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PSEUDOPOTENTIAL AND TIGHT-BINDING CALCULATIONS OF THE BULK
AND SURFACE ELECTRONIC STRUCTURE OF SOLIDS

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ABSTRACT

The electronic structure of semiconductors, alloys, transition metal compounds, and the electronic states associated with surfaces are studied using the empirical pseudopotential and the tight-binding methods. Experimental data are extensively used to obtain information on the pseudopotential and tight-binding parameters, and to check the accuracy of the theoretical calculations. Reflectivity spectra, frequency dependent dielectric constants, densities of states, and charge density distributions are calculated for a number of compounds and compared to corresponding experimental information when available.

A new scheme is developed which results in an appreciable increase in the accuracy of calculations that are frequently encountered in the study of periodic systems. The scheme allows the calculation of various quantities (such as charge density distributions, average energies or dipole matrix elements, etc.) from a knowledge of the values of these quantities at a few optimally chosen states. This is used to derive an expression for the electronic charge density distribution in diamond structure crystals. The method is also very useful in obtaining interpolation formulas and in the construction of localized

Wannier functions from the extended Bloch functions. The method is utilized to study the charge density and also the relationships between ionicity, valence band splittings, and atomic pseudopotentials for a number of binary crystals.

To study systems which do not have long range periodicity an extensive study of the use of the tight-binding method for calculating the electronic structure of diamond and zincblende crystals is made. The method is used to investigate the surface states of these types of crystals. The effects of surface relaxation on the local density of surface atoms, the localization and the character of the various surface states are discussed.

I. INTRODUCTION

We have applied the empirical pseudopotential method¹ (EPM) and the tight-binding method² to study the electronic structure of C, Si, Ge, GaAs, GaP, InSb, ZnSe, CdTe, HgTe, NbC, NbN, HgTe-CdTe alloys, and the (111) surface states of Ge, GaAs and ZnSe. The results of our calculations are compared to available experimental data. A number of calculations, particularly those on the electronic density of states³ were motivated by experimental measurements⁴ showing a need for more accurate theoretical results. These measurements particularly those obtained from the newly developed high-resolution x-ray⁴⁻⁶ and ultraviolet^{7,8} photoemission spectrometers were of great value in giving information on the electronic energy levels over a wide energy range.⁴⁻⁸ This resulted in a better understanding of the energy and angular momentum components of the pseudopotentials^{3,9-12} and more accurate theoretical calculations were made possible.

In section II we discuss our calculations^{3,5} of the band structures and densities of states of Si, Ge, GaAs, InSb, GaP, ZnSe and CdTe. X-ray and ultraviolet photoemission spectra as well as optical reflectivity measurements were used in these calculations. The experimental results^{4,5,7,8} indicated the need for nonlocal (i.e., energy dependent and angular momentum dependent) pseudopotentials. Nonlocal effects were taken into account by the effective mass approximation.³ The experimentally measured gaps, observed¹³ to be related to the ionicity parameter of Phillips and Van Vechten were related¹⁴ to the atomic pseudopotentials and in this way the approximate dependence of ionicity on the pseudopotentials was obtained.

In section III we study the electronic properties of CdTe, HgTe and CdTe-HgTe alloys.^{15,16} The band structures and pseudopotential parameters of the two zincblende compounds were obtained¹⁵ from an analysis of the calculated and measured optical reflectivity spectra and the results were used to study¹⁶ the variation of the band structures, important energy gaps and the electronic charge densities with alloying, in particular near the semiconductor-semimetal transition point. A simple method¹⁶⁻¹⁷ for obtaining the total charge density from a suitable weighted average of the charge density of a few Bloch states is also discussed. A complete generalization¹⁸ of this scheme is developed in section IV where a method for generating optimal or "special points" for arbitrary crystal symmetries is presented. It is shown that the use of these points in calculations involving average energies, matrix elements, or total charge density distributions results in a substantial increase in the accuracy of the results. The usefulness of these points in the construction of Wannier functions¹⁹ is also discussed. The charge densities of a number of semiconductors are calculated²⁰ using only two points and the results are found to agree to a previous many point calculation to within ± 1 per cent. The method is also employed in deriving²¹ an expression (in closed form) for the electronic charge density distribution in group IV crystals. The "special points" are also shown to be useful in the construction of interpolation formulas.²²

The electronic structure, density of states, and the shape of the Fermi surface of the transition metal compounds NbC and NbN are studied²³ in section V. The charge density of electronic states near the Fermi energy are calculated and their possible association with the superconducting transition temperatures of these compounds are discussed.

In section VI we present the results of our study of the application of the tight-binding method to the electronic structure of diamond and zincblende crystals.²⁴ The important interactions are identified and their values are determined for C, Si, Ge, GaAs and ZnSe. The tight-binding parameters are then used to study the (111) surface states^{25,26} of Ge, GaAs and ZnSe. Effects of surface relaxation on the local density of states of surface atoms are also discussed for Ge.

II. CALCULATED VALENCE BAND DENSITIES OF STATES AND PHOTOEMISSION SPECTRA OF DIAMOND AND ZINCBLLENDE CRYSTALS

A. X-ray and Ultraviolet Photoemission Spectra

Abstract

In this section we show the results of some density of states calculations based on recent x-ray and ultraviolet photoemission spectra. We find that a nonlocal pseudopotential is necessary to obtain agreement with the photoemission experiments. Results for the density of states including critical-point assignments and band structures are given for Si, Ge, GaAs, InSb, GaP, ZnSe and CdTe.

1. Introduction

The development of high-resolution ultraviolet^{7,8,27-29} and x-ray^{4-6,30-32} photoemission spectroscopy (UPS and XPS) in recent years have resulted in a much better knowledge of the electronic energy levels and valence band widths of a large number of crystals. Before the UPS and XPS data became available most pseudopotential band structure calculations were primarily based on optical measurements and were concerned mainly with the magnitude of the valence-conduction band separations. The important energy gaps and the position of the prominent structure in $\epsilon_2(\omega)$ (the imaginary part of the frequency dependent dielectric function) which were fit involved only the upper valence bands and the lower conduction bands within a few eV of the Fermi energy. The UPS and XPS data provide valence band energy positions over a much wider energy range and when combined with optical data result in the use of more accurate potentials.

2. Results: Local Pseudopotentials

In Fig. 1 we compare the first high-resolution⁵ valence band x-ray spectra for Ge, GaAs and ZnSe together with theoretical⁵ valence band density of states calculation. The valence band structures and density of states were calculated using the pseudopotential parameters obtained in previous calculations for Ge,³³ GaAs³⁴ and ZnSe.³⁵ These calculations were based only on optical data. A comparison of the experimental and theoretical results in Fig. 1 shows, in general, good agreement between the two. The UPS spectra^{7,8} for Ge and GaAs (not shown) are also very similar to the XPS results. Both types of spectra showed that the widths of the theoretical bands were smaller than the experimental widths, the difference for the upper two valence bands being about 0.7 eV for Ge^{7,8} and GaAs^{7,8} and 1 eV in ZnSe.^{4,5,8} In ZnSe the Zn 3d-states were found^{3,4} to be actually higher in energy than the s-like Se states at the bottom of the calculated valence bands. The position of the lower two valence bands were also found to differ by about 1 eV from the calculated results. These types of discrepancies in the position and width of the valence bands for these and other semiconductors showed the need for more accurate pseudopotentials. In particular, the nonlocal (angular momentum dependent) components of the potential which had been ignored up to this time were found to be necessary to give more accurate results. The use of just one such nonlocal potential (for d-waves) has resulted⁹⁻¹² in an order of magnitude improvement in the accuracy of the band structures of Ge and GaAs and ZnSe. The lowest-order correction^{2,36} to the nonlocal behavior of the pseudopotential can be taken into account by replacing the free electron mass in the Hamiltonian

by an effective mass m^* . This approach works well for a large number of semiconductors and we have applied³ it to obtain valence band densities of states in better agreement with photoemission data for Ge, GaAs, InSb, GaP, ZnSe and CdTe.

3. Effective Mass Approach

We begin by calculating the density of states with a local potential and then fit the nonlocal parameter, i.e. m^* and the form factors of the potential by comparing the density of states with XPS and UPS data. One of the most striking features of the XPS and UPS spectra is that they both mimic the valence band density of states. In addition, the agreement between the two (XPS and UPS) is excellent. Considering that the bulk penetration of electrons is different in the two cases this adds support to the idea that both XPS and UPS measure bulk properties.

After the density of states fits are obtained (reflectivity data is also used as a constraint), a critical point (cp) analysis is done. The sharp structure is identified with the M_0 , M_1 , M_2 , M_3 cp's in the energy band structure. The band structure itself is given for each crystal studied.

The overall agreement is good and the major discrepancies between experiment and the local EPM calculations have been removed especially for the highest bands. The lowest band is the least reliable: this stems partially from the approximate manner in which we have included nonlocal effects.

In the text comparison is made between the present calculation using the nonlocal potential, experimental results and the original calculations using the EPM by Cohen and Bergstresser³³ (CB). More recent EPM calculations since CB have been done which give better agreement with experimental reflectivity spectra. However, in these calculations again very little attention is given to fitting the valence band densities of states. Despite this, the adjustment to fit optical data sometimes yielded a band structure which gave a density of states spectra closer to the XPS value. We have not, however, included these results here, as it is more straightforward and simpler to use the CB values since this reference contains all the crystals of interest and the form factors are not too different from the more recent work. We have also taken the CB form factors as to obtain a good fit to the experimentally determined density of states. The principal optical transitions at Γ , X, L and Σ were constrained to remain near their original values.

Spin-orbit interactions were included for InSb, ZnSe and CdTe. Here the spin-orbit splittings are comparable to the experimental resolution. The method of calculation used was that due to Weisz³⁷ as modified by Bloom and Bergstresser.³⁸ In this procedure two parameters are used to characterize the spin-orbit coupling.³⁹ The metallic spin-orbit parameter is varied until one obtains the experimentally known splittings, while the non-metallic parameter is constrained to a fixed ratio between the two parameters. This ratio is equal to that of the ratio of the spin-orbit interaction for the free atoms as calculated by Herman and Skillman.⁴⁰ The resulting values for the metallic spin-orbit parameters for ZnSe, InSb and CdTe are

0.0006, 0.0019, and 0.0013 respectively.

Once the band structure has been obtained, the density of states, $N(E)$, is calculated from

$$N(E) = \frac{1}{N N_a} \sum_K \sum_{n,\sigma} \delta(E - E_{n,\sigma}(K)) \quad (3)$$

where N is the number of primitive cells, N_a is the number of atoms in the primitive cell, and $N(E)$ is normalized to the number of states per atom. Equation (3) was evaluated by using the Gilat-Raubenheimer technique.⁴¹ The energy derivatives required by this technique were obtained by using $\underline{k} \cdot \underline{p}$ perturbation theory. A grid of 308 points in the irreducible Brillouin zone was used in the calculation.

As in the case of analyzing optical reflectivity spectra, one can identify critical points in the density of states. These points determine the regions of the Brillouin zone responsible for the structure found in the density of states. By observing the relationship of critical point locations in broadened and unbroadened density of states calculations, it is possible to obtain values for the actual positions of the critical points from experimental data.

The resulting form factors, effective mass parameters, and lattice constants used in the calculations are listed in Table I.

4. Results Using m^*

In Figs. 2-8 the calculated densities of states are compared with the experimental results of XPS. The band structures are also presented for each compound. In Tables II-VIII, the resulting values for various characteristic features in the density of states are listed,

and compared with the results of previously calculated form factors from optical data.³³ (For these calculations the matrix size was larger than in the CB case, i.e. $E_1=9$ rather than the CB value $E_1=7$; this gives some slight shifts in the energies.) Tables II-VIII also contain the experimental results from both XPS^{4,5} and UPS.^{7,8} All energy positions are measured relative to the top of the valence band as shown in the figures.

When comparing the calculated density of states using a local pseudopotential (CB) with XPS and UPS data it was found that several bands were in error by as much as 0.5 to 2.0 eV. The largest error is for the lowest lying valence bands. Early workers recognized that the lower valence bands were not expected to be accurate since only interband transitions between the top valence and bottom conduction bands were used in the fitting procedure. As a result they did not publish the values or band structure curves for these lower bands. We have computed these bands using the form factors given in the early papers, and we have extended the energy range in this way.

The addition of an effective mass parameter brings the calculated bands closer to experiment. This is not always the case for the lowest valence band, because our method is approximate and is designed to give the first band (especially near (0,0,0)) a low energy value. A full nonlocal potential which accounts for d-states in the core should work better, but it is a bit more complex. The effective mass approach does, however, remove all the major discrepancies for the higher bands. In particular, the $\chi_1^{\min}$ feature (which is sharp in UPS data) has been improved considerably.

The resulting densities of states are discussed below compound by compound, and critical point identifications are noted in parentheses where unambiguous determination is possible.

Silicon (Fig. 2, Table II)

In the case of Si (only) the original CB form factors were used, without an effective mass, to calculate the density of states. This was done because the resulting density of states agreed quite satisfactorily with the experimental results of both XPS and UPS (see Table II).

The threshold of the valence band contributions to the density of states for Si is -12.6 eV below the top of the valence band, and occurs at $\Gamma_1(M_0)$. The first peak at -10.2 eV is from $L_2(M_1)$. The contributions from the lowest band cease at -8.15 eV at $W_1(M_3)$, while the minimum of the second band occurs at -8.3 eV at $X_1(M_0)$. The large peak at -7.2 eV comes from $L_1(M_2)$. Because of the rather sharp rise of the second valence band in the energy range from -7.2 eV to -4.5 eV there is a rather sharp drop in the density of states from the L_1 peak. The onset of the third band occurs at -4.5 eV near K along Σ , thus the notation $\Sigma_1^{\min}$. The peak near -4.1 eV arises from contributions near $\Sigma_1^{\min}$ and $W_2(M_1)$ at -4.0 eV. The peak at -2.8 eV is due to $X_4(M_2)$. Finally the shoulder at -1.1 eV is from $L_3(M_2)$.

Germanium (Fig. 3, Table III)

The valence band contribution to the density of states for Ge begins at -13.3 eV below the top of the valence band. This point occurs at $\Gamma_1(M_0)$, while the peak at -11.0 eV is due to $L_2(M_1)$. The

contributions from the first band terminates at -9.05 eV at $W_1(M_3)$, and the minimum of the second band occurs at -11.15 eV at $X_1(M_0)$. The sharp peak at -7.8 eV arises from $L_1(M_2)$. Again there is a sharp drop in the density of states from -7.8 eV to -4.4 eV where the threshold of the third band occurs at $\Sigma_1^{\min}$. The peak near -4.0 eV comes from the minimum along with contributions from $W_2(M_1)$. The peak at -3.0 eV is due to $X_4(M_2)$. Finally the shoulder at -1.2 eV comes from $L_3(M_2)$.

From Table III, one notes that the comparison with both UPS and XPS experimental results is quite satisfactory. A considerable improvement has been made from the CB results. Further the discrepancy mentioned by Grobman and Eastman^{7,8} for $\Sigma_1^{\min}$, namely that the previous EPM calculation,³³ and other band structure calculations give a value too close to the top of the valence band, has been removed. The calculated value of -4.4 eV is quite close to the UPS and XPS value of -4.5 eV. The agreement between theory and experiment would even be better if spin-orbit were included. The agreement with experiment for the L_2 , and Γ_1 features has not improved significantly from the CB results.

Gallium Arsenide (Fig. 4, Table IV)

The threshold of the density of states is at -13.8 eV at $\Gamma_1(M_0)$. The shoulder at -12.1 eV arises from $L_1(M_1)$. The main peak at -11.4 eV comes from the entire square face of the zone which turns out to be a surface of nearly constant energy (e.g. the energy change from X_1 to W_4 is less than 0.05 eV). Unlike the case of Ge there is a 4.5 eV gap between the two lowest valence bands. The gap extends from -11.3 eV to -6.8 eV and can be associated with the fact that the antisymmetric

form factors, $V^A(G)$, are no longer zero as in the case of Ge or Si. The minimum of the second band occurs at $X_3(M_0)$. Contributing to the sharp rise, and to the large peak at -6.5 eV are critical points at -6.7 eV and -6.6 eV arising from $L_1(M_1)$ and $W_1(M_1)$ respectively. Just as in the case of Ge, there is a sharp drop near the main peak; this drop continues until the minimum of the third valence band occurring at $\Sigma_1^{\min}$ at -3.9 eV is reached. This, along with W_2 at -3.5 eV, causes the sharp rise at the $\Sigma_1^{\min}$ edge. This fourth band has a minimum at $W_3(M_0)$ which leads to the gradual rise to the $X_5(M_2)$ peak at -2.5 eV. The shoulder at -0.9 eV is from $L_3(M_2)$.

Table IV shows that the agreement of the calculated energies with experiment has improved considerably from the CB results. The discrepancy noted by Grobman and Eastman^{7,8} for $\Sigma_1^{\min}$ has again been removed and would be even smaller if spin-orbit effects were included.

Gallium Phosphide (Fig. 5, Table V)

The calculated density of states for GaP is nearly identical to that of GaAs. The threshold occurs at -13.6 eV $\Gamma_1(M_0)$, while the shoulder at -11.8 eV corresponds to $L_1(M_1)$. As in GaAs the square face of the Brillouin zone causes the huge peak at -10.9 eV. There is a 4 eV gap which extends from -10.9 eV to -6.9 eV between the lowest valence band and the next higher band. The minimum of the second band is at $X_3(M_0)$ which occurs at -6.9 eV. The sharp rise near the main peak at -6.5 eV comes from $L_1(M_0)$ at -6.7 eV and W_1 at -6.6 eV. The contribution of the third band at $\Sigma_1^{\min}$ starting at -4.1 eV causes the sharp rise in the density of states; $W_2(M_1)$ at -3.7 eV also adds to

the rise. The threshold of the fourth band occurs at $W_3(M_0)$ at -3.0 eV and this starts the gradual rise to the $X_5(M_2)$ peak at -2.5 eV. The shoulder at -1.0 eV is from $L_3(M_2)$.

There is good agreement between experiment and the calculated values for the top three bands. There has been a considerable improvement over the CB results for the W_1 and X_3 states. For $\Sigma_1^{\min}$ the change was smaller. This is probably due to the fact that GaP is an indirect semiconductor and the indirect levels were fit roughly to the correct values by Cohen and Bergstresser when they considered the existing optical data.

Zinc Selenide (Fig. 6, Table VI)

Since spin-orbit coupling was included in the following densities of states calculations, the degeneracy of the bands, in certain directions can be removed. Hence, the bands will be labeled 1 through 8 with 1 being the lowest valence band and 8 being the top valence band. To facilitate comparisons with Si, Ge, GaP and GaAs the bands are labeled using non-spin-orbit notation.

The lowest two bands (1,2) are s-like, thus spin-orbit interactions can be neglected. The minimum of the density of states occurs at $\Gamma_1(M_0)$ at -15.8 eV. The shoulder at -14.6 eV is due to $L_1(M_2)$ while the large peak at -14.2 eV is again due to the constant energy surface of the square face of the Brillouin zone. The gap to the next higher band found in zincblende extends from -14.2 eV to -5.9 eV. At -5.9 eV bands (3,4) start to contribute at $L_1(M_0)$. Interestingly enough, X_3 is not the minimum here as was the case in GaP or GaAs. Since L_1 is

lower than X_3 , the large peak at -5.4 eV comes from $X_3(M_1)$ at -5.8 eV and W_1 which is split by the spin-orbit interaction into two peaks: one at -5.3 eV, the other at -5.0 eV. The minimum of band 5 occurs at $\Sigma_1^{\min}$ at -3.8 eV. The doublet peaks at -3.4 eV and -3.2 eV are caused by the splitting of bands (5,6) at W_2 , and the sharp rise at -2.7 eV is from the onset of bands (7,8) at $W_3(M_0)$. The large peak at -2.1 eV is from bands (5,6) at $X_5(M_2)$, while the shoulder at -0.9 eV is from bands (5,6) at $L_3(M_3)$. The spin-orbit splitting here causes another shoulder at -0.7 from bands (7,8) at $L_3(M_3)$.

The agreement as indicated in Table VI is satisfactory except for the lowest band. Again there is marked improvement over the CB results.

Indium Antimonide (Fig. 7, Table VII)

In InSb the spin-orbit coupling was included. The threshold for the lowest band occurs at -11.3 eV at $\Gamma_1(M_0)$, while the shoulder occurring at -10.0 eV is from $L_1(M_1)$. The sharp peak at -9.5 eV comes from the square face of the Brillouin zone as in the other zincblende compounds. Again a gap appears between the two lowest valence bands. It begins at -9.4 eV and terminates at $X_3(M_0)$ at -6.2 eV. Unlike the other calculated densities of states, W_1 lies between X_3 and L_1 . At W_1 spin-orbit interactions split bands 5 and 6 by about 0.2 eV. Both of these points occurring at -6.0 eV and -5.8 eV contribute to the peak at -5.7 eV. $L_1(M_2)$ occurs at -5.7 eV at the height of the peak. Band 5 has a threshold at -3.2 eV at $\Sigma_1^{\min}$. The peaks at -3.1 eV and -2.8 eV are from the spin-orbit split

bands at W_2 (bands 5 and 6). The small peak at -2.4 eV is from bands (7,8) at $W_3(M_0)$ and $X_5(M_2)$ bands (5,6). The peak at -2.1 eV is from bands (7,8) at $X_5(M_2)$, while the shoulder at -1.2 eV is due to $L_3(M_3)$ from bands (5,6).

The comparisons with experimental results found in Table VII are very good. Even the lowest band agrees with the experimental results. It is, perhaps, noteworthy that the d-states lie well below the lowest valence band. XPS data indicates the In 4d level lies about 17 eV below the top of the valence band.

Cadmium Telluride (Fig. 8, Table VIII)

Spin-orbit interactions were again included in the calculations for CdTe. The threshold of the lowest band is at -11.8 eV at $\Gamma_1(M_0)$. The two peaks in the lowest band at -11.0 eV and -10.6 eV are caused by $L_1(M_2)$ and by the nearly constant energy surface of the square face of the Brillouin zone, respectively. The gap between the lowest band and the next lowest band begins at -10.6 eV and terminates at -4.6 eV at $X_3(M_0)$. The spin-orbit splitting between bands 3 and 4 at W_1 causes the doublet peaks at -4.3 eV and -4.0 eV. At -4.4 eV, $L_1(M_1)$ adds to the height of the first peak. The minimum of band 5 again occurs at $\Sigma_1^{\min}$. This causes the sharp rise at -2.7 eV. Spin-orbit splitting between bands 5 and 6 at W_2 causes the peaks at -2.4 eV and -2.0 eV. The peak at -1.8 eV is due to the coincidence of $W_3(M_0)$ from bands (7,8) and $X_5(M_2)$ from bands (5,6). The peak at -1.5 eV is due to $X_5(M_2)$ from bands (7,8). Finally the shoulder at -1.0 eV is due to bands (5,6) at $L_3(M_3)$.

The comparison with experiment is listed in Table VIII. The overall agreement is satisfactory, although the lowest band is in poor agreement with experiment.

5. Discussion of the Results

One can observe some interesting trends by examining the isoelectric series of Ge, GaAs, and ZnSe. The most obvious change from Ge to GaAs is that a gap appears between the first two valence bands. As previously noted⁵ this is due to the localization of electrons in the first band around the strong As ion, and can be related to the antisymmetric form factors $V^A(G)$. This "antisymmetric gap" may also be related to the ionicity.^{13,14} One notes that the gap nearly doubles in size from the 4.5 eV value in GaAs to 8.2 eV in ZnSe which is more ionic.

Another trend observed in the calculated density of states is that the widths of the various peaks decrease as the compound becomes more ionic. For example, the width of the lowest band is 4.1 eV in Ge, 2.4 eV in GaAs, and 1.7 eV in ZnSe. The width of the top three bands also decreases. In Ge the width is 9.1 eV, in GaAs 6.8 eV and in ZnSe 6.0 eV.

The trends in going from InSb to CdTe follow the trends in going from GaAs to ZnSe. Namely, the "antisymmetric gap" for InSb is 3.3 eV, while the gap is 6.0 eV for CdTe. Finally, the width of the lowest band for InSb and CdTe is 1.9 eV and 1.2 eV respectively, and the top three bands also contract: 6.0 eV for InSb, and 4.6 eV for CdTe.

In summary, it has been demonstrated that the EPM, with the addition of an effective mass, can adequately reproduce the experimentally determined density of states for at least the top three valence bands. In addition, complete critical point analysis has been given, and the experimental structure identified.

Table I. Form factors (in Ry), effective mass parameter, and lattice constants (in Å).

	$V^S_{(3)}$	$V^S_{(8)}$	$V^S_{(11)}$	$V^A_{(3)}$	$V^A_{(4)}$	$V^A_{(11)}$	m/m^*	a
Si	-.211	.040	.080	-	-	-	-	5.43
Ge	-.269	.038	.035	-	-	-	1.089	5.65
GaAs	-.252	.000	.080	.068	.060	.012	1.138	5.64
GaP	-.249	.017	.083	.081	.055	.003	1.075	5.45
ZnSe	-.261	-.011	.113	.151	.130	.016	1.291	5.65
InSb	-.250	.010	.044	.049	.038	.010	1.192	6.47
CdTe	-.245	-.015	.073	.089	.094	.006	1.228	6.48

Table II. Energies (in eV) of characteristic features in the valence band of Si (measured relative to the top of the valence band). The theoretical values are Ref. 33. The XPS values are from Refs. 4 and 5. The UPS values are from References 7 and 8.

Si	Theory	Experiment	
		UPS	XPS
$L_{3'}$	- 1.1	-	-
X_4	- 2.8	-	- 2.5 ± 0.3
W_2	- 4.0	-	- 3.9 ± 0.2
$\Sigma_1^{\min}$	- 4.5	- 4.7 ± 0.2	- 4.7 ± 0.3
L_1	- 7.2	- 6.4 ± 0.4	- 6.8 ± 0.2
W_1	- 8.1	-	- 8.1 ± 0.3
$L_{2'}$	-10.2	-	- 9.3 ± 0.4
Γ_1	-12.6	- 12.4 ± 0.6	- 12.5 ± 0.6

Table III. Energies (in eV) of characteristic features in the valence band of Ge (measured relative to the top of the valence band). For a, b, c, see Table II.

Ge	Theory		Experiment	
	Old ^a	New	UPS ^b	XPS ^c
L ₃	- 1.1	- 1.2	- 1.1 ± 0.2	-
X ₄	- 2.4	- 3.0	-	- 2.7 ± 0.3
W ₂	- 3.3	- 4.0	-	- 3.9 ± 0.2
Σ ₁ ^{min}	- 3.8	- 4.4	- 4.5 ± 0.2	- 4.5 ± 0.3
L ₁	- 6.9	- 7.8	- 7.7 ± 0.2	- 7.4 ± 0.2
W ₁	- 8.2	- 9.1	-	- 8.7 ± 0.3
L _{2'}	- 9.9	-11.0	-10.6 ± 0.3	-10.5 ± 0.4
Γ ₁	-12.0	-13.3	-12.6 ± 0.3	-12.8 ± 0.4

Table IV. Energies (in eV) of characteristic features in the valence band of GaAs (measured relative to the top of the valence band). For a, b, c, see Table II.

GaAs	Theory		Experiment	
	Old ^a	New	UPS ^b	XPS ^c
L ₃	- 0.9	- 0.9	- 0.8 ± 0.2	- 1.4 ± 0.3
X ₅	- 2.2	- 2.5	-	- 2.5 ± 0.3
W ₂	- 2.6	- 3.5	-	- 4.0 ± 0.2
Σ ₁ ^{min}	- 3.2	- 3.9	- 4.1 ± 0.2	- 4.4 ± 0.2
W ₁	- 6.0	- 6.6	-	- 6.6 ± 0.2
X ₃	- 6.4	- 6.8	- 6.8 ± 0.2	- 7.1 ± 0.2
X ₁	- 9.7	-11.4	-10.8 ± 0.4	-10.7 ± 0.3
Γ ₁	-12.0	-13.8	-11.9 ± 0.6	-13.8 ± 0.4

Table V. Energies (in eV) of characteristic features in the valence band of GaP (measured relative to the top of the valence band). For a, b, c, see Table II.

GaP	Theory		Experiment	
	Old ^a	New	UPS ^b	XPS ^c
L ₃	- 0.9	- 1.0	-	- 1.4 ± 0.3
X ₅	- 2.3	- 2.5	-	- 2.7 ± 0.2
W ₂	- 3.2	- 3.7	-	- 3.6 ± 0.2
Σ ₁ ^{min}	- 3.8	- 4.1	- 4.2 ± 0.3	- 4.0 ± 0.2
W ₁	- 5.4	- 6.6	-	- 6.5 ± 0.2
X ₃	- 5.8	- 6.9	- 7.0 ± 0.3	- 6.9 ± 0.2
X ₁	-11.5	-10.9	-	- 9.6 ± 0.3
Γ ₁	-13.0	-13.6	-12.0 ± 0.6	-13.2 ± 0.4

Table VI. Energies (in eV) of characteristic features in the valence band of ZnSe (measured relative to the top of the valence band). For a, b, c, see Table II.

ZnSe	Theory		Experiment	
	Old ^a	New	UPS ^b	XPS ^c
L ₃	- 0.9	- 0.9	-	- 1.3 ± 0.3
X ₅	- 1.5	- 2.1	-	- 2.1 ± 0.3
W ₂	- 2.0	- 3.3	-	- 2.6 ± 0.2
Σ ₁ ^{min}	- 2.7	- 3.8	- 4.0 ± 0.3	- 3.4 ± 0.4
W ₁	- 3.4	- 5.3	-	- 5.2 ± 0.2
L ₁	- 3.8	- 5.9	- 5.7 ± 0.3	- 5.6 ± 0.3
X ₁	-13.2	-14.2	-	-12.5 ± 0.4
Γ ₁	-14.2	-15.8	-	-14.5 ± 0.6

Table VII. Energies (in eV) of the characteristic features in the valence band of InSb (measured relative to the top of the valence band). For a, b, c, see Table II.

InSb	Theory		Experiment	
	Old ^a	New	UPS ^b	XPS ^c
L_3	- 0.6	- 1.2	-	- 1.4 ± 0.2
X_5	- 1.4	- 2.1	-	- 2.4 ± 0.4
W_2	-	- 2.8	-	- 3.1 ± 0.2
$\Sigma_1^{\min}$	- 2.1	- 3.2	- 3.3 ± 0.3	- 3.4 ± 0.2
L_1	- 4.9	- 5.7	-	- 5.9 ± 0.2
X_3	- 5.4	- 6.2	- 6.2 ± 0.3	- 6.4 ± 0.2
X_1	- 7.6	- 9.5	- 9.6 ± 0.3	- 9.5 ± 0.2
Γ_1	- 8.9	-11.3	- 10.9 ± 0.5	- 11.7 ± 0.3

Table VIII. Energies (in eV) of the characteristic features in the valence band of CdTe (measured relative to the top of the valence band). For a, b, c, see Table II.

CdTe	Theory		Experiment	
	Old ^a	New	UPS ^b	XPS ^c
L ₃	- 0.4	- 1.0	- 0.7 ± 0.3	- 0.9 ± 0.3
X ₅	- 1.0	- 1.5	-	- 1.8 ± 0.2
W ₂	- 1.4	- 2.0	-	- 2.2 ± 0.3
Σ ₁ ^{min}	- 2.0	- 2.7	- 2.9 ± 0.5	- 2.7 ± 0.3
W ₁	- 2.6	- 4.3	-	- 4.5 ± 0.1
X ₃	- 2.9	- 4.6	- 4.8 ± 0.2	- 5.2 ± 0.2
X ₁	-12.5	-10.6	- 8.8 ± 0.3	-
Γ ₁	-12.9	-11.8	-10.8 ± 0.6	-

FIGURE CAPTIONS

- Fig. 1. X-ray photoemission spectra, band structures, and densities of states of Ge, GaAs and ZnSe. The top row $I(E)$ shows the uncorrected experimental spectra. At the bottom the corresponding band structures $E(\vec{k})$ and densities of states $\rho(E)$ as derived from EPM calculations are shown. The broadened theoretical densities of states $\rho'(E)$ in the second row facilitate comparison with experiment.
- Fig. 2. X-ray photoemission spectra, density of states, and band structure for Si. The top figure shows the corrected experimental XPS spectra of references 4 and 5. The middle figure is the EPM calculated density of states. To facilitate comparison with experiment a broadened density of states is indicated by the dashed line. The bottom figure is the EPM calculated band structure.
- Fig. 3. X-ray photoemission spectra, density of states and band structure of Ge. See also caption for Fig. 2.
- Fig. 4. X-ray photoemission spectra, density of states and band structure of GaAs. See also caption for Fig. 2.
- Fig. 5. X-ray photoemission spectra, density of states and band structure for GaP. See also caption for Fig. 2.
- Fig. 6. X-ray photoemission spectra, density of states, and band structure of ZnSe. The Zn 3d states have been subtracted out, with the peak position indicated by the solid line. See also caption for Fig. 2.

Fig. 7. X-ray photoemission spectra, density of states and band structure of InSb. See also caption for Fig. 2.

Fig. 8. X-ray photoemission spectra, density of states and band structure of CdTe. See also caption for Fig. 2.

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Fig. 1.

XBL 748-7035

Fig. 2.

FIG. 3.

Fig. 4.

Fig. 7.

Fig. 8.

B. Valence-band Splittings, Atomic Pseudopotentials and Ionicity

Abstract

In this section the valence band splittings measured by photo-emission experiments are related to the ionicity parameter of Phillips and Van Vechten and to the atomic pseudopotentials.

1. Introduction

The Phillips and Van Vechten^{42,43} theory of bonding and ionicity in binary crystals makes use of optical and dielectric data in the determination of the parameters of the theory. These parameters are E_h and C which are related respectively to the average homopolar gap and the difference in electronegativities of A and B in $A^N B^{8-N}$ crystals (e.g. GaAs). In terms of pseudopotential theory E_h and C are approximately related to the average symmetric and antisymmetric potentials V_S and V_A (e.g. $2V_S = V_{Ga} + V_{As}$ and $2V_A = V_{Ga} - V_{As}$). The pseudopotentials determine the electronic energy band structure from which E_h and C can be in principle obtained. However, the energy band structure depends in a complicated way on the pseudopotentials. The precise nature of the dependence of E_h and C on the pseudopotentials is therefore not well known. Up to now these parameters have been determined from spectroscopic data. Phillips⁴² has obtained a form for the approximate dependence of E_h and C on the pseudopotential form factors by associating the average energy gap at X between the lowest two conduction bands and the top two valence bands with $|E_h + iC|$. He has also studied the variation of this gap with V_S and V_A .

Here we examine other possible relations between the parameter C and the crystalline pseudopotentials. Measures of C in terms of V_S and V_A are given for 4-fold and 6-fold coordinated crystals in the following two sections. We then briefly suggest, before the concluding section, a condition on the crystal potential for the structural phase transition in these compounds.

2. Measures of C in 4-fold Coordinated Crystals

The approach we follow is related to a suggestion in a recent article of Grobman, Eastman and Cohen¹³ in which they propose a very simple relation between the valence band energy gaps and C . In particular they observe that the experimentally measured gap between the lowest two valence bands at X (denoted X_3-X_1) is a direct measure of C in the zincblende and possibly in the rocksalt crystal structures. This gap can be measured using ultraviolet photoemission spectroscopy (UPS)^{7,8} and x-ray photoemission spectroscopy (XPS).^{4,6} For example in Ge, GaAs and ZnSe, where the lattice constants and ionic cores are nearly the same, XPS measurements⁵ and theoretical⁵ calculations shown in Figures 1-8 of Section II A show an appreciably larger gap between the first two valence bands for ZnSe than for GaAs. In Ge the gap is zero as a result of the symmetry of the diamond structure. We will show in this section that the splitting of this gap is in fact related to the antisymmetric potential (i.e. the difference in the atomic pseudopotentials of the nearest-neighbor atoms). The antisymmetric potential is obviously zero in Ge, and greater in ZnSe than in GaAs. We now use the proposed relationship between C and the X_3-X_1 gap to

obtain the dependence of C on the pseudopotential form factors since this gap is related in a definite way to the form factors. To find this relationship we expand the wavefunctions at X in a plane wave basis:

$$\psi_{\mathbf{X}}(\vec{r}) = \sum_{\vec{G}} \alpha_{\vec{G}} e^{i(\vec{K}_{\mathbf{X}} - \vec{G}) \cdot \vec{r}}$$

where the G's are reciprocal lattice vectors and $\vec{K}_{\mathbf{X}} = (1,0,0) (\frac{2\pi}{a})$. The diagonal matrix elements of the Hamiltonian between these plane waves are of the form $\frac{\hbar^2}{2m} |\vec{K}_{\mathbf{X}} - \vec{G}|^2$. The possible values of $|\vec{K}_{\mathbf{X}} - \vec{G}|^2$ for diamond, zincblende, and rocksalt crystal structures are 1,2,5,6,... in units of $(\frac{2\pi}{a})^2$ where a is the lattice constant. Since we are interested only in the lowest two valence bands we restrict the G's in the expansion to satisfy $|\vec{K}_{\mathbf{X}} - \vec{G}|^2 \leq 2$. This results in a 6x6 secular equation that can be easily solved for the eigenvalues:

$$E(X_1) = \frac{3(1-v_A^4) + v_S^8}{2} - \frac{1}{2} \left[(1-v_A^4 + v_S^8)^2 + 8(v_A^3 - v_S^3)^2 \right]^{1/2}$$

$$E(X_3) = \frac{3(1+v_A^4) + v_S^8}{2} - \frac{1}{2} \left[(1 + v_A^4 + v_S^8)^2 + 8(v_A^3 + v_S^3)^2 \right]^{1/2}.$$

The superscripts on the symmetric and anisymmetric potentials v_S and v_A give the value of $\vec{G}^2$, i.e. $v_A^4 = v_A(\vec{G}^2 = 4)$. The unit of energy

in these expressions is $\frac{\hbar^2}{2m} (\frac{2\pi}{a})^2 = \frac{4\pi^2}{(a/a_0)^2} \text{ Ry}$

where a_0 is the Bohr radius. The antisymmetric pseudopotentials are taken as the difference between the cation and anion pseudopotentials and are positive. The X_3-X_1 energy gap is found to be

$$E_X \equiv E(X_3) - E(X_1) = 3V_A^4 + \frac{1}{2} \left\{ \sqrt{(1 - V_A^4 + V_S^8)^2 + 8(V_A^3 - V_S^3)^2} - \sqrt{(1 + V_A^4 + V_S^8)^2 + 8(V_A^3 + V_S^3)^2} \right\}. \quad (1)$$

The values of E_X calculated from (1) with the Cohen-Bergstresser (CB)³³ values are given in Table I for a number of crystals. In the (CB) calculation all G's satisfying $|\vec{k}-\vec{G}|^2 < 7$ are taken into account exactly, while those G's satisfying $|\vec{k}-\vec{G}|^2 < 20$ are taken into account through Löwdin⁴⁴ perturbation theory. The size of the matrix diagonalized at X is 22x22 in the (CB) case. The "effective" size of this matrix is much larger because of the Löwdin perturbation scheme. The agreement between E_X given by (1) and the CB values is fairly good in most cases (Table I); the largest fractional error is about 10%.

The variation of E_X with the pseudopotential form factors can be obtained from (1). This expression yields the interesting information that $(\partial E_X / \partial V_A^3) \approx 2$ for the usual form factors encountered and $2 < (\partial E_X / \partial V_A^4) < 3$. This dependence of E_X on the antisymmetric form factors is consistent with the increase in the value of C obtained by Phillips⁴² and Van Vechten⁴³ as the valence difference in the isoelectronic AB^N8-N crystals is increased. Assuming that $E_X \approx C$ as proposed by Grobman et al.,¹³ expression (1) gives the approximate dependence of C on the pseudopotential form factors for the zincblende structure compounds.

We now consider whether this dependence on the form factors can be related to real space pseudopotentials. A dependence of C on screened ionic potentials has been proposed by Phillips⁴² and Van Vechten. They find that the following formula works well for tetrahedrally coordinated $A^N B^{8-N}$ crystals:

$$C(AB) = b \frac{Z_A}{r_A} - \frac{Z_B}{r_B} e^{-k_S R} \text{ Ry.} \quad (2)$$

Here Z_A and Z_B are the valence numbers N and $8-N$ of the cation and anion; r_A and r_B are half the homopolar bond length of the group IV element belonging to the same rows of the periodic table as atoms A and B , and $R = (r_A + r_B)/2$. The exponential term gives the Fermi-Thomas screening factor with

$$k_S^2 = \frac{4k_F}{\pi a_0}$$

where k_F is the Fermi momentum of a free electron gas of the same density as that of the valence electrons and a_0 is the Bohr radius. The factor b is equal to 1.5 to an accuracy of 10% or better.⁴² In Table II we list the values of C obtained from this formula for several crystals. Also, "empirical" values of C determined^{42,43} from reflectivity and dielectric constant data are also listed in Table II.

Since the empirically determined pseudopotentials already include¹ screening we may try to see if C is related to the difference of the atomic pseudopotentials at the bond site, in analogy to the Phillips and Van Vechten formula (2). The difference, C_1 , of the atomic pseudopotentials at a point halfway between the atoms is related in a simple way to the antisymmetric potentials $V_A(G)$:

$$C_1 = \sum_{\vec{G}} V_A(G) \cos \vec{G} \cdot \vec{\tau}$$

where $\vec{\tau} = \frac{1}{8} (1,1,1)$ a in zincblende crystal structures. If the antisymmetric potentials corresponding to $G^2 \geq 11 (\frac{2\pi}{a})^2$ are ignored we find

$$C_1 = 2\sqrt{2} V_A^3 \quad (3)$$

for zincblende crystals. Since by definition $V_A^3 = \frac{V_{\text{cation}}^3 - V_{\text{anion}}^3}{2}$ we have

$$C_1 = \sqrt{2} [V_{\text{cation}}(G^2=3) - V_{\text{anion}}(G^2=3)] \quad (4)$$

This expression for C_1 resembles the Phillips and Van Vechten formula (2). In Table II we list the values of C_1 for several crystals obtained from (CB) form factors and from the more recent calculation,³ of section A, which was fit to photoemission data (ultraviolet and x-ray) as well as optical data. The correlation between C_1 and the spectroscopically evaluated value is good in most cases, with the value based on form factors fit to both photoemission and optical data giving better agreement than that based on form factors determined only from optical data.

A different possible relation between C and the antisymmetric pseudopotentials is obtained if we look at the difference of the total crystalline potential at the ionic sites. This difference, D , is also related to the antisymmetric potentials:

$$D = 2 \sum_{\vec{G}} V_A(\vec{G}) \sin^2 \frac{\vec{G} \cdot \vec{r}}{2} \quad (5)$$

For zincblende crystals, neglecting $V_A(G)$ for $G^2 \geq 11$ we find

$$D = 4(2V_A^3 + 3V_A^4) \quad (6)$$

If we assume C is proportional to D then to obtain the correct C for GaAs using the CB form factors, D would have to be multiplied by 0.184.

In Table II we list $C_2 = 0.184D$ for a number of compounds. If the antisymmetric potentials have the form of a Coulomb potential, then

$V_A^4 = \frac{3}{4} V_A^3$ and (6) gives

$$C_2 = 3.12 V_A^3 = 1.56 (V_{\text{cat}}^3 - V_{\text{anion}}^3) \quad (7)$$

This is again very close to the result (4) for C_1 . These results are also consistent with the determination of C using the X_3-X_1 gap. This gap does not depend in a simple way on the antisymmetric potentials alone (see Eq. 1), but is roughly estimated by $E \approx 2(V_A^3 + V_A^4)$. A Coulomb-like potential for the V_A 's gives $E \approx 1.75 (V_{\text{cation}}^3 - V_{\text{anion}}^3)$. These different measures of C , i.e. C_1 , C_2 and E_X are therefore consistent with each other in the zincblende crystals.

3. Measures of C in Rocksalt Structure Crystals

We can also test the dependence of C on the pseudopotentials for the $A_B^{N_B-N}$ rocksalt crystal structures. The quantities of interest, as in the case of the zincblendes are C_1 , D and the energy gap at X between the lowest two valence bands.

To obtain C_1 we take the difference of the ionic potentials of A and B at a point halfway between the two ions. We find:

$$C_1 = \left| \sum_{\vec{G}} V_A(\vec{G}) \cos \vec{G} \cdot \vec{T} \right|$$

where $\vec{T} = \frac{1}{4} (1,1,1)a$ in the rocksalt structures. This is equivalent to

$$C_1 = |6V_A^4 - 8V_A^8| \quad (8)$$

To obtain D, we take the difference of the crystalline potentials at the ionic sites A and B. The result is

$$D = 16V_A^3 \quad (9)$$

The antisymmetric form factors corresponding to $G^2 \gg 11 \left(\frac{2\pi}{a}\right)^2$ have been neglected in the evaluation of C_1 and D. For the zincblende crystals we found that D given by (6) overestimated C by a factor of about 6. For the rocksalt crystals we find that D given by (9) overestimates C by a factor of about 2 when we take NaCl as a test case and use the potentials of Ref. 45 to calculate D. In order to compare C_1 in (8) to D we can assume a Coulombic pseudopotential for the ions. Then $V_A(G)$ is proportional to $\frac{1}{G^2}$ and C_1 may be written in terms of V_A^3

$$C_1 = \frac{3}{2} V_A^3$$

For the zincblende crystals C_1 in (3) was found to be a measure of C . For the rocksalt crystals however, C_1 underestimates C by a factor of nearly 5. For the zincblendes it is the difference of the potentials of A and B near the bond site which approximates C while for the rocksalts the difference in the crystalline potentials at the atomic sites is the better approximation to C .

We now turn to the gap at X between the lowest two valence bands in the rocksalt crystals. The relation between this gap and the form factors can be obtained in the same way as before by using a 6×6 matrix. We find

$$E^R(X_1) = \frac{3(1+v_S^4) + v_S^8}{2} - \frac{1}{2} [(1+v_S^4+v_S^8)^2 + 32 (v_A^3)^2]^{1/2} \quad (10)$$

$$E^R(X_4) = 1 - v_S^4 \quad (11)$$

There is a very interesting relation between the expressions for the X gap in the zincblende and rocksalt crystals. If we make the substitutions $V_S(3) \rightarrow -V_A(3)$ and $V_A(4) \rightarrow -V_S(4)$ in the zincblende formulas we obtain the above expressions for the rocksalts. Since $V_S + V_A = V_{\text{cation}}$ these relations imply that when $V_{\text{cation}} \rightarrow 0$, the gap at X for the rocksalt and zincblende crystals become equal. (Here we are ignoring v_S^8 which is close to zero for most rocksalt and zincblende crystals.)

The energy gap at X for the rocksalts is given by

$$E_X^R \equiv E^R(X_4) - E^R(X_1) = \frac{1}{2} [(1 + v_S^4 + v_S^8)^2 + 32 (v_A^3)^2]^{1/2} - \frac{1 + 5v_S^4 + v_S^8}{2} \quad (12)$$

Because of the crystal symmetry, for the rocksalt crystals E_X^R does not vanish when the antisymmetric potential is set equal to zero.

If as in the case of the zincblendes we associate C with E_X^R in the rocksalts, i.e.,

$$C = E_X^R, \quad (13)$$

then C does not vanish when $V_A \rightarrow 0$. The limit $V_A \rightarrow 0$ is however unphysical for the rocksalt structures since the crystal structure changes much before this limit is reached. We will therefore assume (13) is approximately valid for the rocksalts.

To obtain the dependence of E_X^R on the potentials more accurately than in (12) we can use more plane waves in the expansion of the wavefunctions. When the 14 plane waves corresponding to $|\vec{k} + \vec{G}|^2 \leq 5$ are used in the expansion we find

$$E^R(X_4) = 3 - V_S^4 + \frac{V_S^8 - V_S^{12}}{2} - \frac{1}{2} \sqrt{(4 + V_S^8 - V_S^{12})^2 + 8(V_S^4 - V_S^8)^2}. \quad (14)$$

This expression reduces to (11) when $8(V_S^4 - V_S^8)^2$ is small compared to $(4 + V_S^8 - V_S^{12})^2$. It is interesting that even to this order of approximation $E^R(X_4)$ is independent of the antisymmetric potentials.

A more accurate expression for $E(X_1)$ can be easily obtained only when $V_A = 0$. For this case we find

$$E^R(X_1) = 3 - \sqrt{4 + (V_S^8)^2}; \quad V_A = 0. \quad (15)$$

When $V_A \rightarrow 0$, an expansion of (14) and (15) reveals that the two lowest bands at X come close together.

The approximate value of the lowest X gap in the valence bands for a number of rocksalt crystals has been obtained from photoemission measurements.⁴⁶ A plot of E_X versus C is shown in Fig. 1. It is seen that for the rocksalt crystals most of the points fall below the line $C = E_X$. However, as Phillips⁴² states, when the ionicity $f_i \geq 0.9$ the dispersion theory of ionicity begins to break down and the value of C for such compounds may not be accurate. Most of the rocksalt structure crystals we have plotted have $f_i > 0.9$. For the potassium-halides, the potassium p-core level lies close to the halogen-associated s-level and this can cause E_X to have a value different from that predicted from the approximate expressions given before. For KF the potassium p-core level actually falls in the gap⁴⁶ (between the lowest two valence bands) and this may explain the large value of E_X in this crystal.

4. A Condition on the Crystal Potential for the Structural Phase Transition

It would be interesting to see if the phase transition from the zincblende to the rocksalt crystal structure could be predicted from a knowledge of the pseudopotential form factors. In the Phillips and Van Vechten^{42,43} theory the transition occurs when the ionicity parameter f_i passes through the critical value of 0.785. Since f_i is an increasing function of C we can see if, empirically, this critical value for f_i corresponds to a critical value of C . Looking at the E_h, C plane plot used by Phillips⁴² to separate the fourfold and sixfold coordinated

structures we find that the rocksalt crystal structures occur only for $C \geq 7$ eV. To relate this condition to the pseudopotential form factors the simplest relation to use is probably (3). Equation (3) then implies that for $V_A^3 \geq 0.18$ Ry (in the zincblende crystals) a transition to the rocksalt crystal structure is possible. This limit on V_A^3 seems to be realistic. Recent pseudopotential calculations³ for a number of zincblende compounds with varying degrees of ionicity show that V_A^3 is less than this critical value in all cases.

5. Conclusion

The two main results of this paper are the relation of pseudopotential form factors to the Phillips-Van Vechten ionic band energy C via (1) real space pseudopotentials and (2) the lowest valence band gap at X .

We find that the difference of ionic pseudopotentials midway between nearest neighbors is a good approximation to C for zincblende structure compounds, while for rocksalt structure compounds the case of NaCl indicates that it is the difference between pseudopotentials at the ionic sites which approximates C . The approximation to C for zincblende compounds is generally better if based on pseudopotentials fit to both optical and photoemission data rather than optical data alone.

In deriving the relation between the lowest valence band gap E_x at X and the pseudopotential form factors, and using the relation $E_x \approx C$, we have obtained a new connection between the parameters of dispersion theory and pseudopotential theory. We have briefly indicated one possible use of this relation, namely determination of the condition on the crystal potential for the 4-fold to 6-fold coordination phase transformation.

Table I. Energy gap at X between lowest two valence bands
obtained from 6×6 matrix as compared to the CB values.

	$E_2 - E_1$ (eV) 6 x 6	$E_2 - E_1$ (eV) CB
Si	0	0
Ge	0	0
GaAs	4.18	4.04
GaP	6.02	5.35
GaSb	3.81	4.16
InSb	3.82	4.28
InAs	5.46	5.11
InP	4.09	4.07
ZnSe	9.70	9.60
ZnS	11.04	10.41
ZnTe	8.07	7.90
CdTe	7.86	9.06
AlSb	3.39	3.21

Table II. The parameter C of the Phillips and Van Vechten theory of ionicity as determined from different methods. The values in parenthesis for C_1 and C_2 were obtained from the form factors of Ref. 3. The other values listed for C_1 and C_2 were obtained from the CB form factors of Ref. 33. Energies are in eV.

	C Empirical ⁱ	C Formula(2) ⁱⁱ	C_1 $2\sqrt{2} V_A^3$	C_2 $0.367(4V_A^3 + 6V_A^4)$	$X_3 - X_1$ gap (XPS, UPS)
Ge, Si	0	0	0	0	0
GaAs	2.90	2.72	2.72	2.9	2.9 ± 0.3
GaP	3.28	3.0	4.62 (3.1)	4.53 (3.26)	2.8 ± 0.3
GaSb	2.10	1.71	2.28	2.7	
InSb	2.10	2.0	2.28 (1.9)	2.7 (2.11)	2.6 ± 0.3
InAs	3.34	2.94	3.0	3.1	
InP	3.34	3.25	2.72	2.9	
ZnSe	5.57	5.44	6.84 (5.70)	7.2 (6.9)	6 ± 0.5
ZnTe	4.48	4.02	4.46	5.6	
CdTe	4.40	4.03	5.7 (3.40)	5.7 (4.3)	4.1 ± 0.3

i is reference 43

ii is reference 42 and 43

XBL 748-7018

Fig. 1. The energy gap at X between the lowest two valence bands is plotted against the Phillips-Van Vechten parameter C for several zincblende (circles) and rocksalt (triangles) structure crystals. Typical error ranges for E_X are shown for two compounds.

III. ELECTRONIC STRUCTURES AND CHARGE DENSITIES OF CdTe, HgTe AND CdTe-HgTe ALLOYS

A. Reflectivities and Electronic Band Structures of CdTe and HgTe

Abstract

In this section the electronic band structures and pseudopotential parameters of CdTe and HgTe are determined. The reflectivity spectra are calculated and compared to experimental data. Important features in the reflectivity spectra are identified with critical-point transitions in specific regions of the Brillouin zone.

1. Introduction

The energy band structures of CdTe and HgTe were calculated using the empirical pseudopotential method¹ as modified by Weisz,³⁷ and Bloom and Bergstresser³⁸ to include spin-orbit coupling. In addition the imaginary part of the frequency-dependent dielectric function, $\epsilon_2(\omega)$ and the reflectivity, $R(\omega)$ were calculated. In the energy range considered, almost all the structure in $\epsilon_2(\omega)$ and the reflectivity may be explained by direct electronic transitions at specific regions of the Brillouin zone. We identify structure in $\epsilon_2(\omega)$ and $R(\omega)$ with critical point interband transitions. The symmetry, energy and location in the zone of important critical points are determined and their contributions to $\epsilon_2(\omega)$ and $R(\omega)$ are investigated.

2. Calculation

The initial form factors for CdTe³³ and HgTe⁴⁷ with which the calculations were initially started were slightly modified to improve the agreement between the experimental and theoretical reflectivities.

The two spin-orbit variables³⁹ λ_1 and λ_2 were constrained to have the same ratio as the splittings (of the p-levels) in the free atoms as determined by Herman and Skillman.⁴⁰ This left only one adjustable parameter which was varied to give the correct splitting of the valence bands, at Γ for CdTe, and at L for HgTe.

The energy band structures were calculated at 356 points throughout $1/48$ of the Brillouin zone. Löwdin perturbation theory⁴⁴ as modified by Brust⁴⁸ was used. For CdTe, 15 plane waves were treated exactly at Γ while 98 extra plane waves were taken into account through the Löwdin perturbation scheme. The corresponding values at Γ for HgTe are 59 plane waves treated exactly and 54 plane waves treated through perturbation theory. The energy band structure calculated for HgTe, using the form factors derived in this work, is accurate to within 0.1 eV. For CdTe the identification of reflectivity structure with specific interband transitions, as presented in this paper, is unchanged when more plane waves are treated exactly and the form factors are slightly modified.

The scheme for the calculation of $\epsilon_2(\omega)$ and $R(\omega)$ from the band structure is given in reference 1. The lattice constants (adjusted to 0°K) used in these calculations are 6.48 Å for CdTe and 6.45 Å for HgTe. At the time when the calculations were made high-resolution photoemission data were not available for these compounds and the calculations are therefore based on reflectivity data alone. The most important and interesting states for these compounds are however those near the top of the valence and bottom of the conduction bands and the reflectivity data provides sufficient information for an accurate determination of the band structures in this region.

3. Results

The electronic band structures of CdTe and HgTe in the principal symmetry directions are shown in Figs. 1 and 2. The imaginary part of the dielectric function $\epsilon_2(\omega)$ for CdTe and HgTe appear in Figs. 3 and 4; the experimental and theoretical reflectivities are shown in Figs. 5 and 6. Important features of the experimental and theoretical reflectivities are compared in Tables I and II. Spin-orbit splittings calculated at symmetry points appear in Table III. Table II compares the form factors derived in this work with those with which the calculations were initially started.

4. Interpretation of Reflectivity Structure

a. CdTe. The fundamental gap of 1.59 eV^{49} at $\Gamma(4-5)$, (i.e. between bands 4 and 5), produces the usual M_0 singularity in $\epsilon_2(\omega)$ at the threshold energy of 1.59 eV . The spin-orbit splitting of the valence bands at Γ is $\Delta_0 = 0.91$ determined by several independent experiments.⁵⁰⁻⁵² The value of the spin-orbit parameter was adjusted to reproduce this value.

The two peaks at 3.42 and 3.97 eV in the calculated reflectivity are caused by spin-orbit split $\Lambda(4-5)$ and $\Lambda(3-5)$ transitions respectively. These are consistent with the experimental values of 3.46 and 4.03 eV . The spin-orbit splitting of the valence bands at L is $\Delta_1 = L(3-4) = L_{4,5} - L_6 = 0.57 \text{ eV}$. This agrees very well with the values of 0.57 eV obtained by Cardona and Greenaway⁵¹ at 77°K . The energy of the top valence band at L is -0.40 eV with respect to the energy at Γ_{8v} .

The calculated $R(\omega)$ rises sharply between 5.02 and 5.07 eV. This is caused by $\Delta(4-5)$ transitions occurring at (0.7,0,0) in the zone. The experimental reflectivity also rises sharply in this energy range and has a peak at 5.18 eV. The calculated reflectivity has a peak at 5.27 eV caused by (4-5) transitions from the critical point (0.9, 0.2,0.2) inside the zone.

The calculated $R(\omega)$ has two adjacent peaks at 5.47 and 5.52 eV that correspond to the main peak in the reflectivity data at 5.53 eV. The 5.47 and 5.52 eV peaks are caused mainly by $\Sigma(4-5)$ and $\Delta(3-5)$ transitions respectively. The major contribution to the strength of $\epsilon_2(\omega)$ and $R(\omega)$ comes from the $\Sigma(4-5)$ transitions; $\Delta(3-5)$ transitions account for only 20 percent of the value of $\epsilon_2(\omega)$ at 5.52 eV.

The small shoulder extending from 5.67 to 5.73 eV in the calculated reflectivity is caused by (4-6) transitions from the critical points (0.35, 0.07, 0.07) at 5.63 eV and (0.2,0,0) at 5.73 eV.

The two small peaks at 6.07 and 6.17 eV in $R(\omega)$ result from (3-6) transitions near (0.35,0.07,0.07) and (0.3,0,0) respectively. $\Gamma(4-6)$ transitions at 6.13 eV make a small contribution to the 6.17 eV peak. The corresponding structure in the experimental $R(\omega)$ is a slight shoulder extending from 5.95 to 6.0 eV. The assignment of 6.13 eV to $\Gamma(4-6)$ transitions agrees very well with the results of photoemission experiments.^{53,54}

The large peak in the calculated reflectivity at 6.67 eV is caused by (4-6) transitions from a large volume of the zone centered at (0.6,0.5,0.2). This peak is broadened by $L(4-6)$ transitions at 6.79 eV

and $\Lambda(4-6)$ transitions at 6.89 eV coming from the point (0.36,0.36,0.36) in the zone. Transitions at 6.8 to 7.0 eV near the zone edge from W to K make a negligible contribution to this peak contrary to the suggestion of reference.⁵⁴ The small peak at 7.13 eV in $\epsilon_2(\omega)$ and $R(\omega)$ arises mainly from volume (4-7) transitions near (0.6,0.3,0.14); $\Sigma(2-5)$ transitions also contribute to this peak.

The 7.38 eV peak in the calculated $R(\omega)$ is caused by (3-6) transitions from a large volume centered at (0.6,0.5,0.2) with an average transition energy of about 7.36 eV. The experimental peak occurs at 7.44 eV.

The 7.63 eV peak in $\epsilon_2(\omega)$ corresponds to the 7.6 eV peak in the reflectivity data. This peak is caused by (3-7) transitions from a volume near (0.6,0.2,0.1) and is not related to the 6.82 eV peak through spin-orbit splitting of the bands at L as suggested by Cardona and Greenaway.⁵¹ Our result that the 6.8 and 7.6 eV peaks are caused by transitions to different final states are consistent with the photo-emission studies of Shay and Spicer.⁵⁴

The over-all agreement between the theoretical and experimental reflectivity data is very good for CdTe. The enhancement of the experimental peaks at L may be caused by excitonic effects. We will discuss further in the final section of this paper.

b. HgTe. At the Γ point this compound is a zero-gap semiconductor with the conduction and valence bands degenerate at Γ_8 . Away from Γ , we expect the energy of the top valence band to increase slightly, i.e. HgTe is in principle a semimetal. Unlike CdTe and most other zincblende structures, HgTe has an inverted order of bands Γ_6 and Γ_8 ,

as first suggested by Groves and Paul.⁵⁵ The spin-orbit splitting of the top valence bands at Γ is about 0.30 eV at 1.5°K.^{56,57} This agrees very well with the calculated value of 0.30 eV. The calculated spin-orbit splittings $\Delta_0 = \Gamma_{8V} - \Gamma_{7V}$ and $\Delta_1 = L_{4,5V} - L_{6V}$ are 0.94 and 0.62 eV respectively. The splitting of the valence bands at L was fitted to 0.62 eV by adjusting the spin-orbit parameter. The experimental value of 0.64 eV was obtained by Carbona Greenaway⁵¹ at 77°K.

The peaks occurring at 2.32 and 2.92 eV in the calculated reflectivity are caused by spin-orbit split L(4-5) and L(3-5) transitions at 2.25 and 2.87 eV. These peaks correspond to the experimental peaks at 2.25 and 2.87 eV. The experimental reflectivity has a shoulder starting at 4.18 eV caused by (4-5) transitions extending from 4.0 to 4.2 eV. The matrix element for these transitions has a maximum near 4.03 eV; the theoretical reflectivity does not have conspicuous structure at this energy because of the sharp rise of the reflectivity resulting from other sets of transitions. However, a calculation of the modulated reflectivity, $\frac{1}{R(\omega)} \frac{dR}{d\omega}$ shows that $R(\omega)$ does have a small peak near 4.03 eV.

The calculated reflectivity has a shoulder beginning at 4.47 eV arising from volume (4-5) transitions from a region of the zone centered at (0.8,0.2,0.2) with an average transition energy of 4.42 eV. Transitions from nearly the same region of the zone give rise to the 5.27 eV peak in CdTe and were associated with the critical point (0.9,0.2,0.2). For HgTe the corresponding critical point is at (1,0.2,0.2) and the transition

energy is 4.61 eV. These transitions do not give rise to a peak because of the sharp rise of the reflectivity spectra leading to the main peak at 4.87 eV.

The peak at 4.87 eV in the theoretical $R(\omega)$ is caused mainly by $\Sigma(4-5)$ transitions occurring at points near K. The strength of this peak is increased by $X(3-5)$ transitions at 4.71 eV. The contribution of the $\Sigma(4-5)$ transitions to this peak is more than four times as large as the contribution of the $X(3-5)$ transitions. The corresponding reflectivity peak is at 4.98 eV.

The peak at 5.02 eV in the calculated reflectivity is caused by (4-6) transitions from a large volume of the zone near Γ and around Δ . The $\Gamma(4-6)$ transitions at 4.92 eV and the critical point transitions at 5.00 and 5.02 eV from (0.14,0,0) and (0.14,0.07,0.07) contribute to this peak. The reflectivity decreases very slowly between 5.07 and 5.17 eV because of (4-6) transitions. The $X(4-6)$ transitions at 5.09 eV and (4-6) transitions from a group of points near Δ give rise to a local maximum at 5.12 eV in the matrix element for (4-6) transitions. This is in addition to the larger maximum occurring at 5.02 eV.

The experimental reflectivity has two small peaks at 5.45 and 5.62 eV. The 5.45 eV peak is, most probably, caused by $X(3-6)$ transitions at 5.43 eV and $\Gamma(4-7)$ transitions at 5.44 eV. The contributions of the $X(3-6)$ transitions is about 3 times as large as the contributions of the $\Gamma(4-7)$ transitions. The matrix element for both sets of transitions has a maximum at 5.47 eV, but any associated reflectivity structure seems to have been absorbed in the broad peak centered at

5.57 eV. This 5.57 eV peak is caused by (3-6) critical point transitions at 5.52 eV from (0.2,0,0) and at 5.57 eV from (0.15,0.07,0.07).

The large and broad peak in the reflectivity data at 6.53 eV is caused by volume (4-6) transitions from a region of the zone centered at (0.6,0.5,0.3); L(4-6) transitions at 6.49 eV also contribute to this peak. The theoretical reflectivity peak occurs at 6.63 eV and is in fairly good agreement with the experimental value. Cardona and Greenaway⁵¹ assign the 6.53 eV peak to L(4-6) transitions.

The peak at 7.07 eV in the calculated $R(\omega)$ arises from (3-6) transitions from a region of the zone centered at (0.6,0.5,0.3). The magnitude of this peak is much smaller than the corresponding spin-orbit split volume (4-6) transitions at 6.63 eV. The experimental reflectivity, however, does not show a corresponding peak. There is also no contribution to this peak from L(3-6) transitions at 7.10 eV even though this peak is close in energy.

The peak at 7.57 eV in the calculated reflectivity is caused by volume (4-7) transitions at an average energy of 7.47 eV from a region of the zone centered at (0.6,0.4,0.1). In addition L(3-7) transitions at 7.36 eV also contribute to this peak. The L(3-7) transitions contribute 30 percent of the value of the $\epsilon_2(\omega)$ peak at 7.38 eV. The spin-orbit split L(4-7) transitions at 6.75 eV have weak matrix elements and do not give rise to any peaks. The peak at 7.88 eV in $R(\omega)$ is caused by volume (3-7) transitions from a region of the zone centered at (0.6,0.3,0.1). The experimental reflectivity peak corresponding

to the 7.57 and 7.88 eV peaks in the theoretical reflectivity is the broad peak at 7.6 eV.

The peaks at 8.17 eV in $\epsilon_2(\omega)$ and 8.32 eV in $R(\omega)$ are caused by volume (3-7) transitions from a region of the zone centered at (0.6, 0.3, 0.1). The spin-orbit split (3-7) transitions from this region contribute both to the 7.88 and 8.32 eV peaks.

Scouler and Wright⁵⁸ assign their 7.5 and 8.25 eV peaks to spin-orbit split L(3,4-6) transitions and deduce a Δ_1 value of 0.75 eV. This value for Δ_1 seems to be too large compared to the value of 0.62 eV obtained from the spin-orbit split L(4-5) and L(3-5) transitions at 2.25 and 2.87 eV. The value of Δ_1 obtained from L(4-6), L(3-6) transitions in our case is 0.61 eV, close to the value of 0.62 obtained from L(4-5), L(3-5) transitions.

5. Discussion of Results

The enhancement of some experimental peaks relative to the theoretical peaks, particularly near the first Λ and L transitions, are probably caused by excitons. The effect of the Coulomb interaction between electrons and holes on the four different types of critical points has been investigated by several authors.⁵⁹⁻⁶⁴ The effect of such interactions on an M_1 type critical point occurring at L or "L-like" points where $m_1 = m_2 > 0$ and for the case $|m_3| \gg m_1$ with m_1, m_2, m_3 being the principal effective masses has been calculated by Kane.⁶⁴ His calculations indicate that the most characteristic feature of an M_1 critical point, with electron-hole Coulomb interactions taken into account, is the sharp dropoff in $\epsilon_2(\omega)$ and $R(\omega)$ near the critical point. This is particularly

evident in the case of CdTe where the reflectivity drops sharply at 3.46 and 4.03 eV. According to Kane's calculations the small structure in the measured reflectivity at 3.60 and 4.20 eV actually correspond to the M_1 critical point transitions near L. The prominent peaks at 3.46 and 4.03 eV are to be associated with the electron-hole bound state. The binding energy of the exciton is given by the energy difference between the M_1 structure at 3.60 eV and the main peak at 3.46 eV and is about 0.14 eV. In HgTe the binding energy of the exciton has been assumed to be small⁶⁵ (about 0.04 eV). If this is the case, the corresponding M_1 structure is not expected to be resolvable experimentally.

In many cases our resolution was not sufficient to discuss all the calculated critical points. Tables I and II contain only prominent critical points.

Table I. CdTe. Theoretical and experimental reflectivity structure at 15°K and their identification. The symmetry location in the zone and the transition energy at the critical points are given.

Reflectivity Structure		Associated Critical Points (CdTe)		
Theory	Exper.	Location in Zone	Sym	c_p energy
1.59 eV	1.59 eV	$\Gamma(4-5)$ (0,0,0)	M_0	1.59 eV
3.42	3.46	$\Lambda(4-5)$ (0.43,0.43,0.43)	M_1	3.39
3.97	4.03	$\Lambda(3-5)$ (0.43,0.43,0.43)	M_1	3.95
5.02	-	Volume near $\Delta(4-5)$ (0,7,0,0)	-	5.05
5.27	5.18	$\langle 4-5 \rangle$ (0.9,0.2,0.2)	M_1	5.27
5.47	5.53	$\Sigma(4-5)$ (0,7,0,7,0)	M_2	5.42
5.52		$\Delta(3-5)$ (0,7,0,0)	M_1	5.51
5.37	5.68	$\langle 4-6 \rangle$ (0.35,0.07,0.07)	-	5.63
		$\Delta(4-6)$ (0.2, 0,0)	-	5.73
6.07	5.95	$\langle 3-6 \rangle$ (0.35,0.07,0.07)	-	6.07
6.17		$\Delta(3-6)$ (0.3,0,0)	M_1	6.14
6.87	6.82	Volume $\langle 4-6 \rangle$ (0.8,0.5,0.2)	-	6.62
7.13	-	Volume $\langle 4-7 \rangle$ (0.8,0.3,0.14)	-	7.10
7.38	7.44	Volume $\langle 3-6 \rangle$ (0.6,0.5,0.2)	-	7.38
-	7.6	Volume $\langle 3-7 \rangle$ (0.6,0.2,0.1)	-	7.6

Table II. HgTe. Theoretical and experimental reflectivity structure at 10°K and their identification. The symmetry, location in the zone and the transition energy at the critical points are given.

Reflectivity Structure		Associated Critical Points (HgTe)		
Theory	Exper.	Location in Zone	Sym	c_p energy
0 eV	0 eV	$\Gamma(4-5) (0,0,0)$	M_0	0 eV
2.32	2.25	$L(4-5) (0.5,0.5,0.5)$	M_1	2.25
2.92	2.87	$L(3-5) (0.5,0.5,0.5)$	M_1	2.87
4.03	4.18	Volume near $\Delta(4-5) (0.6,0,0)$	-	4.03
4.47	-	Volume $(4-5) (0.8,0.2,0.2)$	-	4.42
-	-	$X(3-5) (1,0,0)$	M_1	4.71
4.87	4.98	$K(4-5) (0.75,0.75,0)$	M_2	4.82
5.02	5.10	$\Delta(4-5) (0.14,0,0)$	-	5.00
		$(4-5) (0.14,0.07,0.07)$	M_2	5.02
-	5.45	$X(3-5) (1,0,0)$	M_1	5.43
		$\Gamma(4-7) (0,0,0)$	-	5.44
5.57	5.62	$\Delta(3-5) (0.2,0,0)$	M_1	5.52
		$(3-5) (0.15,0.07,0.07)$	-	5.57
6.63	6.53	Volume $(4-5) (0.5,0.5,0.3)$	-	6.53
7.07	-	Volume $(3-5) (0.6,0.5,0.3)$	-	7.02
7.57	7.6	Volume $(4-7) (0.6,0.4,0.1)$	-	7.47
7.88		Volume $(3-7): [5-13]^+ (0.6,0.3,0.1)$		7.75
8.32	8.3	Volume $(3-7): [5-14]^+ (0.6,0.3,0.1)$	-	8.2

*In this notation the bands are numbered consecutively with the doubly degenerate top valence bands at Γ and L numbered 7 and 8.

Table III Calculated spin-orbit splittings for CdTe and HgTe

	CdTe	HgTe
$\Gamma_{8V} - \Gamma_{7V}$	0.91	0.94
$\Gamma_{8C} - \Gamma_{6V}$	-	0.30
$L_{4,5V} - L_{6V}$	0.57	0.62
$X_{7V} - X_{6V}$	0.46	0.35
$\Gamma_{8C} - \Gamma_{7C}$	0.13	0.51
$L_{4,5C} - L_{6C}$	0.06	0.26

Table IV. Comparison of the CdTe and HgTe form factors (in Ry) obtained in the present work (on top) with those of Refs. 33 & 47.

	$V^S(3)$	$V^S(8)$	$V^S(11)$	$V^A(3)$	$V^A(4)$	$V^A(11)$	$V^A(12)$	spin-orbit parameter
CdTe	-0.200	-0.012	0.027	0.168	0.075	0.028	0	0.0014
	-0.20	0.00	0.04	0.15	0.09	0.04	0	--
HgTe	-0.262	-0.035	0.05	0.10	0.042	0.02	0.019	0.0028
	-0.23	-0.025	0.03	0.095	0.08	0.03	0.03	--

Figure Captions

- Fig. 1. Electronic band structure of CdTe in the principle symmetry directions.
- Fig. 2. Electronic band structure of HgTe in the principle symmetry directions.
- Fig. 3. Imaginary part of the dielectric function, $\epsilon_2(\omega)$ of CdTe.
- Fig. 4. Imaginary part of the dielectric function, $\epsilon_2(\omega)$ of HgTe.
- Fig. 5. Experimental and theoretical reflectivity spectra of CdTe.
- Fig. 6. Experimental and theoretical reflectivity spectra of HgTe.

XBL 748-7042

k
Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

NRL 748-7046

XBL 748-7047

Fig. 6.

B. Band Structures and Charge Distributions in CdTe-HgTe Alloys

Abstract

In this section we discuss the results of our calculations of the electronic band structures and charge densities near Γ for the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloy system. We find the energy gap to vary linearly with x , with the semimetal-semiconductor transition occurring at $x = 0.165$. The total electronic charge densities of HgTe and CdTe are calculated by using a weighted sum of the charge densities at a few symmetry points in the Brillouin zone and for the non-symmetry point used by Baldereschi. We show that for a large class of semiconducting compounds the total electronic charge density can be obtained to a very high degree of accuracy using these representative k-points.

1. Introduction

The two zincblende compounds HgTe and CdTe form a continuous series of alloys⁶⁶⁻⁶⁸ denoted by $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ where x is the mole fraction of CdTe in the alloy. This alloy system has been of great interest in recent years because of the wide range of its physical properties. These alloys are a mixture of a semimetal (HgTe) with a semiconductor (CdTe); the energy gap E_G in the alloys varies continuously^{69,70} between the -0.30 eV ⁵⁷ "negative" gap found in HgTe to the 1.60 eV ⁷¹ gap found in CdTe. Narrow gap semiconducting alloys in this system have proved useful as infrared detectors.⁷²

Interest in the band structures of the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys has been concentrated mainly in the region of the Brillouin zone near Γ .

It is in this region where the band structures change most with alloying. The band structures¹⁵ for HgTe and CdTe were discussed in section A. In this section we present detailed results of our calculations of the band structures of the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys along symmetry directions near Γ . The calculation is described briefly in section 2 and the band structures are discussed in section 3. The charge densities for the Γ_6 and Γ_8 levels as well as the total valence band charge density near Γ are discussed in section 4. The way in which the position of the Γ_6 level affects the total charge density at Γ is also discussed in section 4. In section 5 we show how the charge density at a few symmetry points can be used to calculate the total electronic charge density for each band in a crystal. The accuracy of the charge density obtained using representative k-points in this way is discussed in section 6. In this section we also present the results of our calculation for the total electronic charge densities of CdTe and HgTe obtained by the approximation method described in section 5. The results for CdTe are compared with a previous calculation⁷³ using a large number of points in the Brillouin zone.

2. Band Structure Calculation

Our calculation of the band structures of the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys are based on the empirical pseudopotential method and the virtual crystal approximation. The pseudopotential form factors¹⁵ for HgTe and CdTe were obtained in section A by fitting the theoretical optical reflectivity spectra to the experimental data. In the present calculation we have used the same form factors for HgTe as in section A

but the form factors for CdTe have been modified slightly because we have increased the number of plane waves used in the expansion of the wavefunctions. This was done in order to have the same number of plane waves for CdTe as for HgTe. The new form factors for CdTe were constrained to give nearly the same energy differences at Γ , X, L and K as in our previous work. The symmetric and antisymmetric form factors (in Ry) for CdTe used in the present calculations are:

$$V_S(|\vec{G}|^2 = 3) \approx -0.234, V_S(8) = -0.042, V_S(11) = 0.041, V_A(3) = 0.151,$$

$V_A(4) \approx 0.068, V_A(11) = 0.005$ and $V_A(12) = 0$. Spin-orbit interactions were included in the calculation as in section A. The spin-orbit parameter^{15,35} was set equal to 0.0011 (Ry) for CdTe. This gives $\Delta_0 = E(\Gamma_8) - E(\Gamma_7) \approx 1.02$ eV and $\Delta_1 = E(L_{4,5}) - E(L_6) = 0.6$ eV. The band structures were calculated by taking 59 plane waves into account exactly while treating an extra 54 plane waves through the Löwdin⁴⁴ perturbation scheme. The size of the matrix was 118x118 (i.e. 59 plane waves for each spin).

The pseudopotential for the alloys were taken to be the average of the HgTe and CdTe pseudopotentials. The averaging included the spin-orbit component of the Hamiltonian. The pseudopotential form factors were scaled for the small changes in the lattice constant. The lattice constants adjusted to 0°K are 6.45 Å for HgTe and 6.48 Å for CdTe. The lattice constant changes almost linearly with x .⁷⁴

3. Band Structure Results

The calculated variation of the energy gap defined as $E_G = E(\Gamma_6) - E(\Gamma_8)$ was found to be linear with x at 0°K. The energy gap changes sign when x increases from 0.16 to 0.17. The energy gap is -0.01 eV at $x = 0.16$ and is +0.01 eV at $x = 0.17$. The exact value of x at the semimetal-semiconductor transition point is temperature dependent. For both HgTe and CdTe x decreases with temperature^{70,75} thereby lowering the value of x at which the transition occurs at higher temperatures. The calculated value of x at the transition point is $x = 0.165$ at 0°K. This value is in excellent agreement with indirect measurements of the energy gap at low temperatures using magnetoreflexion experiments,⁷⁶ and with the value obtained from the temperature dependence of the Hall constant.⁷⁷ For a highly homogeneous sample with $x = 0.161 \pm 0.003$, Groves and Harman⁷⁶ report $E_G = -0.01$ at $T = 25^\circ\text{K}$ and $E_G = 0.01$ eV at $T \approx 90^\circ\text{K}$. Vérie⁷⁷ estimates $x \approx 0.160 \pm 0.005$ for the transition point at low temperatures.

The calculated variation of the energy gap E_G and the spin-orbit splittings Δ_0 and Δ_1 are shown in Fig. 1, where it is seen that all these energies vary linearly with x . In Fig. 2 we show the band structures for the top two valence bands and the first conduction band for HgTe, CdTe and two alloys near the transition point. The band structures extend from Γ to $|\vec{k}| = 0.18 (\frac{2\pi}{a})$ in the Λ and Δ directions. Near the transition point the variation of energy with wavevector is almost linear in the region near Γ for the Γ_6 level and for the Γ_8 light mass band. This is in agreement with the band structure obtained

from the Kane secular equation⁷⁸ for the case when $E_G \approx 0$.

4. Charge Densities near Γ

The alloys $Hg_{1-x}Cd_xTe$ have an inverted band structure similar to that of grey tin for $x < 0.165$ (Fig. 2). It is interesting to see how the position of the Γ_6 level with respect to the degenerate Γ_8 levels affects the electronic charge density near Γ . Figures 3 and 4 show the charge densities of the Γ_6 and Γ_8 levels for HgTe and CdTe. The charge density has been evaluated at about 1600 points in a $(1, \bar{1}, 0)$ plane which contains both the Hg-Cd and Te sites in the primitive cell. The charge density has been normalized to $\frac{2e}{\Omega}$ where Ω is the volume of the primitive cell. The charge densities of the Γ_6 and Γ_8 levels in HgTe are nearly the same as the corresponding charge densities in CdTe, i.e. the Γ_6 and Γ_8 levels have retained their identity regardless of whether they are part of the valence or conduction bands.

In Fig. 5 we show the charge densities for the sum of the valence bands near Γ for HgTe, CdTe and the alloy $Hg_{0.833}Cd_{0.167}Te$ near the transition point. The charge densities for HgTe and CdTe have different characteristics. For HgTe, the maximum of the charge distribution occurs exactly at the Te site while for CdTe the maximum is shifted toward Cd. The difference in charge densities is directly related to the position of the Γ_6 level in these compounds. In CdTe only the lowest valence band has largely an s-like character, but in HgTe the s-like character of the Γ_6 valence band has been added to the s-like character of the lowest valence band and one of the p-like Γ_8 bands has become the first conduction band. This difference in charge densities persists

in the alloys $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$; the charge density being nearly identical to the HgTe or CdTe charge densities depending on the position of the Γ_6 level. Also shown in Fig. 5 is the charge density for an alloy with a very small positive energy gap. Because of the large mixing of wavefunctions at Γ for this alloy a charge density whose characteristics are intermediate between those of HgTe and CdTe has been obtained.

The charge densities of the sum of valence bands for HgTe and CdTe are shown in Fig. 6. These charge densities were calculated using an approximation scheme described in section 5. The total valence band charge densities of HgTe and CdTe show a greater similarity to each other than the corresponding charge densities calculated near Γ (Fig. 5). Although for HgTe the maximum in the charge density is still at Te, the difference between CdTe and HgTe is less than is implied from the charge distributions near Γ (Fig. 5), where the Γ_6 level has greatly influenced the HgTe charge distribution.

5. Calculation of Charge Densities from a Few Representative Points in the Brillouin Zone

We can ask the question whether it is possible to obtain a good approximation to the charge density by using the charge densities of a small number of points in the Brillouin zone. Baldereschi^{16,17} has recently proposed using only one $\vec{k}$ - point to calculate the average charge density. For fcc crystals the coordinates^{16,17} of this point are $\frac{2\pi}{a}$ (0.622, 0.295, 0). We will show a general method of obtaining the charge density of semiconducting crystals by using the charge density calculated for a few points. We also obtain the representative point chosen by Baldereschi (referred to here as the Baldereschi point)

for fcc crystals when only one point in the Brillouin zone is used for the charge density calculation. The accuracy of this method in obtaining the charge density is discussed in section 6. A more elegant method of obtaining representative $\vec{k}$ points for any crystal structure is discussed in section IV.

The procedure is to express the wavefunctions and charge densities in terms of the Wannier functions. For a given band we can express the Bloch functions in a given band in terms of the Wannier functions for that band:

$$\psi_{\vec{k}}^+(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{m}} e^{i\vec{k} \cdot \vec{R}_{\vec{m}}} a(\vec{r} - \vec{R}_{\vec{m}})$$

where the band index has been suppressed, $\vec{R}_{\vec{m}}$ is a lattice vector, and $a(\vec{r} - \vec{R}_{\vec{m}})$ is a Wannier function centered on $\vec{R}_{\vec{m}}$. The charge density associated with this wavefunction is

$$\begin{aligned} \rho_{\vec{k}}^+(\vec{r}) &= \psi_{\vec{k}}^*(\vec{r}) \psi_{\vec{k}}^+(\vec{r}) = \\ &= \frac{1}{N} \sum_{\vec{m}, \vec{n}} e^{i\vec{k} \cdot (\vec{R}_{\vec{m}} - \vec{R}_{\vec{n}})} a(\vec{r} - \vec{R}_{\vec{m}}) a^*(\vec{r} - \vec{R}_{\vec{n}}) . \end{aligned} \quad (1)$$

The total charge density for the given band is

$$\rho(\vec{r}) = \sum_{\vec{k}} \rho_{\vec{k}}^+(\vec{r}) = \sum_{\vec{m}} |a(\vec{r} - \vec{R}_{\vec{m}})|^2 . \quad (2)$$

The expression for $\rho_{\vec{k}}^+(\vec{r})$ in (1) can be written in the following way:

$$\rho_{\vec{k}}^+(\vec{r}) = \frac{1}{N} \sum_{\vec{m}} |a(\vec{r} - \vec{R}_{\vec{m}})|^2 + \frac{1}{N} \sum_j' \sum_{\vec{m}} e^{i\vec{k} \cdot \vec{R}_j} a(\vec{r} - \vec{R}_{\vec{m}}) a^*(\vec{r} + \vec{R}_j - \vec{R}_{\vec{m}}), \quad (3)$$

where the prime in the sum over j means that the term with $\vec{R}_j=0$ is not included in the sum. The first sum in (3) is proportional to the total charge density for the given band and is actually the average charge density of an electron in that band. Our purpose is therefore to try to minimize the second sum in (3). To do this, consider the set of wavevectors obtained from a general wavevector $\vec{k}=(k_1 k_2 k_3)$ by performing all possible permutations and sign changes on the components. We can generate up to 48 different $\vec{k}$ vectors from a given one using these operations, which will be specified by T . The charge densities $\rho_{\vec{k}}^+(\vec{r})$ associated with each one of these wavevectors can be calculated easily once the charge density for one of them is known by using the symmetry operations of the Hamiltonian. The sum of charge densities obtained in this way from the charge density $\rho_{\vec{k}}^+(\vec{r})$ is given by

$$\begin{aligned} \sum_T \rho_{T\vec{k}}^+(\vec{r}) &= \frac{1}{N} \sum_T \sum_{\vec{m}} |a(\vec{r} - \vec{R}_{\vec{m}})|^2 + \\ &\quad \frac{1}{N} \sum_j' \sum_{\vec{m}} \sum_T e^{i(T\vec{k}) \cdot \vec{R}_j} a(\vec{r} - \vec{R}_{\vec{m}}) a^*(\vec{r} + \vec{R}_j - \vec{R}_{\vec{m}}). \end{aligned} \quad (4)$$

The first term in (4) is independent of any sign changes and permutations of $\vec{k}$ so the sum over T just multiplies this term by 48. Let $F(\vec{r})$ be the second sum in (4), then $F(\vec{r})$ can be expressed in the following way:

$$F(\vec{r}) = \frac{1}{N} \sum_j e^{i\vec{k} \cdot \vec{R}_j} \sum_m \sum_T a(\vec{r} - \vec{R}_m) a^*(\vec{r} + T\vec{R}_j - \vec{R}_m) . \quad (5)$$

For any given $\vec{R}_j$, $T\vec{R}_j$ is a lattice vector of the same magnitude as $\vec{R}_j$, therefore the sum

$$S(\vec{r}) = \sum_m \sum_T a(\vec{r} - \vec{R}_m) a^*(\vec{r} + T\vec{R}_j - \vec{R}_m) \quad (6)$$

in (5), for a given $\vec{R}_j$, remains constant under all permutations and sign changes of $\vec{R}_j$. The condition that $F(\vec{r})$ be zero can be fulfilled if we require the wavevector $\vec{k}$ to satisfy the following set of equations:

$$\sum_{|\vec{R}_j| = c_m} e^{i\vec{k} \cdot \vec{R}_j} = 0 \quad m = 1, 2, 3, \dots \quad (7)$$

where $c_m = m^{\text{th}}$ nearest neighbor distance. In the case where two lattice vectors, such as $\vec{R}_1 = (2 \frac{1}{2} \frac{1}{2})a$ and $\vec{R}_2 = (\frac{3}{2} \frac{3}{2} 0)a$ in the fcc structure, have the same magnitude but the coordinates are not related by any permutations or sign changes, Eq. (7) must be satisfied for each set of lattice vectors separately.

For the fcc crystal structure, letting $\vec{k} = \frac{2}{a} (k_1 \ k_2 \ k_3)$, the equations to be satisfied are of the following form for the first three nearest neighbors:

$$\cos k_1 \cos k_2 + \cos k_1 \cos k_3 + \cos k_2 \cos k_3 = 0 \quad (8)$$

$$\cos 2k_1 + \cos 2k_2 + \cos 2k_3 = 0 \quad (9)$$

$$\cos 2k_1 \cos k_2 \cos k_3 + \cos k_1 \cos 2k_2 \cos k_3 + \cos k_1 \cos k_2 \cos 2k_3 = 0 . \quad (10)$$

The point $\frac{2\pi}{a}$ (0.622, 0.295, 0) proposed by Baldereschi satisfies (8) and (9). It is possible to show that for the fcc crystal structure there is no $\vec{k}$ which will satisfy (8) - (10) simultaneously. We can, however, use more points in the Brillouin zone in order to satisfy a greater number of the conditions of (7). In fact we can use the weighted sum of the charge density at a few points in the Brillouin zone to do this. If the charge density is going to be approximated by

$$\rho(\vec{r}) = \sum_T \sum_{i=1} \alpha_i \rho_{T\vec{k}_k}(\vec{r}) \quad (11)$$

then the conditions, similar to those in (7), to be satisfied are

$$\sum_{i=1}^n \sum_{|\vec{R}_j|=c_m} \alpha_i e^{i\vec{k}_i \cdot \vec{R}_j} = 0 \quad m = 1, 2, 3, \dots, \quad (12)$$

where

n is the number of points being used and as before $c_m = m^{\text{th}}$ nearest neighbor distance. We must also require

$$\sum_{i=1}^n \alpha_i = \frac{1}{48} \quad (13)$$

in order to have the proper normalization for the charge density. The conditions (12) are most easily satisfied by symmetry points. For example, the three symmetry points Γ , X and L can be used in this way to calculate the charge density. The charge density is then given by

$$\rho(\vec{r}) = \frac{1}{8} \rho_{\Gamma}(\vec{r}) + \frac{3}{8} \rho_X(\vec{r}) + \frac{1}{2} \rho_L(\vec{r})$$

where by $\rho_X(\vec{r})$ and $\rho_L(\vec{r})$ we mean the symmetrized charge densities at these points, (i.e., $\rho_X(\vec{r}) = \frac{1}{48} \sum_T \rho_{T(1,0,0)}(\vec{r})$, T being the set of 48 permutations and sign changes of the coordinates of a general wavevector; for X this gives $\rho_X(\vec{r}) = \frac{1}{3} (\rho_{(1,0,0)}(\vec{r}) + \rho_{(0,1,0)}(\vec{r}) + \rho_{(0,0,1)}(\vec{r}))$). The symmetry points Γ , X , and L used in this combination satisfy the conditions (12) for the first three nearest neighbors and should therefore give a better charge density than the Baldereschi point; furthermore, the calculation of wavefunctions and charge densities is simpler for symmetry points than for general points. A better scheme with three symmetry points is obtained by using a weighted sum of the symmetrized charge densities at $\vec{k}_1 = (0.5, 0, 0)$, $\vec{k}_2 = (1.0, 0.5, 0)$ and $\vec{k}_3 = (0.5, 0.5, 0)$ with the weighting factors $\alpha_1 = \frac{1}{4}$, $\alpha_2 = \frac{1}{4}$ and $\alpha_3 = \frac{1}{2}$ respectively.

6. Accuracy of the Representative k-Point Scheme for Charge Density

The scheme outlined in section V for the calculation of charge densities from a few representative points in the Brillouin zone is clearly valid only for completely filled bands and therefore is not very useful for metals. It will give accurate results when the Wannier functions representing the bands are well-localized. The magnitude of the error in the charge density is given by $F(\vec{r})$ in (5). This error will decrease rapidly when the conditions (7) or (12) are satisfied beyond the nearest neighbor shells in which the Wannier

functions are well localized. The Wannier function for a band is not unique; it is related to the Bloch functions in the band by

$$a(\vec{r}) = \sum_{\vec{k}} \psi_{\vec{k}}(\vec{r}) e^{i\theta(\vec{k})}, \quad (14)$$

where the $\theta(\vec{k})$ are arbitrary real numbers. The localization of the Wannier function $a(\vec{r})$ depends on the choice of the $\theta(\vec{k})$. The localization of the Wannier functions for the one-dimensional case has been treated by Kohn⁷⁹ and the general case has been treated by Blount.⁸⁰

We have used the approximation schemes described in section V to calculate the electronic charge densities for HgTe, CdTe and some other semiconductors. A comparison of our results for the sum of the valence band charge densities of CdTe with previous calculations⁷³ using a large number of points in the Brillouin zone, shows excellent agreement between the two. The total charge densities for CdTe and HgTe were calculated in two different ways: first by using the Baldereschi point $\frac{2\pi}{a}$ (0.622, 0.295, 0) and then by using a weighted sum of the charge densities at $\frac{2\pi}{a}$ (0.5, 0, 0), $\frac{2\pi}{a}$ (1.0, 0.5, 0) and $\frac{2\pi}{a}$ (0.5, 0.5, 0), as described in section V. For CdTe the total charge densities obtained in these two ways were found to agree with one another and with the 71 point calculation⁷³ to about $\pm 1\%$. The sum of the valence band charge densities for HgTe and CdTe obtained in this way are shown in Fig. 6.

The accuracy of the approximation schemes is less for the individual valence band charge densities than for the sum of the valence band charge densities. The scheme using the weighted sum of charge densities at (0.5, 0, 0), (1.0, 0.5, 0) and (0.5, 0.5, 0) (in units of $\frac{2\pi}{a}$) gives individual

valence band charge densities to an accuracy of $\pm 5\%$ for many crystals. The accuracy of the Baldereschi point is lower than the three point scheme as may be expected. The reason why the total charge density turns out to be more accurate than individual band charge densities is that even though the Wannier functions for the individual bands may not be localized, we can construct a set of composite Wannier functions from these bands such that they are more localized and such that they will give the total charge density. For n interacting bands we can construct n composite Wannier functions:

$$a_i(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} \sum_{m=1}^n U_{im}(\vec{k}) \psi_{k,m}(\vec{r}), \quad i = 1, \dots, n, \quad (15)$$

with the requirement that $U(\vec{k})$ be a unitary matrix for each $\vec{k}$. These Wannier functions are constructed from a combination of Bloch functions from different bands m , and satisfy the usual properties of Wannier functions. The Bloch wavefunctions can be expressed in terms of these composite Wannier functions:

$$\psi_{k,m}^*(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{i=1}^n \sum_j U_{im}^*(\vec{k}) e^{i\vec{k} \cdot \vec{R}_j} a_i(\vec{r} - \vec{R}_j). \quad (16)$$

The sum of the charge densities of the n bands is then given by

$$\sum_{m=1}^n \sum_{\vec{k}} \psi_{k,m}^*(\vec{r}) \psi_{k,m}(\vec{r}) = \sum_{i=1}^n \sum_j |a_i(\vec{r} - \vec{R}_j)|^2. \quad (17)$$

This expression is similar to (2) with the exception that in (17), $a_i(\vec{r})$ does not represent the Wannier function of any given band. There is considerably more freedom in constructing the composite Wannier

function (15) than the simple Wannier functions (14). This extra degree of freedom can be used to make the composite functions very localized particularly if the bands from which they are constructed do not interact strongly with other bands. The approximation schemes described in section V can be easily extended to these new Wannier functions for the calculation of the total charge density. The representative points in the Brillouin zone giving the total charge density are again found to satisfy the conditions (7) or (12). These localized Wannier functions provide at least some explanation for the fact that the calculation of the valence band charge densities using only a few representative points turn out to be so accurate.

Figure Captions

- Fig. 1. Variation of the energy gap E_G and spin-orbit splittings at Γ and L with alloying for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys.
- Fig. 2. Band structures near Γ for HgTe, CdTe and two alloys near the semimetal-semiconductor transition region. The band structures extend from Γ to $|\vec{k}| = 0.18 \left(\frac{2\pi}{a}\right)$ in the Λ and Λ directions.
- Fig. 3. HgTe charge densities near Γ for the Γ_8 conduction and valence levels (top), and the Γ_6 valence level (bottom).
- Fig. 4. CdTe charge densities near Γ for the Γ_6 conduction level (top) and the Γ_8 valence level (bottom).
- Fig. 5. Sum of valence band charge densities near Γ for HgTe, $\text{Hg}_{0.167}\text{Cd}_{0.833}\text{Te}$ and CdTe.
- Fig. 6. Total valence band charge densities for HgTe and CdTe. These charge densities have been normalized to $8e/\Omega$.

XBL 748-7048

Fig. 1.

Fig. 2.

XRL 748-7014

XBL 748-7010

Fig. 3.

XBL 748-7013

Fig. 4.

ABL 748-7050

Fig. 5.

Fig. 6.

ARI 7-18-7049

IV. NEW METHOD FOR THE CALCULATION OF AVERAGES OF PERIODIC FUNCTIONS

A. Special Points in the Brillouin Zone

Abstract

In this section we present sets of special points in the Brillouin zone from which the average over the Brillouin zone of a periodic function of wave vector (e.g., energy, charge density, dipole matrix elements, etc.) can be determined in a simple and accurate way once the values of the function at these points are specified. We discuss a method for generating the special-point sets and apply it to the case of crystals with cubic and hexagonal Bravais lattices.

1. Introduction

Many calculations in crystals involve the averaging over the Brillouin zone of a periodic function of wave vector. Such calculations are often long and complicated and in principle require a knowledge of the value of the function at each $\vec{k}$ point in the Brillouin zone. In practice the functional values are known or determined over a set of points in the zone and the values at other points are found by using various types of approximation and interpolation methods. To obtain sufficient accuracy in these calculations it is necessary, in general, to know the functional values over a large set of points.

In this section we present a systematic way of choosing sets of points in the Brillouin zone which makes possible simpler and more accurate calculations of averages over the Brillouin zone of periodic functions of wave vector. With these points one may avoid the use of interpolation in the calculation of averages.

This paper is organized in the following way. In section 2 we discuss the conditions to be satisfied by the special-point sets, and the method for obtaining these sets. A number of special-point sets for crystals with cubic or hexagonal Bravais lattices are derived in section 3. The accuracy of the special-point scheme is discussed briefly in section 4 and the use of these points in obtaining interpolation formulas is discussed in section 5. Results of some calculations using the special points is given in section 6.

2. Generation of Special Points

Special points in the Brillouin zone from which average values (i.e., averaged over the Brillouin zone) of various quantities, such as the charge density^{16,17,81} or energy, can be calculated have recently been proposed, and the conditions to be satisfied by these points have been specified. Up to now no systematic way of satisfying an arbitrary number of these conditions has been suggested. In this section we restate these conditions and develop a method of generating successive sets of points which will satisfy as many of these conditions as one may require for a given accuracy. This method is a generalization of the one we have previously used¹⁶ in charge-density calculations.

We restrict ourselves to smoothly varying periodic functions of wave vector (with periodicity $\vec{G}$, where $\vec{G}$ is any reciprocal-lattice vector). Assuming $g(\vec{k})$ to be such a function we can expand it in a Fourier series:

$$g(\vec{k}) = f_0 + \sum_{m=1}^{\infty} g_m e^{i\vec{k} \cdot \vec{R}_m} \quad (1)$$

From $g(\vec{k})$ we can construct a function $f(\vec{k})$ which has the complete symmetry of the lattice, i.e.,

$$f(\vec{k}) = \frac{1}{n_T} \sum_i g(T_i \vec{k}) , \quad (2)$$

where the T_i 's range over all the operations of the lattice point group T and where n_T is the number of elements in T . We can express $f(\vec{k})$ in the form

$$f(\vec{k}) = f_0 + \sum_{m=1}^{\infty} f_m A_m(\vec{k}) , \quad (3)$$

where

$$A_m(\vec{k}) = \sum_{|\vec{R}|=C_m} e^{i\vec{k} \cdot \vec{R}} , \quad m = 1, 2, \dots \quad (4)$$

The sum in (4) is over equivalent lattice vectors $\vec{R}$ related to each other through the operations of T . The lattice vectors are ordered so that $0 < C_m \leq C_{m+1}$. Equation (4) associates each $A_m(\vec{k})$ with a particular "shell" of lattice vectors. The $A_m(\vec{k})$ are real functions which can be written out in terms of sums and products of cosines and they satisfy the following relations:

$$\frac{\Omega}{(2\pi)^3} \int_{BZ} A_m(\vec{k}) d^3k = 0, \quad m=1, 2, \dots \quad (5)$$

$$\frac{\Omega}{(2\pi)^2} \int_{BZ} A_m(\vec{k}) A_n(\vec{k}) d^3k = N_n \delta_{mn} , \quad (6)$$

$$A_m(\vec{k} + \vec{G}) = A_m(\vec{k}) , \quad (7)$$

$$A_m(\vec{k}) = A_m(\vec{k}'), \quad (8)$$

$$A_n(\vec{k})A_n(\vec{k}) = \sum_j a_j(m,n)A_j(\vec{k}), \quad (9)$$

In these expressions Ω is the volume of the primitive cell, N_n is the number of lattice vectors in shell n , $\vec{G}$ is any reciprocal-lattice vector, T is any element of the lattice point group, and the $a_j(n,m)$'s are integers which can be determined for a specific choice of n and m . We define

$$A_0(\vec{k}) = 1$$

so that $a_j(m,n)$ is defined for $j, m, n \geq 0$. By the average over the Brillouin zone, $\bar{f}$, of f we mean

$$\bar{f} = \frac{\Omega}{(2\pi)^3} \int_{BZ} f(\vec{k}) d^3k. \quad (10)$$

Using (3) and (5) we find $\bar{f} \approx f_0$. The average over the Brillouin zone of $g(\vec{k})$ in (1) is obviously also equal to f_0 . We now present a method for obtaining the approximate value of the integral in (10) by performing a sum over a finite number of optimally chosen $\vec{k}$ points. The approximation can be made as accurate as desired.

The exact value of the integral in (10) would be obtained immediately if there were a point $\vec{k}_0$ which satisfied

$$A_m(\vec{k}_0) = 0, \quad m = 1, 2, \dots, N \quad (11)$$

for $N=\infty$. Then using (3) we would immediately have $\bar{f}=f_0=f(\vec{k}_0)$. Such a point does not in fact exist. The expansion coefficients f_m normally drop rapidly in magnitude as m becomes large so that we actually require (11) to be satisfied for a finite value of N . Baldereschi¹⁷ has obtained for the cubic crystals the point $\vec{k}_0$, which satisfies (11) for $N=2$ or $N=3$ depending on the lattice symmetry. This point, called the "mean-value point" by Baldereschi, gives surprisingly good results when used to calculate the average electron charge density^{16,17} and energy¹⁷ in a number of diamond and zinc-blende crystals. We have previously¹⁶ used three points (called "representative k points" in Ref. 2) which satisfy (11) for the first seven nearest neighbors of an fcc-lattice-structure crystal in charge-density calculations. We show in section 3 a better scheme which involves the use of only two points.

To satisfy (11) for large values of N , a many-point scheme becomes necessary. We impose the following conditions on the points $\vec{k}_i$ and their weighting factors α_i :

$$\sum_{i=1}^n \alpha_i A_m(\vec{k}_i) = 0 \quad m = 1, \dots, N \quad (12)$$

$$\sum_{i=1}^n \alpha_i = 1. \quad (13)$$

With these conditions on $\vec{k}_i$ and α_i one can easily show by using (3), (12), and (13) that the average over the Brillouin zone, f_0 , of $f(\vec{k})$ is

$$f_0 = \sum_{i=1}^n \alpha_i f(\vec{k}_i) = \sum_m \sum_i \alpha_i f_m A_m(\vec{k}_i), \quad (14a)$$

where the prime on the sum over m indicates that those m for which $A_m(k)$ satisfies (12) are excluded from the sum. The first f_m to appear in (14a) is f_{N+1} . Since the expansion coefficients f_m normally drop rapidly in magnitude when m becomes large, by making N in (12) large enough we should have to a good approximation

$$f_0 = \sum_{i=1}^N \alpha_i f(\vec{k}_i) . \quad (14b)$$

Equation (14b) presents a simple way of calculating the average over the Brillouin zone of a periodic function $f(\vec{k})$. All we need are the values of $f(\vec{k})$ for certain $\vec{k}$ points. We define the special points to be those which satisfy (12) by using a minimum number of points for a given value of N . The special points and their corresponding weighting factors are derived for the cubic and hexagonal Bravais-lattice crystals in section 3. In the following we discuss how one can generate sets of points that satisfy (12) for N as large as one may require.

Suppose that the points $\vec{k}_1$ and $\vec{k}_2$ satisfy $A_m(\vec{k}) = 0$ for certain values of m denoted by $\{N_1\}$ (for $\vec{k}_1$) and $\{N_2\}$ (for $\vec{k}_2$). From these two points we can generate a new set of points that will satisfy (12) for m in either $\{N_1\}$ or $\{N_2\}$. One can easily show (see section 7) that the new points $\vec{k}_i$ are related to $\vec{k}_1$ and $\vec{k}_2$ by

$$\vec{k}_i = \vec{k}_1 + \tau_i \vec{k}_2 , \quad (15)$$

with

$$\alpha_i = \text{const.}$$

and with T_1 ranging over all the operations of the lattice point group. The new points $\vec{k}_1$ obtained in this way can be used in a similar process to generate larger sets of points which will satisfy (12) for larger values of N . In each such process each one of the original points gives rise to a number of new points. These points can always be transformed to equivalent points lying in the irreducible part of the Brillouin because the $A_m(\vec{k})$'s satisfy (7) and (8). When this is done the resulting points do not all necessarily have identical weighting factors. This arises from the fact that several of the original points may have been transformed into a single point of the irreducible zone.

When $\vec{k}_2$ in (15) is a symmetry point the set of points $T\vec{k}_2$ does not contain too many elements. However, when this is not the case the number of points generated from an application of (15) can increase rapidly (e.g., by a factor of 48 in the cubic crystals). By a proper choice of $\vec{k}_1$ and $\vec{k}_2$ this can be avoided. We will now apply (15) to generate the special-point sets for the cubic and hexagonal Bravais-lattice structures.

3. Special Points

a. Face-Centered-Cubic Bravais Lattice. This Bravais lattice includes the diamond, zinc-blende, and rocksalt crystal structures. A good choice for a starting point $\vec{k} = (k_x, k_y, k_z)$ is $\vec{k}_1 = (\frac{1}{2}, \frac{1}{2}, 0)$ (units of $2\pi/a$, where a is the lattice constant). Another possible starting point is the point $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. These points are better than other possible starting points because they appear to lead to the smallest possible point sets. With the choice of $\vec{k}_1 = (\frac{1}{2}, \frac{1}{2}, 0)$ or $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ Eq. (11)

is satisfied for the infinite set of nearest-neighbor shells represented by the lattice vectors $\vec{R} = (R_1, R_2, R_3)$ (units of a) whenever at least one R_i is a half-integer. Equation (11) is therefore satisfied for $m=1,3,5,7$, etc. We will choose our second point so that (11) is satisfied for the even m 's. The point $\vec{k}_2 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ satisfies (11) for $m=2,4,6$, etc. The set of points $T\vec{k}_2$ consists of eight different elements. Combining $\vec{k}_1 = (\frac{1}{2}, \frac{1}{2}, 0)$ or $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with $\vec{k}_2$ as in (15) we should get eight points. We find, however, that for either choice of $\vec{k}_1$ these eight points are related by the symmetry operations of T to only two distinct points of the irreducible zone. Six of these points correspond to $\vec{k}_1 = (\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ and the other two to $\vec{k}_2 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. The normalized weighting factors for $\vec{k}_1$ and $\vec{k}_2$ are therefore $\alpha_1 = \frac{3}{4}$ and $\alpha_2 = \frac{1}{4}$, respectively. This leads to the simplest possible two-point scheme for the approximate determination of f_0 in the fcc Bravais-lattice crystals; i.e., we have from (14b)

$$f_0 = \frac{1}{4}[3f(\vec{k}_1) + f(\vec{k}_2)] .$$

The accuracy of these two points in determining f_0 is at least as good as the three-point scheme we have previously¹⁶ used. These two points satisfy (12) for an infinite number of m , but not for all m . The first failure occurs for $m=8$, corresponding to the eighth-largest nearest-neighbor shell represented by the lattice vector $\vec{R} = (2,0,0)$ (units of a). Other failures occur for $\vec{R} = (2,2,0)$, $(2,2,2)$, $(4,0,0)$, etc. The point $\vec{k} = (\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ satisfies (11) for the lattice vectors $(2,0,0)$, $(2,2,0)$, and $(2,2,2)$. The points $\vec{k}_1$ and $\vec{k}_2$ can be used with this point as in (15)

to generate a set of ten points from which the average over the zone of $f(\vec{k})$ can be found with a higher degree of accuracy. The coordinates and relative weights of these points are

$$\vec{k}_1 = (\frac{7}{8}, \frac{3}{8}, \frac{1}{8}), \quad \alpha_1 = \frac{3}{16}; \quad \vec{k}_2 = (\frac{7}{8}, \frac{1}{8}, \frac{1}{8}), \quad \alpha_2 = \frac{3}{32};$$

$$\vec{k}_3 = (\frac{5}{8}, \frac{5}{8}, \frac{1}{8}), \quad \alpha_3 = \frac{3}{32}; \quad \vec{k}_4 = (\frac{5}{8}, \frac{3}{8}, \frac{3}{8}), \quad \alpha_4 = \frac{3}{32};$$

$$\vec{k}_5 = (\frac{5}{8}, \frac{3}{8}, \frac{1}{8}), \quad \alpha_5 = \frac{3}{16}; \quad \vec{k}_6 = (\frac{5}{8}, \frac{1}{8}, \frac{1}{8}), \quad \alpha_6 = \frac{3}{32};$$

$$\vec{k}_7 = (\frac{3}{8}, \frac{3}{8}, \frac{3}{8}), \quad \alpha_7 = \frac{1}{32}; \quad \vec{k}_8 = (\frac{3}{8}, \frac{3}{8}, \frac{1}{8}), \quad \alpha_8 = \frac{3}{32};$$

$$\vec{k}_9 = (\frac{3}{8}, \frac{1}{8}, \frac{1}{8}), \quad \alpha_9 = \frac{3}{32}; \quad \vec{k}_{10} = (\frac{1}{8}, \frac{1}{8}, \frac{1}{8}), \quad \alpha_{10} = \frac{1}{32}.$$

These ten points satisfy (12) for all m except those which correspond to nearest-neighbor shells represented by lattice vectors of the form $\vec{R} = (4n_1, 4n_2, 4n_3)$, where the n_i 's are integers. The first failure occurs for $m=37$, corresponding to the lattice vector $(4,0,0)$. Other failures occur for $\vec{R} = (4,4,0)$, $(4,4,4)$, etc. Thus, for the first 150 different nearest neighbors, these ten points satisfy (12) except for the three lattice vectors $(4,0,0)$, $(4,4,0)$ and $(4,4,4)$. If desired, the accuracy of these special points can be further increased by using the point $\vec{k} = (\frac{1}{16}, \frac{1}{16}, \frac{1}{16})$, which satisfies (11) for the three lattice vectors $(4,0,0)$, $(4,4,0)$ and $(4,4,4)$. The ten points combined with $\vec{k}$ as in (15) give rise to a grid of 60 points in the Brillouin zone. For these 60 points (12) is satisfied except for lattice vectors

of the form $\vec{R} = (8n_1, 8n_2, 8n_3)$ (n_i 's being integers). The first error for these points occurs for $\vec{R} = (8,0,0)$, corresponding to $m \approx 150$. For over the first 500 nearest neighbors these 60 points satisfy (12) except for $\vec{R} = (8,0,0)$, $(8,8,0)$ and $(8,8,8)$. The extension to higher point sets can be carried out by using the $\vec{k}$ points $\frac{1}{16} (1/2^n, 1/2^n, 1/2^n)$, $n=1,2,\dots$. In each such extension the magnitude of the smallest lattice vector for which (12) is not satisfied is doubled.

The weighing factor α_i of each special point $\vec{k}_i$ is easily determined by the following general rule. Let n_i be the number of different (i.e., not related by a reciprocal-lattice vector) wavevectors obtained when $\vec{k}_i$ is acted upon by every element of T . Then α_i is proportional to n_i and the normalized weighing factors are given by

$$\alpha_i = n_i / \sum_j n_j . \quad (16)$$

As an example of the use of (16) consider the two special points $\vec{k}_1 = (\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ and $\vec{k}_2 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ discussed above. We see that there are 24 different wave vectors related to $\vec{k}_1$ through the operations of T and eight different wave vectors related to $\vec{k}_2$. We have therefore $n_1 = 24$ and $n_2 = 8$ and using (16) we get

$$\alpha_1 = \frac{24}{24 + 8} = \frac{3}{4}$$

and

$$\alpha_2 = \frac{8}{24 + 8} = \frac{1}{4} .$$

The weighting factor α_1 is also proportional to the volume of $\vec{k}$ space occupied by $\vec{k}_1$.

The special point $\vec{k} = (0.6223, 0.2953, 0) (2\pi/a)$ proposed by Baldereschi¹⁷ satisfies (12) for $m=1, 2$ and gives a minimum for $m=3$. This is the best single point for the calculation of averages in crystals with the fcc Bravais lattice when the expansion coefficients are significant only for the first few nearest-neighbor shells.

b. Body-Centered-Cubic Bravais Lattice. The points $(\frac{1}{2}, 0, 0)$, and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (units of $2\pi/a$, where a is the lattice constant) are equally suitable as starting points. All three points lead to identical special-point sets. Choosing $\vec{k}_1$ to be any one of these points (11) is satisfied for all lattice vectors $\vec{R} = \frac{1}{2} (R_1, R_2, R_3)$ (units of a) whenever R_1, R_2 and R_3 are all odd (for the bcc lattice structures R_1, R_2, R_3 are simultaneously odd or even). The point $\vec{k}_2 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ can be used with $\vec{k}_1$ to generate, as in (15), a new set of points. These points correspond to only two distinct points of the irreducible zone. They are

$$\vec{k}_1 = (\frac{3}{4}, \frac{1}{4}, \frac{1}{4}), \quad \alpha_1 = \frac{1}{2}; \quad \vec{k}_2 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}), \quad \alpha_2 = \frac{1}{2}.$$

where the α_1 's are the weighting factors. These two points satisfy (12) except for the shells represented by lattice vectors of the form $\vec{R} = (2n_1, 2n_2, 2n_3)$, where the n_i 's are integers. The first error occurs for $\vec{R} = (2, 0, 0)$, which is the sixth-largest lattice vector. Other errors occur for $\vec{R} = (2, 2, 0)$ and $(2, 2, 2)$. The two points $\vec{k}_1$ and $\vec{k}_2$ above have the same coordinates as the two points found for the fcc Bravais lattice. The weighting factors are different because of

differences in symmetry. To go beyond the two-point scheme we can use $\vec{k} = (\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$, which satisfies (11) for the lattice vectors (2,0,0), (2,2,0), and (2,2,2). This point can therefore be used with $\vec{k}_1$ and $\vec{k}_2$ to obtain the higher set of special points. When this is done we find the following eight points:

$$\vec{k}_1 = (\frac{1}{8}, \frac{1}{8}, \frac{1}{8}), \quad \alpha_1 = \frac{1}{16}; \quad \vec{k}_2 = (\frac{3}{8}, \frac{1}{8}, \frac{1}{8}), \quad \alpha_2 = \frac{3}{16};$$

$$\vec{k}_3 = (\frac{3}{8}, \frac{3}{8}, \frac{1}{8}), \quad \alpha_3 = \frac{3}{16}; \quad \vec{k}_4 = (\frac{3}{8}, \frac{3}{8}, \frac{3}{8}), \quad \alpha_4 = \frac{1}{16};$$

$$\vec{k}_5 = (\frac{5}{8}, \frac{1}{8}, \frac{1}{8}), \quad \alpha_5 = \frac{3}{16}; \quad \vec{k}_6 = (\frac{5}{8}, \frac{3}{8}, \frac{1}{8}), \quad \alpha_6 = \frac{3}{16};$$

$$\vec{k}_7 = (\frac{5}{8}, \frac{3}{8}, \frac{3}{8}), \quad \alpha_7 = \frac{1}{16}; \quad \vec{k}_8 = (\frac{7}{8}, \frac{1}{8}, \frac{1}{8}), \quad \alpha_8 = \frac{1}{16};$$

where the α_i 's are the relative weighting factors. These points satisfy (12) except for lattice vectors of the form $\vec{R} = (4n_1, 4n_2, 4n_3)$. The first error occurs for $\vec{R} = (4,0,0)$, which corresponds to $m = 28$ in (12). Larger point sets can be constructed in a similar way by using the points $\vec{k} = \frac{1}{8} (1/2^n, 1/2^n, 1/2^n)$, $n=1,2,\dots$. The weighting factor of each special point can be determined from (16).

The special point $\vec{k} = (\frac{1}{6}, \frac{1}{6}, \frac{1}{6})$ ($2\pi/a$) suggested by Baldereschi¹⁷ satisfies (12) for $m=1,2$ and minimizes (12) for $m=3$. This is the best single point for the calculation of averages in crystals with the bcc Bravais lattice.

c. Simple-Cubic Bravais Lattice. The best starting point is $\vec{k}_1 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ (units of $2\pi/a$, where a is the lattice constant), which is identical with the special point obtained by Baldereschi.¹⁷ This point satisfies (11) for all lattice vectors $\vec{R} = (R_1, R_2, R_3)$ whenever at least one of the components R_i is odd. To satisfy (11) for lattice vectors with even R_i we use the point $\vec{k}_2 = (\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ to generate a new set of points as in (15). we find the following four points:

$$\begin{aligned} \vec{k}_1 &= (\frac{1}{8}, \frac{1}{8}, \frac{1}{8}), \quad \alpha_1 = \frac{1}{8}; \quad \vec{k}_2 = (\frac{3}{8}, \frac{1}{8}, \frac{1}{8}), \quad \alpha_2 = \frac{3}{8}; \\ \vec{k}_3 &= (\frac{3}{8}, \frac{3}{8}, \frac{1}{8}), \quad \alpha_3 = \frac{3}{8}; \quad \vec{k}_4 = (\frac{3}{8}, \frac{3}{8}, \frac{3}{8}), \quad \alpha_4 = \frac{1}{8}. \end{aligned}$$

These four points satisfy (12) except for the shells represented by lattice vectors of the form $\vec{R} = (4n_1, 4n_2, 4n_3)$, where the n_i 's are integers. The first error occurs for $\vec{R} = (4, 0, 0)$, which corresponds to the fourteenth-largest shell.

Higher point sets can be obtained in a similar way by using the points $\vec{k}_1 = \frac{1}{8} (1/2^n, 1/2^n, 1/2^n)$ for $n=1, 2, \dots$. The weighting factors for points in the larger special-point sets can be obtained from (16).

d. Hexagonal Bravais Lattice. The system of crystals with a hexagonal Bravais lattice includes the wurtzite and the hexagonal-close-packed crystal structures.

To describe the special-point sets we pick the origin of coordinates such that the primitive translation vectors in real and reciprocal space are given by:

$$\vec{R}_1 = \frac{1}{2} a\hat{x} + \frac{1}{2} \sqrt{3} a\hat{y}, \quad \vec{R}_2 = \frac{1}{2} a\hat{x} - \frac{1}{2} \sqrt{3} a\hat{y}, \quad \vec{R}_3 = c\hat{z}.$$

$$\vec{G}_1 = (2\pi/a)(\hat{x} + \frac{1}{3} \sqrt{3} \hat{y}), \quad \vec{G}_2 = (2\pi/a)(\hat{x} - \frac{1}{3} \sqrt{3} \hat{y}),$$

$$\vec{G}_3 = (2\pi/c)\hat{z}.$$

We will represent a special point $\vec{k} = (2\pi/a)(k_x, k_y, (a/c)k_z)$ of the Brillouin zone by $\vec{K} = (k_x, \sqrt{3} k_y, k_z)$ to avoid the repetition of the various factors.

A good starting point is $\vec{K} = (\frac{1}{3}, \frac{1}{3}, \frac{1}{4})$, which satisfies (11) for the first nearest neighbors in the z direction and in the $z=0$ plane. The best choice for a second point is $\vec{K}' = (\frac{2}{9}, 0, 0)$. When $\vec{K}$ and $\vec{K}'$ are combined according to (15) and the resulting points are taken to the irreducible part of the Brillouin zone we find the following three points:

$$\vec{K}_1 = (\frac{2}{9}, 0, \frac{1}{4}), \quad \vec{K}_2 = (\frac{4}{9}, 0, \frac{1}{4}), \quad \vec{K}_3 = (\frac{5}{9}, \frac{1}{3}, \frac{1}{4}).$$

The weighting factor for each point is $\frac{1}{3}$. These three points satisfy (12) for the first-eight nearest-neighbor "shells." (In ordering the nearest-neighbor shells we are assuming a c/a ratio close to $\frac{2}{3} \sqrt{6}$; the exact value of this ratio is, however, immaterial in the scheme for generating the special points.) The first failure occurs for the sixfold ring of nearest neighbors represented by $\vec{R} = 3\vec{R}_1$. To satisfy (12) for this ring we use the point $K = (\frac{1}{9}, \frac{1}{9}, 0)$ with the three points above to generate the following six points:

$$\begin{aligned}\vec{k}_1 &= (\frac{1}{9}, \frac{1}{9}, \frac{1}{4}), & \alpha_1 &= \frac{1}{9}; & \vec{k}_2 &= (\frac{2}{9}, \frac{2}{9}, \frac{1}{4}), & \alpha_2 &= \frac{1}{9}; \\ \vec{k}_3 &= (\frac{4}{9}, \frac{4}{9}, \frac{1}{4}), & \alpha_3 &= \frac{1}{9}; & \vec{k}_4 &= (\frac{1}{3}, \frac{1}{9}, \frac{1}{4}), & \alpha_4 &= \frac{2}{9}; \\ \vec{k}_5 &= (\frac{5}{9}, \frac{1}{9}, \frac{1}{4}), & \alpha_5 &= \frac{2}{9}; & \vec{k}_6 &= (\frac{4}{9}, \frac{2}{9}, \frac{1}{4}), & \alpha_6 &= \frac{2}{9}.\end{aligned}$$

For the first 30 nearest neighbors these six points satisfy (12) except when $|\vec{R}| = 2c$. The point $\vec{k} = (0, 0, \frac{1}{8})$ satisfies (12) for this lattice vector and when combined with the above six points results in the following set of 12 points:

$$\begin{aligned}\vec{k}_1 &= (\frac{1}{9}, \frac{1}{9}, \frac{1}{9}), & \alpha_1 &= \frac{1}{18}; & \vec{k}_2 &= (\frac{1}{9}, \frac{1}{9}, \frac{3}{8}), & \alpha_2 &= \frac{1}{18}; \\ \vec{k}_3 &= (\frac{2}{9}, \frac{2}{9}, \frac{1}{8}), & \alpha_3 &= \frac{1}{18}; & \vec{k}_4 &= (\frac{2}{9}, \frac{2}{9}, \frac{3}{8}), & \alpha_4 &= \frac{1}{18}; \\ \vec{k}_5 &= (\frac{4}{9}, \frac{4}{9}, \frac{1}{8}), & \alpha_5 &= \frac{1}{18}; & \vec{k}_6 &= (\frac{4}{9}, \frac{4}{9}, \frac{3}{8}), & \alpha_6 &= \frac{1}{18}; \\ \vec{k}_7 &= (\frac{1}{3}, \frac{1}{9}, \frac{1}{8}), & \alpha_7 &= \frac{1}{9}; & \vec{k}_8 &= (\frac{1}{3}, \frac{1}{9}, \frac{3}{8}), & \alpha_8 &= \frac{1}{9}; \\ \vec{k}_9 &= (\frac{5}{9}, \frac{1}{9}, \frac{1}{8}), & \alpha_9 &= \frac{1}{9}; & \vec{k}_{10} &= (\frac{5}{9}, \frac{1}{9}, \frac{3}{8}), & \alpha_{10} &= \frac{1}{9}; \\ \vec{k}_{11} &= (\frac{4}{9}, \frac{2}{9}, \frac{1}{8}), & \alpha_{11} &= \frac{1}{9}; & \vec{k}_{12} &= (\frac{4}{9}, \frac{2}{9}, \frac{3}{8}), & \alpha_{12} &= \frac{1}{9}.\end{aligned}$$

For these 12 points the first failure to satisfy (12) occurs for m corresponding to $|\vec{R}_m| = 4c$. Succeeding failures occur for $|\vec{R}|^2 = 27a^2$, $|\vec{R}|^2 = 27a^2 + 16c^2$, $|\vec{R}|^2 = 81a^2$, etc. Larger sets of points can be constructed to remove these failures by using the points $\vec{k} = (0, 0, 1/2^{n+3})$, $(2/3^{n+2}, 0, 0)$, and $(1/3^{n+2}, 1/2^{n+2}, 0)$, $n \geq 1$. The weighting factors for the larger point sets can be obtained from (16).

It should be noted again that the coordinates of the special points $\vec{k} = (2\pi/a)(k_x, k_y, (a/c)k_z)$ of the Brillouin zone are related to the coordinates of $\vec{K} = (K_x, K_y, K_z)$ by $k_x = K_x$, $k_y = \frac{1}{3} \sqrt{3} K_y$, $k_z = K_z$.

4. Accuracy of Averages Obtained from the Special-Point Scheme

How accurate is the special-point scheme in determining the average over the Brillouin zone, f_0 , of a periodic function $f(\vec{k})$? How does the accuracy change with successive approximations when the number of point are increased? In this section we examine the accuracy of the special-point scheme using two complementary approaches which will prove useful.

The error ϵ in the value of f_0 using the point schemes described in section 3 can be obtained from (14a) and (14b) and is equal to

$$\epsilon = \sum_i \sum_m \alpha_i A_m(\vec{k}_i) f_m. \quad (17)$$

When (12) is not satisfied, the special points have the property that

$$\sum_i \alpha_i A_m(\vec{k}_i) = S_m N_m, \quad S_m = \pm 1 \quad (18)$$

with N_m defined as in (6). Using this in (17) we find

$$\epsilon = \sum_m S_m N_m f_m. \quad (19)$$

To obtain an estimate of this error we need the behavior of f_m . Using (3) and (6) we find

$$f_m = \frac{1}{N_m} \frac{\Omega}{(2\pi)^3} \int f(\vec{k}) A_m(\vec{k}) d^3k.$$

Assuming $f(k)$ to be a smoothly varying function we can expand it in a Taylor series and perform the integral over the Brillouin zone to obtain the asymptotic behavior of f_m . We will consider here only the case of the cubic crystals. The smallest vectors R_m associated with those f_m which appear in (19) are then of the form $(R,0,0)$, $(R,R,0)$, (R,R,R) . For these lattice vectors we find, on carrying out the integration for the case of the fcc lattice structure, that f_m drops at least as fast as $(1/N_m)(1/|R_m|^3)$ for large $|R_m|$. This implies that

$$\epsilon \approx \sum_m \frac{S_m}{|R_m|^3} . \quad (20)$$

The error therefore decreases rapidly as (12) is satisfied for larger N (and hence larger $|R_m|$). In going from one set of special points to the next higher set of points the magnitude of the smallest R_m 's occurring in (20) is increased by a factor of 2. We therefore expect the error ϵ to get reduced by a factor of nearly 8 for each successive approximation. This result can also be obtained in a different way.

Let D be the difference in the value of the average f_0 obtained from two consecutive approximations. Let $F_1^{(0)}$ be the value of $f(k)$ at one of the original points k_1 and let $F_1^{(j)}$ for $j=1, \dots, 8$ be the values of $f(k)$ at the eight points obtained from k_1 in going to the higher-order approximation. These eight points actually lie on the corners of a cube centered at the original point k_1 for the case of the cubic crystals. The value of D is

$$D = \sum_i \alpha_i (F_i^{(0)} - \frac{1}{8} \sum_{j=1}^8 F_i^{(j)}) ,$$

where the α_1 's are the weighting factors for the original points $\vec{k}_1$. Assuming $f(\vec{k})$ to be a smoothly varying function that can be expanded in a Taylor series about each point $\vec{k}_1$, we find in going to third order in the expansion

$$D = \frac{1}{2} (\Delta k/2)^2 \sum_1 \alpha_1 v_k^2 f(\vec{k}_1), \quad (21)$$

where Δk is the length of the cube about each point $\vec{k}_1$. We found previously that the magnitude of the error ϵ is reduced by a factor of about 8 in each successive approximation. Since D is the difference in the errors of two successive approximations, if we ignore the smaller error, which is about 10% of the larger one, then we can take $D = \epsilon$. Therefore to minimize ϵ we will try to minimize D .

A reduction in the value of D can occur if we are interested in sums of averages. For example, the sum of the average energies of several bands can usually be more accurately determined than the average energy of each band individually. This is because the different bands do not have the same curvature everywhere; in particular, the lowest band normally has a different sense of curvature than the next few higher bands. This causes cancellations in (21) when taking sums of averages for these bands. The same effect appears in charge-density calculations based on a small number of points.¹⁶

The difference in the value of f_0 obtained from two nonconsecutive approximations can also be expressed in the form of (21) with $(\Delta k)^2$ replaced by some mean value $(\Delta k)^2$. This implies that if the Taylor expansion of $f(\vec{k})$ to third order were sufficient then the "best" single point k_0 would satisfy

$$\nabla_{\vec{k}}^2 f(\vec{k}_0) = 0$$

Since the functional dependence of $f(\vec{k})$ on $\vec{k}$ is not known, in general, this equation cannot be used to determine $\vec{k}_0$. The best thing to do to minimize D is therefore to restrict $\vec{k}_0$ to satisfy the condition (11) for N as large as possible. This has been done by Baldereschi¹⁷ for the cubic crystals.

We can also derive a different expression for D . By using (3) and (4) we find that

$$\nabla_{\vec{k}}^2 f(\vec{k}) = - \sum_{\vec{m}} (a/2\pi)^2 |\vec{R}_{\vec{m}}|^2 f_{\vec{m}} A_{\vec{m}}(\vec{k}), \quad (22)$$

where the lattice vectors are of the form $a\vec{R}_{\vec{m}}$ and $\vec{k}$ is measured in units of $2\pi/a$.

Using (12) and (18) we get

$$D \approx - \frac{1}{2} (\Delta k/2)^2 \sum_{\vec{m}} |\vec{R}_{\vec{m}}|^2 S_{\vec{m}} N f_{\vec{m}}, \quad (23)$$

where the summation is only over those $\vec{m}$ for which (12) is not satisfied. In each set of successive approximations, (12) is satisfied for a larger set of $\vec{m}$ values and the number of terms in D decreases. Furthermore the length of the cubes (Δk) about each point is reduced by a factor of 2 in each successive approximation. The asymptotic behavior of $f_{\vec{m}}$ was found to be of the form $(1/N_{\vec{m}})(1/|\vec{R}_{\vec{m}}|^3)$. Substitution in (23) therefore gives

$$D \approx (\Delta k)^2 / |\vec{R}_{\vec{m}}|, \quad (24)$$

where $|\mathbf{R}_m|$ is the smallest lattice vector for which (12) is not satisfied. Since the magnitude of this lattice vector increases by a factor of 2 in each successive approximation and (Δk) decreases by a factor of 2, D decreases by a factor of about 8 in each successive approximation. It is interesting to note that the number of special points increases by a factor of nearly 8 for each consecutive approximation as the number of special points becomes large.

In conventional calculations of averages a reduction in the value of D takes place mainly through a reduction in the size of Δk as more points are used. The "effective" $|\mathbf{R}_m|$ occurring in (24) is much smaller in these calculations than is the case when a set of special points containing a comparable number of points are employed. For a given accuracy one therefore needs a smaller number of points if one chooses the grid of points in the Brillouin zone to coincide with the special points.

5. Interpolation Formula

Equation (3) of section 2 can be considered as an interpolation formula for $f(\vec{k})$ if the expansion coefficients f_m are known. The special points make it possible to evaluate these coefficients in a simple and accurate way. The expansion coefficients (as already noted in section 4) are given by

$$f_m = \frac{1}{N_m} \frac{\Omega}{(2\pi)^3} \int f(\vec{k}) A_m(\vec{k}) d^3k \quad (25)$$

Except for the constant N_m in front of the integral, f_m is nothing but the average of $f(\vec{k}) A_m(\vec{k})$ over the Brillouin zone. Since $f(\vec{k})$ and

$A_m(\vec{k})$ are both periodic in $\vec{k}$ (Eqs. 3,4, and 7) the product also has the same periodicity. This means that the method we have developed in the previous sections for the evaluation of averages of a periodic function can be used to obtain the f_m 's. The f_m 's can therefore be approximated by

$$f_m \approx \frac{1}{N_m} \sum \alpha_i f(\vec{k}_i) A_m(\vec{k}_i) \quad (26)$$

where the $\vec{k}_i$ are the special points and the α_i are their corresponding weighting factors as before. Equation (26) can be used to obtain a good approximation for all f_m 's with $m < \frac{N}{2}$ where $\vec{k}_i$ is the largest lattice vector for which (12) is satisfied. This condition on the maximum value of m arises if we write the exact equation (similar to Eq. 14a) for the f_m 's. When this is done we find that in order to solve the system of linear equations we need to assume $f_m \approx 0$ for $m > \frac{N}{2}$. If N is large enough then this is a good approximation since the f_m 's normally vanish for large m .

6. Results of Calculations Using Special Points

We have tested the accuracy of the special points⁸² by calculating the charge density of Ge, GaAs and ZnSe using only two $\vec{k}$ -points in the Brillouin zone and comparing the results to those obtained from more accurate calculations⁷³ involving 71 points in the Brillouin zone. The results are very impressive. We find that the two special points reproduce the charge density of individual bands to within a few percent accuracy in all three compounds. One reason for the success of such a small number of points is that the variation of the charge density of individual $\vec{k}$ -states with respect to changes in $\vec{k}$ is not large.

The charge density (at an arbitrarily chosen point in the primitive cell) of different $\vec{k}$ -states fluctuate by about $\pm 15\%$ about their mean value. Therefore, it is not surprising that a few well chosen $\vec{k}$ -points give good results. The special point scheme has also been successfully used for other crystals in obtaining charge densities.⁸³⁻⁸⁵

7. Appendix

We want to show that if

$$A_m(\vec{k}) = \sum_{|\vec{R}|=C_m} e^{i\vec{k} \cdot \vec{R}} = 0 \quad (A1)$$

is satisfied by $\vec{k}_1$ for $m=m_1$ and by $\vec{k}_2$ for $m=m_2$ then the set consisting of the n_T points obtained from

$$\vec{k}_i = \vec{k}_1 + T_i \vec{k}_2 \quad (A2)$$

for $i=1, \dots, n_T$ satisfy

$$\sum_i \alpha_i A_m(\vec{k}_i) = 0 \quad (A3)$$

with $\alpha_i = 1/n_T = \text{const.}$ for $m=m_1$ and for $m=m_2$. The sum in (A1) is over equivalent lattice vectors related to each other by the operations T_i of the lattice point group T , which has n_T elements.

From our choice of $\vec{k}_1$ and $\vec{k}_2$ we know that

$$A_m(\vec{k}_1) A_m(\vec{k}_2) = 0 \quad (A4)$$

is satisfied for $m=m_1$ and for $m=m_2$. Using (A1) this can be expressed

$$\left(\sum_{|\vec{R}|=C_m} e^{i\vec{k}_1 \cdot \vec{R}} \right) \left(\sum_{|\vec{R}|=C_m} e^{i\vec{k}_2 \cdot \vec{R}} \right) = 0 . \quad (A5)$$

This equation is equivalent to

$$\left(\sum_{|\vec{R}|=C_m} e^{i\vec{k}_1 \cdot \vec{R}} \right) \left(\sum_j e^{i\vec{k}_2 \cdot T_j \vec{R}} \right) = 0 . \quad (A6)$$

The dot product $\vec{k}_2 \cdot (T_j \vec{R})$ is equal to $(T_j \vec{k}_2) \cdot \vec{R}$, where $T_j = T_j^{-1}$. We can therefore rewrite (6) in the form:

$$\sum_l \sum_{|\vec{R}|=C_m} e^{i(\vec{k}_1 + T_l \vec{k}_2) \cdot \vec{R}} = 0 . \quad (A7)$$

Using the definition (A1) of $A_m(\vec{k})$ in Eq. (A7) is seen to be identical to

$$\sum_l A_m(\vec{k}_1 + T_l \vec{k}_2) = 0 . \quad (A8)$$

Using (A2) this can be expressed as

$$\sum_l A_m(\vec{k}_l) = 0 . \quad (A9)$$

Equation (A9), except for a constant multiplicative factor, is equivalent to (A3), which we wanted to show.

B. Approximate Wannier Functions

Abstract

In this section we discuss a method for constructing approximate Wannier functions from finite sets of Bloch functions specified at the special points of the Brillouin zone which were derived in the previous section.

The usual definition of a Wannier function (WF), $w(\vec{r})$, in terms of Bloch functions (BFs), $\psi(\vec{k}, \vec{r})$, is

$$w(\vec{r}) = N^{-1/2} \sum_{\vec{k}} \psi(\vec{k}, \vec{r}) \quad , \quad (1)$$

where the band index on $w(\vec{r})$ and $\psi(\vec{k}, \vec{r})$ has been suppressed for convenience. This equation has not been very useful for obtaining WFs because of difficulties involved in summing over all $\vec{k}$ states.

In this paper we describe a method for constructing approximate WFs, $a(\vec{r})$, by taking a sum over a finite number of special $\vec{k}$ points in (1). We show that $a(\vec{r})$ can be used in place of $w(\vec{r})$ in many calculations involving the WFs. In section A we have,¹⁸ in a different but closely related context, described a method for obtaining the special point sets. Here we discuss how these points arise in the construction of the approximate WFs and we give the procedure for generating these points for the cubic crystals.

We define $\{\psi(\vec{k}, \vec{r})\}$ to be a sum over all BFs whose wavevectors are related to $\vec{k}$ by the operations of the lattice point group Γ . We restrict each wavevector to appear only once in the sum. Two wavevectors $\vec{k}$ and $\vec{k} + \vec{G}$ differing by a reciprocal lattice vector $\vec{G}$ will be

considered to be identical so that if $\Psi(\vec{k}, \vec{r})$ occurs in the sum $\Psi(\vec{k}+\vec{G}, \vec{r})$ will be excluded. The relative phases of the Bloch functions appearing in the sum can be taken to be completely arbitrary. We will show that

$$a(\vec{r}) = N^{-1/2} \sum_i \{\Psi(\vec{k}_i, \vec{r})\} \quad (2)$$

can under certain conditions be a useful WF when the $\vec{k}$'s are the special points of the Brillouin zone.

To find the conditions on the $\vec{k}_i$'s we start by expressing $a(\vec{r})$ as a general linear combination of BFs:

$$a(\vec{r}) = \sum_i \beta_i^{1/2} \Psi(\vec{k}_i, \vec{r}) \quad (3)$$

where β_i 's are constants to be determined.

We want $a(\vec{r})$ to satisfy the usual properties of a WF, i.e.,

$$\int_V a^*(\vec{r}) a(\vec{r}) d^3r = 1, \quad (4)$$

$$\int_V a^*(\vec{r}-\vec{R}) a(\vec{r}) d^3r = 0, \quad |\vec{R}| \neq 0 \quad (5)$$

The integrals in (4) and (5) are over the crystal volume V and $\vec{R}$ is a lattice vector. Substitution of (3) in (4) and (5) gives

$$\sum_i \beta_i = 1, \quad (6)$$

$$\sum_i \beta_i \exp(i\vec{k}_i \cdot \vec{R}) = 0. \quad (7)$$

The equations one obtains from (7) for "equivalent" lattice vectors related to one another through the operations of the lattice point group can be reduced to a single equation if instead of (3) we take

$$a(\vec{r}) \sum_i \beta_i^{1/2} \{\psi(\vec{k}_i, \vec{r})\} . \quad (8)$$

Equations (6) and (7) should then be changed to

$$\sum_i \beta_i n_i = 1 , \quad (9)$$

$$\sum_i \beta_i \{\exp(i\vec{k}_i \cdot \vec{R})\} = 0 \quad (10)$$

with n_i being the number of BFs in $\{\psi(\vec{k}_i, \vec{r})\}$ and $\{\exp(i\vec{k}_i \cdot \vec{R})\}$ being defined in the same way as $\{\psi(\vec{k}_i, \vec{r})\}$.

If we define

$$\alpha_i = n_i \beta_i \quad (11)$$

and

$$A_m(\vec{k}) = \sum_{|\vec{R}|=C_m} \exp(i\vec{k} \cdot \vec{R}) \quad m = 1, 2, \dots \quad (12)$$

then Eqs. (9) and (10) can be expressed in the form

$$\sum_i \alpha_i = 1 , \quad (13)$$

$$\sum_i \alpha_i A_m(\vec{k}_i) = 0 \quad m = 1, 2, \dots \quad (14)$$

Each $A_m(\vec{k})$ is associated with a "shell" of equivalent lattice vectors of length c_m . We order these shells so that $0 < c_m \leq c_{m+1}$. Ideally, we would like to satisfy (14) for all m by using a finite number of $\vec{k}_i$. This is not however possible. In section A we developed¹⁸ a systematic method for determining the α_i 's and $\vec{k}_i$'s which satisfy (13) and (14) for all lattice vector shells specified by $m \leq M$, $|\vec{R}| \leq c_M$ where M can be made as large as desired. The special point sets are designed to use the smallest number of $\vec{k}$ points to obtain the largest value for c_m . These points have the property that the β_i are all the same,

$$\beta_i = \alpha_i / n_i = \text{Constant} = N^{-1}$$

where N is the total number of wavefunctions that appears in (8). Equation (8) therefore reduces to Eq. (2).

The function $a(\vec{r})$ given by (2) is an approximate WF in that it fails to satisfy (5) for all lattice vectors. If the magnitude of the smallest $\vec{R}$ for which (5) is not satisfied is made large enough then, in many calculations, $a(\vec{r})$ can give accurate results when used in place of $w(\vec{r})$. As an example the average energy of electrons in a given band defined as

$$\bar{E} = N^{-1} \sum_{\vec{k}} E(\vec{k}) \quad (15)$$

can be obtained from $w(\vec{r})$:

$$\bar{E}_w = \bar{E} = \langle w(\vec{r}) | H | w(\vec{r}) \rangle \quad (16)$$

where H is the Hamiltonian operator. If we use $a(\vec{r})$ instead of $w(\vec{r})$ in (16) we have

$$\tilde{E}_a = \sum_i \alpha_i E(\vec{k}_i) \quad (17)$$

where $\alpha_i = n_i/N$. Equation (17) is an example (which uses WFs) of an application of the method¹⁸ for determining averages which we have discussed in more detail in Sec. A. (If $E(\vec{k})$ does not have the complete symmetry of the lattice then Eq. (17) is slightly modified). We have shown in section A that the accuracy of (17) increases as higher order special points are used.

The approximate WFs can also be used to obtain other moments of the energy, the charge density,¹⁶ etc.

We can now ask whether $a(\vec{r})$ "converges" to $w(\vec{r})$ as more BFs are used in (2). If we let

$$D_V = \int_V |a(\vec{r}) - w(\vec{r})|^2 d^3r \quad (18)$$

be a measure of the convergence between $a(\vec{r})$ and some WF, $w(\vec{r})$, then we can easily see that D_V does not go to zero when a finite number of BFs are used in (2) and when we require the region of integration to be the crystal volume. Using Eqs. (1) and (2) in (18) one obtains integrals of the form

$$I_V = \int_V \psi^*(\vec{k}, \vec{r}) \psi(\vec{k} + \Delta\vec{k}, \vec{r}) d^3r \quad (19)$$

which are zero even for an arbitrarily small $|\Delta\vec{k}|$ when the region of integration is over the infinite crystal volume (if $I_v = 1$, $D_v = 0$). If we restrict the limits of integration to a finite region of space, v , and require $\vec{k}$ and $\vec{k} + \Delta\vec{k}$ to be in the same irreducible zone, by the proper choice of phase for the BFs we can have

$$\lim_{\Delta\vec{k} \rightarrow 0} I_v = 1.$$

Assuming that $w(\vec{r})$ has been constructed from BFs which have this property and using these BFs at the special points in (2) it can be shown that

$$D_v = \int_v |a(\vec{r}) - w(\vec{r})|^2$$

approaches zero as the number of BFs used in (2) increases. The region ΔR over which $a(\vec{r})$ approximates $w(\vec{r})$ is determined by

$$(\Delta k) (\Delta R) \ll \pi$$

where (Δk) is the spacing between the special points. Therefore over a finite region ΔR we can make an $a(\vec{r})$ as close to a $w(\vec{r})$ (with a certain choice of phase in (1)) as we like.

We expect the Wannier functions to be useful in calculations involving surfaces and impurities.

C. Analytic Expression for the Electron Charge Density Distribution in Diamond Structure Crystals

Abstract

In this section we obtain the explicit dependence of the valence band electronic charge density distribution on the pseudopotential form factors for the diamond structure crystals using a weighted sum of the charge densities at the symmetry points Γ , X, and L of the Brillouin zone. The charge densities and energies for the bands at Γ , X and L and their dependence on the lattice constant and pseudopotentials are also discussed.

1. Introduction

Knowledge of the electronic charge distribution in crystals provides valuable insight into many physical and chemical properties of a crystal. Differences in these properties between two crystals of the same family as well as information on bonding and relative ionicities of the atoms in crystals can often be inferred from charge density distributions.

The charge density distribution, $\rho(\vec{r})$, can be obtained once the energy band structure and wavefunctions have been determined. The charge density has the form

$$\rho(\vec{r}) = \sum_{n, \vec{k}} e |\psi_{\vec{k}, n}(\vec{r})|^2 \quad (1)$$

where $\psi_{\vec{k}, n}$ is a Bloch function of wavevector $\vec{k}$ belonging to band n. A particularly simple and successful method of obtaining $\psi_{\vec{k}, n}$ and the band structure has been the empirical pseudopotential method (EPM)¹. The EPM can in principle yield the exact one electron energies but the pseudowavefunctions approximate the true wavefunctions only in the

region outside the atomic cores. Since for diamond structure crystals, such as Ge and Si, the region of interest for the charge density is at and near the bond sites, the pseudowavefunctions give the essential information of interest. The Bloch functions for a general $\vec{k}$ have a complicated dependence on the atomic pseudopotentials and the explicit dependence of $\rho(\vec{r})$ on the pseudopotentials is not generally known.

In this paper we use an approximation scheme to obtain the explicit dependence of $\rho(\vec{r})$ on the atomic potentials for the simple case of the diamond structure crystals. The approximation involved is the change of the sum over all $\vec{k}$ in (1) to a sum over a small number of suitably chosen $\vec{k}$ points. We have already discussed such approximations in detail in sections III.C and IV.A. These approximation schemes not only result in a large reduction in computation time but they also make it possible to obtain a better understanding of the origin of the structure in $\rho(\vec{r})$. For example we will show that it is possible to obtain an expression for the explicit dependence of the charge density on the atomic pseudopotentials.

The approximation scheme we use is based on a weighted sum of the charge densities at the symmetry points Γ , X, and L of the Brillouin zone. Such a scheme has been previously suggested and utilized by Kleinman and Phillips⁸⁶ as a method for successive approximations. Our use of these points is based on a different set of considerations,¹⁶ i.e., the minimization of the overlap between Wannier functions based on different lattice sites. It should be noted that Γ , X, and L are not the optimum points to use. In fact as we have already (section A) discussed in more detail the two points $(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, (units of $\frac{2\pi}{a}$, a = lattice

constant) are expected to give more accurate results.¹⁸ However, the explicit dependence of energies and wavefunctions on the atomic pseudopotentials can be determined more easily and more accurately for Γ , X and L than for less symmetric points. The results for the energies of all valence and some conduction bands are summarized in Table I. The wavefunctions are given in section 2 and are used in section 3 to obtain an approximate analytic expression for the total electronic charge distribution. We have taken the spin-orbit interaction into account only at Γ and neglected it at X and L. The spin-orbit coupling is weak in C and Si; in Ge it modifies the total valence band charge density only slightly. For the gray-tin case however, the spin-orbit interaction appreciably modifies the band structure at Γ . We have determined the energies and wavefunctions at Γ with and without spin-orbit interactions.

2. Wavefunctions and Energies at Γ , X, and L.

We take the pseudopotential Hamiltonian for an electron in a crystal to consist of a kinetic energy term plus a weak local pseudopotential arising from the superposition of spherically symmetric atomic pseudopotentials centered on the atoms. The pseudopotential can be expressed as the product of a structure factor times a pseudopotential form factor $V(|\vec{G}|)$, where $\vec{G}$ is a reciprocal lattice vector. The pseudopotential is assumed to be sufficiently weak so that $V(|\vec{G}|^2 > 16)$, ($\vec{G}$ measured in units of $\frac{2\pi}{a}$, a = lattice constant) can be neglected. We take the origin of coordinates halfway between the atoms in the basis. For this choice of coordinates the matrix elements of the Hamiltonian between plane wave states are real and depend on the symmetric form

factors. The truncation $V(|\vec{G}|^2 > 16)$ leaves only four form factors with non-zero structure factors. These are V_0 , V_3 , V_8 and V_{11} where the subscripts refer to the value of $|\vec{G}|^2$. The form factor V_0 appears on the diagonal elements of the Hamiltonian. Its value can be set equal to zero without affecting energy differences or wavefunctions. We will therefore choose $V_0 = 0$ in the following.

We expand the wavefunction of each band in a symmetrized combination of plane waves. At points where several bands are degenerate, this expansion is not unique. The sum of the charge densities of the degenerate bands is however independent of the choice of the expansion when the wavefunctions are made orthonormal. The number of plane waves in the expansion is restricted so that the secular equation for the energy of each band can be reduced to a 2×2 matrix. In the following we represent a plane wave $e^{i\vec{k} \cdot \vec{r}}$ by

$$(k_1 k_2 k_3) = e^{i\vec{k} \cdot \vec{r}}$$

where

$$\vec{k} = \frac{2\pi}{a} (k_1, k_2, k_3) .$$

The unit of energy is taken equal to

$$\frac{\hbar^2}{2m} \left(\frac{2\pi}{a}\right)^2 = \left(\frac{2\pi a_0}{a}\right)^2 \text{ Ry} \quad (2)$$

where a_0 is the Bohr radius, a is the lattice constant, and m is the free electron mass. The volume of the crystal is taken equal to unity in the following expressions.

3. Wavefunctions and Energies at Γ

a. Without Spin-orbit

The expansion coefficients of the plane waves for the Γ_1 , $\Gamma_{25'}$, and Γ_2 , levels are listed in Table II. The subscript n in $\psi_n(\Gamma)$ denotes the band index. The $\Gamma_{25'}$ level is triply degenerate in the absence of spin-orbit interactions and the assignment, in Table II, of a band index to the $\Gamma_{25'}$ wavefunctions is arbitrary. The coefficients, a_1 and a_2 , of the plane waves (Table II) for the Γ_1 level are given by

$$a_1 = \frac{2V_3}{\sqrt{E^2(\Gamma_1) + 4V_3^2}}, \quad a_2 = -\frac{1}{2\sqrt{2}} \frac{E(\Gamma_1)}{\sqrt{E^2(\Gamma_1) + 4V_3^2}} \quad (3)$$

where

$$E(\Gamma_1) = \frac{3}{2} (1+V_8) - \sqrt{\frac{9}{4}(1+V_8)^2 + 4V_3^2} \quad (4)$$

is the energy of the Γ_1 level. The coefficients b_1 and b_2 (Table II) for the triply degenerate $\Gamma_{25'}$ levels are given by:

$$b_1 = \frac{V_3 - V_{11}}{2\sqrt{A^2(\Gamma_{25'}) + 2(V_3 - V_{11})^2}}, \quad b_2 = -\frac{A(\Gamma_{25'})}{\sqrt{2A^2(\Gamma_{25'}) + 4(V_3 - V_{11})^2}}$$

$$A(\Gamma_{25'}) = 3 - V_8 - E(\Gamma_{25'})$$

and

$$E(\Gamma_{25'}) = \frac{7}{2} (1-V_8) - \sqrt{\left(\frac{1+V_8}{2}\right)^2 + 2(V_3 - V_{11})^2}$$

is the energy of the degenerate $\Gamma_{25'}$ levels. The coefficients c_1 and c_2 of the Γ_2 conduction band are given by

$$c_1 = \frac{\sqrt{3}}{2} \frac{v_3 - v_{11}}{\sqrt{6(v_3 - v_{11})^2 + A^2(\Gamma_2)}} \quad c_2 = \frac{A(\Gamma_2)}{\sqrt{6}} \frac{1}{\sqrt{6(v_3 - v_{11})^2 + A^2(\Gamma_2)}}$$

where $A(\Gamma_2) = 3(1+v_8) - E(\Gamma_2)$

and

$$E(\Gamma_2) = \frac{7}{2} (1+v_8) - \sqrt{\left(\frac{1+v_8}{2}\right)^2 + 6(v_3+v_{11})^2}$$

b. With Spin-orbit

The spin-orbit interaction can be incorporated into the pseudopotential calculation by using the method of Weisz.³⁷ In this method the spin-orbit Hamiltonian which operating on the real wavefunctions would give the spin-orbit splitting is transformed into a new Hamiltonian H^{s-o} which can be used on the pseudowavefunctions instead. The effect of H^{s-o} on the energies and wavefunctions at Γ can be easily obtained if we take

$$H = H_0 + \frac{\hbar}{4m c} \vec{\nabla} \cdot \vec{V}^{eff} \vec{x} \cdot \vec{\sigma} \quad (5)$$

where H_0 is the non-spin-orbit Hamiltonian used before and V^{eff} is some effective localized pseudopotential. This Hamiltonian is different than the one used by Weisz³⁷ but the final results are the same for both cases.

The Hamiltonian (5) leaves the energies of the Γ_1 and Γ_2 levels unchanged and it does not mix these states with the Γ_{25} levels. To obtain the effect of (5) on the Γ_{25} levels we take as a basis the following combinations of the $\psi_i(\Gamma_{25})$'s listed in Table II:

$$|I\rangle = \frac{|\psi_2 - i\psi_3\rangle + \rangle}{\sqrt{2}}, \quad |II\rangle = |\psi_4\rangle$$

$$|III\rangle = \frac{|\psi_2 + i\psi_3\rangle + \rangle}{\sqrt{2}}$$

$$|IV\rangle = \frac{|-\psi_2 + i\psi_3\rangle + \rangle}{\sqrt{2}}, \quad |V\rangle = |\psi_4\rangle$$

$$|VI\rangle = \frac{|\psi_2 - i\psi_3\rangle + \rangle}{\sqrt{2}}.$$

The 6×6 matrix can be written in the form

$$\begin{vmatrix} H' & 0 \\ 0 & H' \end{vmatrix}$$

with

$$H' = \begin{vmatrix} E_0 - \frac{\Delta}{3} - E & \frac{\sqrt{2}}{3} \Delta & 0 \\ \frac{\sqrt{2}}{3} \Delta & E_0 - E & 0 \\ 0 & 0 & E_0 + \frac{\Delta}{3} - E \end{vmatrix} \quad (6)$$

where E_0 is the energy of the Γ_{25} levels in the absence of spin-orbit interactions, and

$$\Delta = \frac{3\hbar^4}{4m^2 c^2} \langle \psi_2(\Gamma_{25'}) | \frac{\partial v^{\text{eff}}}{\partial x} p_y - \frac{\partial v^{\text{eff}}}{\partial y} p_x | \psi_3(\Gamma_{25'}) \rangle$$

is the spin-orbit splitting of the valence bands. Equation (6) is the same as the one derived by Kane⁸⁷ for InSb and the basis functions are also similar to those used by him. The new wavefunctions and energies at Γ are:

$$|\psi_{2a}\rangle = \frac{1}{\sqrt{3}} (\sqrt{2} |I\rangle - |II\rangle); E_{2a} = E_{2b} = E_0 - \frac{2}{3} \Delta$$

$$|\psi_{2b}\rangle = \frac{1}{\sqrt{3}} (\sqrt{2} |IV\rangle - |V\rangle)$$

$$|\psi_{3a}\rangle = |III\rangle = |\psi_{3b}\rangle = |VI\rangle; E_{3a} = E_{3b} = E_0 + \frac{\Delta}{3}$$

$$|\psi_{4a}\rangle = \frac{1}{\sqrt{3}} (|I\rangle + \sqrt{2} |II\rangle); E_{4a} = E_{4b} = E_0 + \frac{\Delta}{3}$$

$$|\psi_{4b}\rangle = \frac{1}{\sqrt{3}} (|IV\rangle + \sqrt{2} |V\rangle)$$

Comparing these wavefunctions to those in Table II it can be seen the sum of the charge densities of the triply degenerate $\Gamma_{25'}$ bands does not change when spin-orbit interactions are included in the Hamiltonian.

4. Wavefunctions and Energies at X

For the diamond structure crystals, the bands are always doubly degenerate at X. For the lowest two bands we use 6 plane waves in the expansion of the wavefunction. The plane waves $e^{i(\vec{k}_X + \vec{G}) \cdot \vec{r}}$ occurring in the expansion satisfy $|\vec{k}_X + \vec{G}|^2 \leq 2$ (units of $(\frac{2\pi}{a})^2$). For the third and fourth bands fourteen plane waves corresponding to $|\vec{k}_X + \vec{G}| \leq 5$ are

used in the expansion. The secular equation for the energy is however reduced to 2×2 matrices for all four bands by using the symmetry properties of the wavefunctions. For the calculation of the charge density we need the wavefunctions for the equivalent X points $(1,0,0)$, $(0,1,0)$ and $(0,0,1)$. The wavefunctions at these points and the energies of the X_1 and X_4 levels are given below.

X_1 bands

$$\psi_1(1,0,0) = a_1(100) + a_2[(011) - (0\bar{1}\bar{1}) + (01\bar{1}) + (0\bar{1}1)]$$

$$\psi_1(0,1,0) = a_1(010) + a_2[(101) - (\bar{1}0\bar{1}) + (10\bar{1}) + (\bar{1}01)]$$

$$\psi_1(0,0,1) = a_1(001) + a_2[(110) - (\bar{1}\bar{1}0) + (1\bar{1}0) + (\bar{1}10)]$$

$$\psi_2(1,0,0) = \psi_1^*(100), \text{ etc.}$$

$$a_1 = \frac{\sqrt{2} v_3}{\sqrt{A^2(X_1) + 2v_3^2}} \quad a_2 = -\frac{1}{2} \frac{A(X_1)}{\sqrt{A^2(X_1) + 2v_3^2}} \quad (7)$$

$$A(X_1) = 1 - E(X_1)$$

$$E(X_1) = \frac{1}{2}(3 + v_8) - \frac{1}{2} \sqrt{(1 + v_8)^2 + 8v_3^2}$$

Slightly away from $X = (1,0,0)$, for example for $\vec{k} = (1 - \frac{\Delta}{2}, 0, 0)$ the degeneracy of the bands is lifted and the energies are given by

$$E = \frac{1}{2} (3 + v_8 \pm \Delta) - \frac{1}{2} \sqrt{(1 + v_8 \mp \Delta)^2 + 8v_3^2}$$

The wavefunctions retain their form given above, except that the coefficients a_1 and a_2 which depend on the band energies through A

should now be determined by using the appropriate energies for each band.

X₄ bands

$$\psi_3(1,0,0) = b_1[(011)+(0\bar{1}\bar{1})+(0\bar{1}1)-(01\bar{1})] + b_2[(120)+(1\bar{2}0)+(\bar{1}02)+(\bar{1}0\bar{2})]$$

$$\psi_3(0,1,0) = b_1[(101)+(\bar{1}0\bar{1})+(\bar{1}01)-(10\bar{1})] + b_2[(210)+(\bar{2}10)+(0\bar{1}2)+(0\bar{1}\bar{2})]$$

$$\psi_3(0,0,1) = b_1[(110)+(\bar{1}\bar{1}0)+(\bar{1}10)-(1\bar{1}0)] + b_2[(201)+(\bar{2}01)+(02\bar{1})+(02\bar{1})]$$

$$\psi_4(1,0,0) = \psi_3^*(100), \text{ etc.}$$

$$b_1 = \frac{v_3 - v_{11}}{\sqrt{2}} \frac{1}{\sqrt{A^2(X_4) + 2(v_3 - v_{11})^2}} \quad b_2 = -\frac{1}{2} \frac{A(X_4)}{\sqrt{A^2(X_4) + 2(v_3 - v_{11})^2}}$$

$$A(X_4) = 2 - v_8 - E(X_4)$$

$$E(X_4) = \frac{1}{2} (7 - v_8) - \frac{1}{2} \sqrt{(3 + v_8)^2 + 8(v_3 - v_{11})^2}$$

These bands remain degenerate along the $(k,0,0)$, $(1,k,0)$ and $(1,0,k)$ directions and the assignment of a band index to the wavefunctions is arbitrary. Table I contains the energies for the 14×14 and the 6×6 matrix.

5. Wavefunctions at L.

The wavefunctions of the lowest two bands are expanded in 8 plane waves corresponding to $|\vec{k}_L + \vec{G}|^2 \leq \frac{11}{4}$. For the next two higher bands 14 plane waves corresponding to $|\vec{k}_L + \vec{G}|^2 = \frac{19}{4}$ are used in the expansion. For the calculation of the charge density we need the wavefunctions for the equivalent L points $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $(\frac{\bar{1}}{2}, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, \frac{\bar{1}}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{\bar{1}}{2})$. The wavefunctions and energies of the valence bands are given below.

Band 1: L_2 level

$$\psi_1(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) = a_1 [(\frac{1}{2} \frac{1}{2} \frac{1}{2}) - (\frac{1}{2} \frac{1}{2} \frac{1}{2})]$$

$$+ a_2 [(\frac{3}{2} \frac{1}{2} \frac{1}{2}) - (\frac{3}{2} \frac{1}{2} \frac{1}{2}) + (\frac{1}{2} \frac{3}{2} \frac{1}{2}) - (\frac{1}{2} \frac{3}{2} \frac{1}{2}) + (\frac{1}{2} \frac{1}{2} \frac{3}{2}) - (\frac{1}{2} \frac{1}{2} \frac{3}{2})]$$

$$\psi_1(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) = a_1 [(\frac{1}{2} \frac{1}{2} \frac{1}{2}) + (\frac{1}{2} \frac{1}{2} \frac{1}{2})]$$

$$+ a_2 [(-\frac{3}{2} \frac{1}{2} \frac{1}{2}) - (\frac{3}{2} \frac{1}{2} \frac{1}{2}) + (\frac{1}{2} \frac{3}{2} \frac{1}{2}) + (\frac{1}{2} \frac{3}{2} \frac{1}{2}) + (\frac{1}{2} \frac{1}{2} \frac{3}{2}) + (\frac{1}{2} \frac{1}{2} \frac{3}{2})]$$

$$\psi_1(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) = a_1 [(\frac{1}{2} \frac{1}{2} \frac{1}{2}) + (\frac{1}{2} \frac{1}{2} \frac{1}{2})]$$

$$+ a_2 [(-\frac{3}{2} \frac{1}{2} \frac{1}{2}) - (\frac{3}{2} \frac{1}{2} \frac{1}{2}) + (\frac{3}{2} \frac{1}{2} \frac{1}{2}) + (\frac{3}{2} \frac{1}{2} \frac{1}{2}) + (\frac{1}{2} \frac{1}{2} \frac{3}{2}) + (\frac{1}{2} \frac{1}{2} \frac{3}{2})]$$

$$\psi_1(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) = a_1 [(\frac{1}{2} \frac{1}{2} \frac{1}{2}) + (\frac{1}{2} \frac{1}{2} \frac{1}{2})]$$

$$+ a_2 [(-\frac{3}{2} \frac{1}{2} \frac{1}{2}) - (\frac{1}{2} \frac{1}{2} \frac{3}{2}) + (\frac{3}{2} \frac{1}{2} \frac{1}{2}) + (\frac{3}{2} \frac{1}{2} \frac{1}{2}) + (\frac{1}{2} \frac{3}{2} \frac{1}{2}) + (\frac{1}{2} \frac{3}{2} \frac{1}{2})]$$

$$a_1 = \frac{\sqrt{3}}{2} \frac{v_3}{\sqrt{A^2(L_2,) + \frac{3}{2} v_3^2}}, \quad a_2 = -\frac{1}{\sqrt{6}} \frac{A(L_2,)}{\sqrt{A^2(L_2,) + \frac{3}{2} v_3^2}} \quad (9)$$

$$A(L_2,) = \frac{3}{4} + \frac{v_3}{\sqrt{2}} - E(L_2,)$$

$$E(L_2,) = \frac{7}{4} + v_8 - \frac{v_3 + v_{11}}{2\sqrt{2}} - \sqrt{(1 + v_8 - \frac{3v_3 + v_{11}}{2\sqrt{2}})^2 + \frac{3}{2} v_3^2}$$

Band 2: L_1 level

$$\psi_2(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) = b_1[(\frac{1}{2} \frac{1}{2} \frac{1}{2}) + (\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{\bar{1}}{2})]$$

$$+ b_2[(\frac{3}{2} \frac{\bar{1}}{2} \frac{\bar{1}}{2}) + (\frac{\bar{3}}{2} \frac{1}{2} \frac{1}{2}) + (\frac{\bar{1}}{2} \frac{3}{2} \frac{\bar{1}}{2}) + (\frac{1}{2} \frac{\bar{3}}{2} \frac{1}{2}) + (\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{3}{2}) + (\frac{1}{2} \frac{1}{2} \frac{\bar{3}}{2})]$$

$$\psi_2(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) = b_1[(\frac{\bar{1}}{2} \frac{1}{2} \frac{1}{2}) - (\frac{1}{2} \frac{\bar{1}}{2} \frac{\bar{1}}{2})]$$

$$+ b_2[-(\frac{\bar{3}}{2} \frac{\bar{1}}{2} \frac{\bar{1}}{2}) + (\frac{3}{2} \frac{1}{2} \frac{1}{2}) + (\frac{1}{2} \frac{3}{2} \frac{\bar{1}}{2}) - (\frac{\bar{3}}{2} \frac{\bar{3}}{2} \frac{1}{2}) + (\frac{1}{2} \frac{\bar{1}}{2} \frac{3}{2}) - (\frac{\bar{1}}{2} \frac{1}{2} \frac{\bar{3}}{2})]$$

$$\psi_2(\frac{1}{2}, \frac{\bar{1}}{2}, \frac{1}{2}) = b_1[(\frac{1}{2} \frac{\bar{1}}{2} \frac{1}{2}) - (\frac{\bar{1}}{2} \frac{1}{2} \frac{\bar{1}}{2})]$$

$$+ b_2[-(\frac{\bar{1}}{2} \frac{\bar{3}}{2} \frac{\bar{1}}{2}) + (\frac{1}{2} \frac{3}{2} \frac{1}{2}) + (\frac{3}{2} \frac{1}{2} \frac{\bar{1}}{2}) - (\frac{\bar{3}}{2} \frac{\bar{1}}{2} \frac{1}{2}) + (\frac{\bar{1}}{2} \frac{1}{2} \frac{3}{2}) - (\frac{1}{2} \frac{\bar{1}}{2} \frac{\bar{3}}{2})]$$

$$\psi_2(\frac{1}{2}, \frac{1}{2}, \frac{\bar{1}}{2}) = b_1[(\frac{1}{2} \frac{1}{2} \frac{\bar{1}}{2}) - (\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{\bar{1}}{2})]$$

$$+ b_2[-(\frac{\bar{1}}{2} \frac{\bar{1}}{2} \frac{\bar{3}}{2}) + (\frac{1}{2} \frac{1}{2} \frac{3}{2}) + (\frac{3}{2} \frac{\bar{1}}{2} \frac{1}{2}) - (\frac{\bar{3}}{2} \frac{1}{2} \frac{\bar{1}}{2}) + (\frac{\bar{1}}{2} \frac{3}{2} \frac{1}{2}) - (\frac{1}{2} \frac{\bar{3}}{2} \frac{\bar{1}}{2})]$$

where

$$b_1 = \frac{\sqrt{3}}{2} \frac{v_3}{A^2(L_1) + \frac{3}{2} v_3} \quad , \quad b_2 = - \frac{1}{\sqrt{6}} \frac{A(L_1)}{A^2(L_1) + \frac{3}{2} v_3^2} \quad (10)$$

$$A(L_1) = \frac{3}{4} - \frac{v_3}{\sqrt{2}} - E(L_1)$$

$$E(L_1) = \frac{7}{4} + v_8 + \frac{v_3 + v_{11}}{2\sqrt{2}} - \sqrt{(1 + v_8 + \frac{3v_3 + v_{11}}{2\sqrt{2}})^2 + \frac{3}{2} v_3^2}$$

Bands 3 and 4 at L: L_3, v level

For these bands the eigenfunctions of the Hamiltonian at $\vec{k} = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$ are of the form

$$\psi_1(\vec{r}) = c_1 [(\bar{1} \ 1 \ \bar{1}) - (\bar{1} \ \bar{1} \ 1) - (0 \ \bar{2} \ 0) + (0 \ 0 \ \bar{2})] (\frac{1}{2} \frac{1}{2} \frac{1}{2})$$

$$+ c_2 [(1 \ 1 \ \bar{1}) - (1 \ \bar{1} \ 1) - (\bar{2} \ \bar{2} \ 0) + (\bar{2} \ 0 \ \bar{2})] (\frac{1}{2} \frac{1}{2} \frac{1}{2})$$

$$\psi_2(\vec{r}) = c_1 [(\bar{1} \ 1 \ \bar{1}) - (1 \ \bar{1} \ \bar{1}) + (\bar{2} \ 0 \ 0) - (0 \ \bar{2} \ 0)] (\frac{1}{2} \frac{1}{2} \frac{1}{2})$$

$$+ c_2 [-(1 \ \bar{1} \ 1) + (\bar{1} \ 1 \ 1) + (\bar{2} \ 0 \ \bar{2}) - (0 \ \bar{2} \ \bar{2})] (\frac{1}{2} \frac{1}{2} \frac{1}{2})$$

and

$$\psi_3(\vec{r}) = c_1 [-(\bar{1} \ \bar{1} \ 1) + (1 \ \bar{1} \ \bar{1}) - (\bar{2} \ 0 \ 0) + (0 \ 0 \ \bar{2})] (\frac{1}{2} \frac{1}{2} \frac{1}{2})$$

$$+ c_2 [(1 \ 1 \ \bar{1}) - (\bar{1} \ 1 \ 1) - (\bar{2} \ \bar{2} \ 0) + (0 \ \bar{2} \ \bar{2})] (\frac{1}{2} \frac{1}{2} \frac{1}{2})$$

These three functions are not linearly independent. They are related to each other by permutations of the coordinates (r_1, r_2, r_3) of $\vec{r}$. In fact we have

$$\psi_1 = \psi_2 + \psi_3 \quad . \quad (11)$$

The ψ 's are furthermore not orthogonal to one another. Taking the ψ 's to be normalized we can construct three sets of two orthogonal functions.

$$\phi_1 = \psi_1 + \psi_2 \quad \phi_3 = \psi_1 + \psi_3 \quad \phi_5 = \psi_2 + \psi_3$$

$$\phi_2 = \psi_1 - \psi_2 \quad \phi_4 = \psi_1 - \psi_3 \quad \phi_6 = \psi_2 - \psi_3$$

The wavefunctions of bands 3 and 4 can be taken to be proportional to ϕ_1, ϕ_2 or to ϕ_3, ϕ_4 or to ϕ_5, ϕ_6 . Using the relation (11) between the ψ 's we find:

$$\begin{aligned} \phi_1 &= \psi_1 + \psi_2 & \phi_3 &= \psi_1 + \psi_3 & \phi_5 &= \psi_1 \\ & & ; & & ; & \\ \phi_2 &= \psi_3 & \phi_4 &= \psi_2 & \phi_6 &= \psi_2 - \psi_3 \end{aligned} \quad (13)$$

Under the permutation of coordinates these functions transform into one another. Since the permutation of coordinates is a symmetry operation of the Hamiltonian the total charge density is also symmetric under this operation. The charge density at $\vec{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ for the L_3, ν levels should therefore be associated with an average of the charge densities of $\phi_1, \dots, \phi_6$. When the ϕ_i 's are normalized it is simple to verify that this average is simply proportional to $\frac{1}{3}(\psi_1\psi_1^* + \psi_2\psi_2^* + \psi_3\psi_3^*)$. In this way the charge densities at $\vec{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ of bands 3 and 4 remain invariant under the permutation of coordinates. The expansion coefficients are given by the following expressions:

$$c_1 = \frac{v_3 - v_{11}}{2} \frac{1}{\sqrt{2A^2(L_3, \nu) + (v_3 - v_{11})^2}} \quad (14)$$

$$c_2 = \frac{1}{\sqrt{2}} \frac{A(L_3, \nu)}{\sqrt{2A^2(L_3, \nu) + (v_3 - v_{11})^2}} \quad (15)$$

where

$$A(L_3, \nu) = \frac{11}{4} - v_8 + \frac{1}{\sqrt{2}} (v_3 - v_{11}) - E(L_3, \nu)$$

and

$$E(L_3, \nu) = \frac{15}{4} + \frac{v_3 - 2v_{11}}{2\sqrt{2}} - v_8 - \frac{1}{2} \sqrt{2(v_3 - v_{11})^2 + (2\frac{v_3}{\sqrt{2}})^2}$$

is the energy of the degenerate L_{3v} bands. The 8×8 results are given in Table I.

We now need the wavefunctions for $\vec{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, etc.

It is sufficient to find the wavefunction for

$\vec{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; the other wavefunctions can be obtained from the permutations of the coordinates (r_1, r_2, r_3) of $\psi(\vec{k}, \vec{r})$ or from time-inversion symmetry. The wavefunction for $\vec{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ can be obtained from the wavefunction for $\vec{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ by using symmetry operations of the Hamiltonian. Three possible wavefunctions for $\vec{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ are

$$\psi_1(\vec{r}) = c_1[(\bar{1} \bar{1} \bar{1}) - (\bar{1} \bar{1} 1) + (0 \ 0 \ 2) - (0 \ 2 \ 0)](\frac{1}{2} \frac{1}{2} \frac{1}{2})$$

$$+ c_2[(1 \bar{1} \bar{1}) - (1 \bar{1} 1) + (\bar{2} \ 0 \ 2) - (\bar{2} \ 2 \ 0)]$$

$$\psi_2(\vec{r}) = c_1[(\bar{1} \bar{1} \bar{1}) + (1 \ 1 \ 1) + (\bar{2} \ 0 \ 0) + (0 \ 0 \ 2)](\frac{1}{2} \frac{1}{2} \frac{1}{2})$$

$$- c_2[(1 \bar{1} \bar{1}) + (\bar{1} \bar{1} \bar{1}) + (\bar{2} \ 2 \ 0) + (0 \ 2 \ 2)]$$

$$\psi_3(\vec{r}) = -c_1[(\bar{1} \bar{1} \bar{1}) + (1 \ 1 \ 1) + (\bar{2} \ 0 \ 0) + (0 \ 2 \ 0)](\frac{1}{2} \frac{1}{2} \frac{1}{2})$$

$$+ c_2[(1 \bar{1} \bar{1}) + (\bar{1} \bar{1} \bar{1}) + (\bar{2} \ 0 \ 2) + (0 \ 2 \ 2)](\frac{1}{2} \frac{1}{2} \frac{1}{2})$$

These three wavefunctions are not linearly independent. They transform into one another under the symmetry operations of the Hamiltonian which have the effect of leaving $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ invariant. The charge densities of 3 and 4 for this $\vec{k}$ point should each be associated with

$\frac{1}{3}(\psi_1^* + \psi_2^* + \psi_3^*)$. The wavefunctions obtained for the other equivalent L points should be treated in the same way.

6. Charge Density

The total valence band charge density $\rho(\vec{r})$ can be approximated¹⁶ by the following weighted sum of the charge densities at Γ , X, and L:

$$\rho(\vec{r}) = \frac{1}{8} \rho(\Gamma) + \frac{3}{8} \rho(X) + \frac{1}{2} \rho(L) \quad (16a)$$

where

$$\rho(\Gamma) = \sum_{n=1}^4 \rho_n(\Gamma) \quad (16b)$$

$$\rho(X) = \frac{1}{3} \sum_{n=1}^4 [\rho_n(1,0,0) + \rho_n(0,1,0) + \rho_n(0,0,1)] \quad (16c)$$

$$\rho(L) = \frac{1}{4} \sum_{n=1}^4 [\rho_n(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + \rho_n(\frac{\bar{1}}{2}, \frac{1}{2}, \frac{1}{2}) + \rho_n(\frac{1}{2}, \frac{\bar{1}}{2}, \frac{1}{2}) + \rho_n(\frac{1}{2}, \frac{1}{2}, \frac{\bar{1}}{2})] \quad (16d)$$

In these expressions n indicates the band index. The charge density of each band should be multiplied by a factor of two to include for both spin states.

For the Group IV compounds, the most important region of charge concentration occurs at and around the bond sites. To obtain the correct charge density in this region, the wavefunctions need to be expanded in a large number of plane waves. The expansion of the wavefunctions of section II has been limited to two sets of symmetrized combinations of plane waves (SCPWs) in order to have simple results for

for the energy and the wavefunctions. The coefficients of higher SCFWs and the change in energy resulting from these extra plane waves can be easily obtained from Löwdin⁴⁴ perturbation theory.

Denoting H_{mn} to be the matrix element of the Hamiltonian between two plane waves of the form $|\vec{k} + \vec{G}_m\rangle$ and $|\vec{k} + \vec{G}_n\rangle$, the coefficient of the latter is given by

$$c_n = \sum_m \frac{H_{nm}}{E - H_{mm}} \quad (17)$$

where the sum on m is over those plane waves which have been taken into account without perturbation theory and c_n is the coefficient of a higher plane wave. Equation (17) can also be used to obtain the relative phase factors between the plane waves of the higher SCFWs, i.e., it can be used to construct the higher SCFWs for a given $\vec{k}$ -vector. The energy E occurring in (17) is in principle the exact energy of the band in question. However it is a good first approximation to use the energy obtained from limited plane wave expansions instead of the exact energy. The change in the energy when larger plane waves are taken into account is also easy to obtain from the Löwdin theory.⁴⁴ The size of the 2×2 secular equations remains unchanged but the elements of the 2×2 matrix are modified with the inclusion of the higher SCFWs.

We find that the energy differences between the bands at a given $\vec{k}$ point can be determined fairly accurately by using the expressions in Table I. The application of perturbation theory does not appreciably alter these energy differences. However the energies of individual levels are usually lowered when higher plane waves are used (all energies

are measured relative to $V_0 = V(\vec{G} = 0)$ which was taken equal to zero in section III. This lowering of the energies has an important effect on the bonding charge. When Eq. (16) is applied directly to the wavefunctions of section II the resulting charge density at the bond site is found to be smaller than the correct⁷³ value by about 35% for the case of Ge. If we lower the energies of all levels by 0.16 Ry (in an attempt to simulate the effects of perturbation theory) we obtain a remarkable improvement in the charge density. For Ge we obtain a charge density of 21 at the bond site compared to the correct value of about 26 (normalized to $8e/\Omega$, $\Omega = \frac{a^3}{4}$ = volume of primitive cell). At the atomic site we obtain a value of 10 as compared to the value of 12 of reference 88. Since our wavefunctions have been expanded in a limited number of SCFWs it is not surprising that we do not obtain as localized a charge density as in the exact calculation⁷³ where each wavefunction has been expanded in about 90 plane waves.

The values of $\rho(\Gamma)$, $\rho(X)$ and $\rho(L)$ for Ge at the bond and atomic sites are given in Table III. We have used the CB form factors,³³ i.e. $V_j = -0.23$, $V_2 = 0.01$ and $V_{11} = 0.06$. The energies of all bands were shifted downward by 0.16 Ry before being used in the calculation. The average of the charge densities of bands 3 and 4 at Γ , X and L are shown in Table IV and compared to the exact values of Ref. 88.

Although Eqs. (16) do not provide the exact values of the charge density $\rho(r)$ they are nevertheless useful in obtaining information about $\rho(\vec{r})$ induced by changes in the pseudopotential parameters or the lattice constant can be determined fairly accurately from the results of sections 2 and 3. An example is the problem of the pressure

dependence⁸⁹ of the charge density. Under high hydrostatic pressure the charge density becomes more spread out and metallic-like.⁹⁰ Using the expressions of sections II and III we can easily check the dependence of the charge density on the lattice constant and the pseudopotentials. We find that the bonding charge, $\rho(0)$, decreases (almost linearly) with a decrease in the lattice constant. The rate of decrease of $\rho(0)$ (i.e. the charge density at the bond) is about a tenth of the rate of decrease of the lattice constant. The charge density at the atomic sites decreases twice as fast as the bonding charge. We have also examined the pseudopotential dependence of the charge density for Si. The pressure dependence of the pseudopotentials has been analyzed by C. V. de Alvarez and M. L. Cohen.⁹⁰ For Si, they have determined the scaling of form factors which gives rise to the correct variation of the optical gaps with pressure. We have used their pseudopotentials for zero and 20 kbar pressures in calculating the charge density. We find that at 20 kbars the change in the lattice constant, together with the resultant change in the form factors decreases $\rho(0)$ (i.e. the charge density at the bond) by 1% from its value at zero pressure. This is two and a half times larger than the decrease resulting from a change in the lattice constant alone. This indicates that the change in the pseudopotentials has a greater effect in reducing the bonding charge than the change in the lattice constant. This rate of decrease of the bonding charge with pressure is nearly the same as that obtained in Ref. 90 and the calculations here using analytic expressions are much simpler.

The expressions of sections 2 and 3 may be useful in calculating changes in energies, wavefunctions and charge densities resulting from

other possible changes in the pseudopotential parameters or the lattice constant. The use of Löwdin⁴⁴ perturbation may be necessary in some calculations in order to obtain more accurate results. The expressions of sections 2 and 3, however, predict the correct trends in most cases.

Table I. Explicit dependence of energies on pseudopotential form factors for the symmetry points Γ , X , and L . The unit of energy is $(2\pi a_0/a)^2$ Ry. Some of these expressions are also given in the text.

Energies at Γ , X , L	
<u>Matrix size</u>	<u>$\Gamma = (0,0,0)$</u>
15×15	$E(\Gamma_1) = \frac{3(1+V_8)}{2} - \sqrt{\frac{9}{4}(1+V_3)^2 + 4V_3^2}$
15×15	$E(\Gamma_{25'}) = \frac{7(1-V_8)}{2} - \frac{1}{2} \sqrt{(1+V_3)^2 + 8(V_3-V_{11})^2}$
15×15	$E(\Gamma_{2'}) = \frac{7(1+V_8)}{2} - \sqrt{\left(\frac{1-V_8}{2}\right)^2 + 6(V_3+V_{11})^2}$
	<u>$X = (1,0,0) \frac{2\pi}{a}$</u>
6×6	$E_V(X_1) = \frac{3+V_8}{2} - \frac{1}{2} \sqrt{(1+V_3)^2 + 8V_3^2}$
	$E_V(X_4) = 2 - V_8$
	$E_C(X_1) = \frac{3+V_8}{2} + \frac{1}{2} \sqrt{(1+V_3)^2 + 8V_3^2}$
14×14	$E_V(X_4) = \frac{7-V_8}{2} - \frac{1}{2} \sqrt{(3+V_3)^2 + 8(V_3-V_{11})^2}$

Table I (Cont.)

	$L = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right) \frac{2\pi}{a}$
8 × 8	$F(L_{21}) = \frac{7}{4} + V_8 - \frac{V_3 + V_{11}}{2\sqrt{2}} - \sqrt{\left(1 + V_8 - \frac{3V_3 + V_{11}}{2\sqrt{2}}\right)^2} + \frac{3}{2} V_3^2$
	$E(L_1) = \frac{7}{4} + V_8 + \frac{V_3 + V_{11}}{2\sqrt{2}} - \sqrt{\left(1 + V_8 + \frac{3V_3 + V_{11}}{2\sqrt{2}}\right)^2} + \frac{3}{2} V_3^2$
	$E(L_{3V}) = \frac{11}{4} - V_8 + \frac{V_3 - V_{11}}{\sqrt{2}}$
	$E(L_{1c}) = \frac{7}{4} + V_8 + \frac{V_3 + V_{11}}{2\sqrt{2}} + \sqrt{\left(1 + V_8 + \frac{3V_3 + V_{11}}{2\sqrt{2}}\right)^2} + \frac{3}{2} V_3^2$
	$E(L_{2c}) = \frac{11}{4} - V_8 - \frac{(V_3 - V_{11})}{\sqrt{2}}$
14 × 14	$F(L_{21c}) = \frac{7}{4} + V_8 - \frac{V_3 + V_{11}}{2\sqrt{2}} - \sqrt{\left(1 + V_8 - \frac{3V_3 + V_{11}}{2\sqrt{2}}\right)^2} + \frac{3}{2} V_3^2$
	$F(L_{3V}) = \frac{15}{4} + \frac{V_3 - 2V_{11}}{2\sqrt{2}} - V_8 - \frac{1}{2} \sqrt{2(V_3 - V_{11})^2} + \left(2 + \frac{V_3}{\sqrt{2}}\right)^2$
	$E(L_{3c}) = \frac{15}{4} - \frac{V_3 - 2V_{11}}{2\sqrt{2}} - V_8 - \frac{1}{2} \sqrt{2(V_3 - V_{11})^2} + \left(2 + \frac{V_3}{\sqrt{2}}\right)^2$

Table II. Wavefunctions for $\Gamma_1, \Gamma_{25'}$, and Γ_2 , levels. The expansion coefficients are given in Sec. 2.

$\psi_n \bar{G}$	(000)	(111)	($\bar{1}\bar{1}\bar{1}$)	(11 $\bar{1}$)	($\bar{1}\bar{1}1$)	(1 $\bar{1}\bar{1}$)	($\bar{1}11$)	($\bar{1}\bar{1}1$)	(11 $\bar{1}$)	(200)	($\bar{2}00$)	(020)	(0 $\bar{2}0$)	(002)	(00 $\bar{2}$)
$\psi_1(\Gamma_1)$	a_1	a_2	a_2	$-a_2$	$-a_2$	$-a_2$	$-a_2$	$-a_2$	$-a_2$	0	0	0	0	0	0
$\psi_2(\Gamma_{25'})$	0	b_1	b_1	c_1	b_1	b_1	b_1	$-c_1$	$-c_1$	c_2	c_2	0	0	0	0
$\psi_3(\Gamma_{25'})$	0	b_1	b_1	c_1	b_1	$-b_1$	$-b_1$	c_1	b_1	0	0	b_2	b_2	0	0
$\psi_4(\Gamma_{25'})$	0	b_1	b_1	$-b_1$	$-b_1$	b_1	b_1	b_1	b_1	0	0	0	0	b_2	b_2
$\psi_5(\Gamma_2)$	0	c_1	$-c_1$	c_1	$-c_1$	c_1	$-c_1$	c_1	$-c_1$	c_2	$-c_2$	c_2	$-c_2$	c_2	$-c_2$

Table III. Symmetrized charge densities of all valence bands at Γ , X, and L. The charge density

$$\rho(\vec{r}) = \frac{1}{8} \rho(\Gamma) + \frac{3}{8} \rho(X) + \frac{1}{2} \rho(L);$$

(see Eq. 16 of text). The values of $\rho(\vec{r})$ in parenthesis are the exact values obtained from Ref. 73.

	$\rho(\Gamma)$	$\rho(X)$	$\rho(L)$	$\rho(\vec{r})$
Band	29.3	14.5	23.3	21.0 (20)
Atom	7.8	5.7	13.9	10.1 (12)

Table IV. Average of the charge densities of bands 3 and 4 at Γ , X and L. The values in parenthesis are the exact values of Ref. 88.

	$\rho_{3,4}(\Gamma)$	$\rho_{3,4}(X)$	$\rho_{3,4}(L)$	$\rho_{3,4}(\vec{r})$
Band	8(11)	5(7)	8(10)	7(9)
Atom	0(0)	0(0)	0(0)	0(0)

V. ELECTRONIC BAND STRUCTURES AND CHARGE DENSITIES OF NbC AND NbN

Abstract

In this section we present non-local pseudopotential calculations of the electronic band structures and charge densities of NbC and NbN. The major contribution to the charge density of the bands near the Fermi energy comes from C or N 2p-states. The charge density for the first partially filled Nb 4d-band and the shape of the Fermi surface for this band are also discussed.

1. Introduction

Transition metal compounds have been the object of much research for some time because of their unusual physical properties. Some of these compounds are high temperature superconductors with superconducting transition temperatures that vary appreciably with composition.⁹¹ Despite the great practical and theoretical interest in these compounds, the electronic structure of many transition metal compounds have not been studied in detail as yet.

In this paper we apply the empirical pseudopotential method (EPM) to the study of two transition metal compounds: NbC and NbN. The band structure and density of states of NbN have been recently calculated by the APW^{92,93} and the EPM⁹⁴ methods. The band structure and density of states of NbN presented in this paper are the same as those of Ref. 94. For NbC only the density of states has been presented previously (calculated using the APW method).⁹⁵

Usual EPM calculations are based on experimental data such as optical reflectivity spectra, which provide information on critical point energy gaps, and on photoemission data which give information on the density of states. Such experimental information is lacking for NbN and some other transition metal compounds. The EPM band structure calculation⁹⁴ for NbN was therefore fitted to a self-consistent⁹³ APW calculation and the results indicated that the non-local EPM method could be used to obtain accurate band structures for transition metal compounds of interest. Our calculations on NbC are an extension of the EPM calculation⁹⁴ on NbN. We find the band structures of NbC and NbN to be very similar. The important difference between the two compounds appears to be the position of the Fermi energy which determines the occupancy and electronic charge distribution in the partially filled Nb 4d-bands. The band structures, charge density distributions and Fermi surfaces of NbC and NbN are discussed in the section II in more detail.

The pseudopotentials used in the NbC calculation were obtained from previous EPM calculations on NbN⁹⁴ and C. The non-local d-pseudopotential of the NbN calculation was used in NbC to treat the Nb 4d-states. The non-local p-pseudopotential needed for the C 2p-states was obtained from the previous EPM calculation on C and adjusted for the lattice constant change. All the relevant pseudopotential parameters for NbC are listed in Table I and their significance is discussed in Ref. 94 which also includes the NbN pseudopotentials.

The energy band structure of NbC was calculated on a grid of 46 points in 1/48 of the irreducible part of the Brillouin zone. To obtain sufficient convergence for the charge density calculation the wavefunctions for NbC and NbN were expanded in a basis set of about 150 plane waves. The band structure, charge density and Fermi surface results are discussed in the next section.

2. Results

The band structures and densities of state of NbC and NbN are shown in Figs. 1-4. In discussing the band structures and charge densities of these compounds we will number the bands according to their energies. This can cause a band (such as band 3 in NbC and NbN) to be mostly p-like in some part of the Brillouin zone and d-like in another part of the zone, as can be seen by following band 3 from Γ to X.

The lowest valence band in NbC arising from C 2s-states is not shown in Fig. 1. This band is separated by a large energy difference from the higher bands and does not mix with them. This is consistent with other APW^{92,93} calculations on NbN; however the precise energy of this band relative to the higher bands does not seem to be well established. High energy photoemission experiments would be very useful in determining the position of this band. The next three higher bands with Γ_{15} symmetry at $\vec{k} = 0$ arise mainly from C or N 2p-states together with some Nb 5p-states. In addition, there is a small overlap and mixing between these bands and Nb 4d-states as can be seen in going from Γ to X in the Brillouin zone. This type of overlap is also present

in the self-consistent APW calculation of Schwarz⁹³ for NbN but is absent in the APW calculation of Mattheiss.⁹² Some measurements of NbC valence band X-ray emission spectra^{97,98} indicate that the Nb 4d-states overlap with the C 2p-states more than our calculation⁹⁹ indicates. To obtain better agreement with these experimental results the C 2p-states would have to be moved closer to the Fermi energy.

The band structures and band orderings for NbC and NbN shown in Figs. 1-2 are seen to be very similar in the region below the Fermi energy E_F . The partially filled bands at E_F come from a mixture of Nb 4d-states and C or N 2p-states. The Nb 5s state is high in energy and lies above the Fermi energy in both NbC and NbN. The electronic charge in this state has been transferred to the Nb 4d-levels while some Nb 4d-electrons have dropped into the C 2p-states. The position of the Nb 5s level relative to the 5d-levels is seen to be lower in NbC than in NbN (Figs. 1-2). This tends to make the dispersion of the bands above E_F somewhat different in NbC and NbN because of interactions between the bands. Other calculations on NbN^{92,93} and TiC^{100,101} also reveal the transition metal s-states to be above the Fermi energy.

The densities of states, $N(E)$, of NbC and NbN (Figs. 3-4) are also seen to be very similar. The Fermi energy, E_F , measured relative to the energy of $\Gamma_{25'}$ state, is higher in NbN than in NbC because of the extra electron in NbN. In both crystals E_F lies in a dip of $N(E)$ and NbN has a larger density of states at E_F than NbC. This could, perhaps, be related to the higher superconducting transition temperature found in NbN. The large peak on the low energy side of $N(E)$ comes

mainly from C or N 2p-states. The lowest lying C or N 2s-states are not shown in Figs. 3-4.

The charge densities for several bands in NbC and NbN are shown for the (100) and (110) planes in Figs. 5-13. The charge densities for the lowest bands are strongly concentrated on the non-metal ions and are not shown in these figures. The charge densities for the p-like bands (i.e. bands 2, 3, and 4) are very similar in NbC and NbN. The charge densities of the three bands are also very similar to one another. In Fig. 5 we show the charge density in the (100) plane for one of these bands in NbC. The charge density is p-like around C; it rises to a maximum as we go away from C and then gradually decreases. This is similar to the behavior of the p-like charge densities in semiconductors^{73,102} although the shape of the contours depends on crystal symmetry. The d-states of Nb contribute to the small charge density around Nb. The outermost closed contour around C contains approximately 60% of the total charge in band 3 while the corresponding contour around Nb contains only about 15% of the total charge. The remaining 25% of the charge is spread out almost uniformly in the rest of the unit cell.

The higher bands in NbC and NbN are each only partially filled. The first partially filled band (i.e. band 5 with symmetry Γ_{25} , at $\vec{k} = 0$) contains nearly all the remaining electron in NbC and over 80% of the two remaining electrons in NbN. The charge density of this band in the (100) and (110) planes are shown in Figs. 6-9. The interesting feature of these figures are the local maxima in the charge density occurring along the Nb-Nb direction. The magnitude of the charge in

the maxima is strongly dependent on the number of electrons per unit cell and is twice as large in NbN (with 10 electrons) than in NbC (with 9 electrons). These maxima arise from the Nb 4d-states and have d_{xy} symmetry about the Nb atoms. The charge density of band 5 is not purely d-like. There is a large mixture of C 2p-states in the wavefunction which gives the p-like charge distribution around C.

The sum of the charge densities of all occupied states in NbC and NbN are shown in Figs. 10-13. The strong concentration of charge on C or N evident in these figures arises from the first s-like valence bands in NbC and NbN. The C or N 2s-bands could be too low in energy in our calculation and this would tend to make the charge localization on C or N stronger than it should be. Since the Nb 5s-state lies above the Fermi energy there is no charge localization on Nb; the charge contours around Nb coming from the Nb 4d and 5p states have much lower values than the combination of s,p-contours around C or N. Figures 10-13 show the charge distribution of NbC and NbN to be strongly ionic in character. A spread out metallic-like charge distribution outside the closed contours around the ions can also be seen in these figures. This seems to indicate that bonding in NbC and NbN results mainly from a combination of ionic and metallic charge distributions. The C-C, N-N and Nb-Nb metal and non-metal nearest neighbor distances are too large for the formation of localized covalent bonds as in the case of the diamond or zincblende crystals where the bonding is characterized by a peak in the magnitude of the charge density on the line joining the nearest neighbor atoms. The overlap between the bonding orbitals on the ions in NbC and NbN are small and do not produce a

maximum in the charge density. The overlap results, instead, in a region, centered halfway between like atom nearest neighbors, with a slowly varying charge distribution which appears metallic-like. The bonding configuration for NbC and NbN (and probably in other transition metal compounds as well) can be described as having ionic, covalent and metallic components.

A very interesting property of NbC, NbN and some other transition-metal carbides is the occurrence of anomalies in the phonon dispersion curves of those compounds and the association of these with a high superconducting^{103,104} transition temperature, T_c . These phonon anomalies have been interpreted by Weber, Bilz and Schröder¹⁰⁵ as resulting from resonances in the $\vec{q}$ -dependent polarizability of the metal ions. They attribute the coupling between the metal ions as arising from a charge density with d_{xy} symmetry. This is consistent with the charge density of band 5 in NbC and NbN (Figs. 6-9) which we have obtained. Because of the extra electron in NbN compared to NbC the magnitude of the charge in the d_{xy} peak is larger in NbN than in NbC. The coupling between the Nb atoms is therefore expected to be larger in NbN than in NbC. If the number of valence electrons is reduced from 9 to 8 (as in going from NbC to NbC_{0.75}) the magnitude of the charge in the d_{xy} peak becomes nearly zero. It is interesting to note that no phonon anomalies are observed in¹⁰³ NbC_{0.75}. If the phonon anomalies and high values of T_c are related to resonances in $\vec{q}$ -dependent polarizability of the metal ions then it appears that it is band 5 which is most important in determining the superconducting properties of NbC, NbN and other transition-metal carbides.

A cross-section of the Fermi surface of NbC for band 5 is shown in Fig. 14. The Fermi surface of NbN for various bands at the Fermi energy is given in Ref. 94. An interesting feature of the NbC Fermi surface is the magnitude of wavevectors separating the occupied and empty states. The wavevectors AD and BC (Fig. 14) with $\vec{q} \cong \frac{2\pi}{a} (\frac{2}{3}, 0, 0)$ and the wavevector GH with $\vec{q} \cong \frac{2\pi}{a} (0.5, 0.5, 0)$ are in good agreement with the $\vec{q}$ values at which the anomalies in the phonon dispersion curves have been observed.¹⁰³ It is possible that the shape of the Fermi surface in NbC and NbN can lead to an enhancement of the observed phonon anomalies in these compounds. It should be noted, however, that experimentally the phonon anomalies disappear without any shift in their position when the number of valence electrons is diminished.¹⁰³ We expect the shape of the Fermi surface and the wavevectors at which resonance behavior may occur to change with the number of valence electrons.

Table I. Pseudopotential parameters for NbC. Non-local d and p-pseudopotentials were used in addition to the local pseudopotentials in calculating the band structure of NbC.

Local Pseudopotentials	Parameters for non-local d-pseudopotential (See Ref. 5)	Parameters for non-local p-pseudopotential (See Ref. 7)
$V^A(G^2 = 3) = 0.444$	$V_{NL} = \begin{cases} A_2 & r \leq R_s \\ 0 & r > R_s \end{cases}$	$V_{NL} = \begin{cases} A r e^{-\alpha r} & r \leq R_s \\ 0 & r > R_s \end{cases}$
$V^A(11) = 0.06$	$R_s = 1.18 \text{ \AA}$	$R_s = 0.20 \text{ \AA}$
$V^B(4) = -0.14$	$A_2 = -4.65 \text{ Ry}$	$A = -0.19 \text{ Ry}$
$V^C(8) = -0.11$	$\alpha = 0.118$	$\alpha = 1.10 \text{ \AA}^{-1}$
$V^S(12) = -0.066$	$\kappa = 1.74$	
$a = 4.47 \text{ \AA}$		

Figure Captions

- Fig. 1. Electronic energy band structure of NbC along principal symmetry directions. The lowest C 2s-band is not shown. The zero of energy is at the Γ_{25} level.
- Fig. 2. Electronic energy band structure of NbN. This band structure was obtained from Ref. 5. The zero of energy is at the Γ_{15} level.
- Fig. 3. Density of states of NbC. The density of states of the lowest band is not shown.
- Fig. 4. Density of states of NbN. The density of states of the lowest band is not shown.
- Fig. 5. Electronic charge density of band 3 in the (100) plane of NbC. The charge density arises mainly from C 2p-states with the Nb 4d-state making a small contribution. Charge density is normalized to $2e/\Omega$ = primitive cell volume.
- Fig. 6. Charge density of the first partially filled band in NbC for the (100) plane.
- Fig. 7. Charge density of the first partially filled band in NbC for a (110) plane. The "empty" region in the middle with no contours has a nearly uniform charge density of about $0.7(e/\Omega)$.
- Fig. 8. Charge density of the first partially filled band in NbN for a (100) plane.
- Fig. 9. Charge density of the first partially filled band in NbN for a (110) plane.

Fig. 10. Total charge density of occupied states in NbC for a (100) plane.

Fig. 11. Total charge density in NbC plotted for a (110) plane.

Fig. 12. Total charge density of NbN for a (100) plane.

Fig. 13. Total charge density of NbN for a (110) plane.

Fig. 14. A cross section of the Fermi surface for the first partially filled band in NbC.

XBL 748-7022

Fig. 1.

Fig. 2.

XBL 748-7008

XBL 748-7030

Fig. 3.

Fig. 4.

Fig. 17

XBL 748-7051

Fig. 6.

XRL 748-7052

Fig. 7.

Fig. 8.

XBL 748-7053

Fig. 9.

XBL 748-7031

Fig. 10.

XBL 748-7032

Fig. 11.

XBL 748-7035

Fig. 12.

XBL 748-7034

Fig. 13.

NbC BAND 5 FERMI SURFACE

$\Gamma (0,2,0)$

$\Gamma (2,2,0)$

XBL 748-7028

Fig. 14.

VI. TIGHT-BINDING CALCULATIONS OF BULK AND SURFACE STATES

A. Tight-Binding Calculations of the Valence Bands of Diamond and Zincblende Crystals

Abstract

In this section we use the tight-binding method, to calculate the valence band structures and densities of states of C, Si, Ge, GaAs and ZnSe. We obtain very good agreement with other calculations when we include all nearest and one second nearest neighbor interactions. The effects of the various interactions on the density of states are discussed.

1. Introduction

The tight-binding approach to the problem of the electronic energy levels in solids is intuitively very appealing. The method provides a real space picture of the electronic interactions which give rise to the particular features of the energy band structure, density of states, etc. This is extremely useful in studies of how these features change when the electronic configuration is altered. The tight-binding method is most practical when only a few types of electronic interactions are dominant. In such a case an adequate description of the system of interest can be obtained by specifying a small number of interaction parameters. In this way a qualitative description of the valence bands can be obtained^{2,105-110} for materials in the diamond, zincblende and other structures.

In this paper we show that a tight-binding method using a few interaction parameters gives accurate results for the valence bands of the diamond and zincblende crystals C, Si, Ge, GaAs, and ZnSe. The tight-binding method we use is equivalent to that of Slater and Koster.² It can also be regarded as a more complete version of the Weaire and Thorpe¹⁰⁷ model in which interactions between more distant directed orbitals are included.^{111,112} It is necessary to include these extra interactions for a more complete description of the valence bands. In section 2 we give a brief review of the method and consider the effects of the various interactions on the density of states. We show that the inclusion of all the possible nearest neighbor interactions¹¹³ between s and p-tight-binding states is not sufficient to broaden the "p-like" bands along all symmetry directions. The resulting error in the energies is about 1 eV and occurs mostly for states near the surface of the Brillouin zone. With the inclusion of only one second-nearest-neighbor interaction, the accuracy is greatly improved and the resulting valence band structures and densities of states exhibit all the structures obtained in other calculations.

The band structures, densities of states and interaction parameters for C, Si, Ge, GaAs and ZnSe are discussed in section 3. The dependence of the energy levels, along several symmetry directions and at some symmetry points, on the interaction parameters are also given in section 3. These expressions are useful for obtaining information about the interaction parameters.

2. Tight-Binding Method

In diamond and zincblende crystals, every atom is tetrahedrally coordinated and there are two atoms in the primitive cell. For each tight-binding basis function centered on these atoms, two Bloch functions can be constructed. For example for a tight-binding basis function $b(\mathbf{r})$ we have the two Bloch functions

$$\psi_0(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} b_0(\mathbf{r} - \mathbf{R}), \quad (1)$$

and

$$\psi_1(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} b_1(\mathbf{r} - \mathbf{R} - \mathbf{l}) \quad (2)$$

where $\mathbf{l}$ is the vector joining the two atoms in the primitive cell and the subscripts on b refer to the atoms in the primitive cell. In the diamond structure crystals we take $b_0(\mathbf{r}) = b_1(\mathbf{r})$, but in the zincblende crystals the two functions are different.

In order to have

$$\langle \psi_i(\mathbf{k}, \mathbf{r}) | \psi_j(\mathbf{k}, \mathbf{r}) \rangle = \delta_{ij} \quad i, j = 0, 1 \quad (3)$$

we must require that the tight-binding functions on different atomic sites be orthonormal:

$$\langle b_0(\mathbf{r} - \mathbf{R}_m) | b_1(\mathbf{r} - \mathbf{R}_n - \mathbf{l}) \rangle = 0 \quad (4)$$

$$\langle b_i(\mathbf{r}) | b_i(\mathbf{r}) \rangle = 1 \quad (5)$$

These conditions can always be accomplished by a method due to Löwdin² without affecting the symmetry of the basis functions.

The basic problem of the tight-binding method is to find the matrix elements of the Hamiltonian between the various basis states. For example, if we place s-states on each atomic site and take only nearest-neighbor interactions, we find the following 2x2 matrix for the eigenvalues:

$$\begin{vmatrix} E_{s_0} - E(k) & V_{ss} g_0(k) \\ V_{ss} g_0^*(k) & E_{s_1} - E(k) \end{vmatrix} \approx 0. \quad (6)$$

The parameters E_{s_0} and E_{s_1} are the energies of the tight-binding s-states:

$$E_{s_0} = \langle s | H | s \rangle, \quad E_{s_1} = \langle s_1 | H | s_1 \rangle.$$

In diamond structure crystals $E_{s_0} = E_{s_1}$ and will be denoted simply by E_s . The parameter

$$V_{ss} = 4 \langle s_0(\mathbf{r}) | H | s_1(\mathbf{r}-\mathbf{r}) \rangle$$

measures the strength of the nearest neighbor interaction (the factor of 4 is used for convenience) and

$$g_0(\mathbf{k}) = \frac{1}{4} \sum_{j=1}^4 e^{i\mathbf{k} \cdot \mathbf{r}_j} \quad (7)$$

results from the phase difference between the atoms at the four corners of the tetrahedron defined by $\mathbf{r}_1 = \frac{1}{4}(1,1,1)a$, $\mathbf{r}_2 = \frac{1}{4}(1,\bar{1},\bar{1})a$, $\mathbf{r}_3 = \frac{1}{4}(\bar{1},1,\bar{1})a$ and $\mathbf{r}_4 = \frac{1}{4}(\bar{1},\bar{1},1)a$ where a is the lattice constant. (To obtain g_0 we assign a phase factor $e^{i\mathbf{k}\cdot\mathbf{r}_j}$ to each orbital in Fig. 1. In this way the phase of the Bloch function changes by $e^{i\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_1)} = e^{i\mathbf{k}\cdot\mathbf{R}}$ in going from atom i to j ($i, j = 1, 2, \dots, 4$), which is consistent with Eqs. 1-2.)

In a similar way, we can obtain the matrix elements of the interactions between the other orbitals. We will consider here only the case where we have only one set of s , p_x , p_y and p_z orbitals at each atomic site. We will denote these by s_0, x_0, y_0, z_0 or s_1, x_1, y_1, z_1 where the subscripts as before refer to the atoms in the primitive cell. The Hamiltonian matrix elements between an s and a p -state on the same atom or two different p -states on the same atom are zero because of symmetry in diamond and zincblende crystals. To describe the interaction of an s -state on one atom with the p -state of a nearest neighbor atom we need one parameter for the group IV crystals and two parameters for the zincblende crystals, where there are different s and p orbitals on the basis atoms. We will denote the interactions between s and p_x orbitals by $V_{s_0p}g_1$ and $V_{s_1p}g_1$ where

$$V_{s_0p} = 4 \langle s_0(\mathbf{r}) | H | x_1(\mathbf{r}-\mathbf{r}_1) \rangle \quad (8)$$

$$V_{s_1p} = -4 \langle s_1(\mathbf{r}-\mathbf{r}_1) | H | x_0(\mathbf{r}) \rangle \quad (9)$$

$$g_1(k) = \frac{1}{4} (e^{ik \cdot r_{1+e}} e^{ik \cdot r_{2-e}} e^{ik \cdot r_{3-e}} e^{ik \cdot r_{4}}) . \quad (10)$$

For the group IV crystals $V_{s_0 p} = V_{s_1 p}$ and will be denoted simply by V_{sp} . The minus sign in front of some of the phase factors result from the fact that the sign of the matrix elements $\langle s_0(x) | H | x_1(x - r_j) \rangle$ and $\langle s_1(x - r_j) | H | x_0(x) \rangle$ depend² on the sign of $(r_j)_x$. For r_1 and r_2 the sign is positive, for r_3 and r_4 it is negative. These differences in sign are incorporated into g_1 . To obtain the matrix elements for the $s-p_y$ and $s-p_z$ interactions g_1 should be replaced by

$$g_2(k) = \frac{1}{4} (e^{ik \cdot r_{1-e}} e^{ik \cdot r_{2+e}} e^{ik \cdot r_{3-e}} e^{ik \cdot r_{4}}) \quad (11)$$

for $s-p_y$ type interactions, and

$$g_3(k) = \frac{1}{4} (e^{ik \cdot r_{1-e}} e^{ik \cdot r_{2-e}} e^{ik \cdot r_{3+e}} e^{ik \cdot r_{4}}) \quad (12)$$

for $s-p_z$ type interactions. The matrix elements between s , p and d basis functions have been derived in Ref. (2). The 8×8 secular matrix representing all possible nearest neighbor interactions between the tight-binding s and p orbitals centered on each atom in the crystal is:

	s_0	s_1	x_0	y_0	z_0	x_1	y_1	z_1
s_0	$E_{s_0} - E(\tilde{k})$	$V_{ss}g_0$	0	0	0	$V_{s_0p}g_1$	$V_{s_0p}g_2$	$V_{s_0p}g_3$
s_1	$V_{ss}g_0^*$	$E_{s_1} - E(\tilde{k})$	$-V_{s_1p}g_1^*$	$-V_{s_1p}g_2^*$	$-V_{s_1p}g_3^*$	0	0	0
x_0	0	$-V_{s_1p}g_1$	$E_{p_0} - E(\tilde{k})$	0	0	$V_{xx}g_0$	$V_{xy}g_3$	$V_{xy}g_1$
y_0	0	$-V_{s_1p}g_2$	0	$E_{p_0} - E(\tilde{k})$	0	$V_{xy}g_3$	$V_{xx}g_0$	$V_{xy}g_1$
z_0	0	$-V_{s_1p}g_3$	0	0	$E_{p_0} - E(\tilde{k})$	$V_{xy}g_1$	$V_{yy}g_2$	$V_{xx}g_0$
x_1	$V_{s_0p}g_1^*$	0	$V_{xx}g_0^*$	$V_{xy}g_3^*$	$V_{xy}g_1^*$	$E_{p_1} - E(\tilde{k})$	0	0
y_1	$V_{s_0p}g_2^*$	0	$V_{xy}g_3^*$	$V_{xx}g_0^*$	$V_{xy}g_2^*$	0	$E_{p_1} - E(\tilde{k})$	0
z_1	$V_{s_0p}g_3^*$	0	$V_{xy}g_1^*$	$V_{xy}g_2^*$	$V_{xx}g_0^*$	0	0	$E_{p_1} - E(\tilde{k})$

= 0

(13)

For diamond structure crystals $E_{s_0} = E_{s_1}$, $E_{p_0} = E_{p_1}$ and $V_{s_0p} = V_{s_1p}$ and from this point we will drop the subscripts for these crystals.

The functions g_0 , g_1 , g_2 and g_3 which we have previously defined can also be expressed in the following way:

$$g_0(k) = \cos\frac{k_1}{2} \cos\frac{k_2}{2} \cos\frac{k_3}{2} - i \sin\frac{k_1}{2} \sin\frac{k_2}{2} \sin\frac{k_3}{2} \quad (14)$$

$$g_1(k) = -\cos\frac{k_1}{2} \sin\frac{k_2}{2} \sin\frac{k_3}{2} + i \sin\frac{k_1}{2} \cos\frac{k_2}{2} \cos\frac{k_3}{2} \quad (15)$$

$$g_2(k) = -\sin\frac{k_1}{2} \cos\frac{k_2}{2} \sin\frac{k_3}{2} + i \cos\frac{k_1}{2} \sin\frac{k_2}{2} \cos\frac{k_3}{2} \quad (16)$$

$$g_3(k) = -\sin\frac{k_1}{2} \sin\frac{k_2}{2} \cos\frac{k_3}{2} + i \cos\frac{k_1}{2} \cos\frac{k_2}{2} \sin\frac{k_3}{2} \quad (17)$$

where $k = \frac{2\pi}{a} (k_1, k_2, k_3)$.

For diamond structure crystals, the parameters appearing in (13) are related to those of Slater and Koster² by

$$\begin{aligned} E_s &= E_{s,s}(000), & E_p &= E_{x,x}(000) \\ V_{ss} &= 4E_{s,s} \left(\frac{1}{2} \frac{1}{2} \frac{1}{2}\right), & V_{xx} &= 4E_{x,x} \left(\frac{1}{2} \frac{1}{2} \frac{1}{2}\right) \\ V_{xy} &= 4E_{x,y} \left(\frac{1}{2} \frac{1}{2} \frac{1}{2}\right), & V_{sp} &= 4V_{s,x} \left(\frac{1}{2} \frac{1}{2} \frac{1}{2}\right). \end{aligned} \quad (18)$$

Before describing the total interaction between s and p states, it is interesting to look at each one separately. If we set the s-p interaction parameters V_{s_0p} and V_{s_1p} equal to zero the 8x8 matrix (13) decouples into a 2x2 (Eq. 6) and a 6x6 matrix. The energy eigenvalues of the 2x2 matrix which describes the s-states is given by

$$E(k) = E_s \pm V_{ss} |g_0(k)| \quad (19)$$

for diamond structure crystals. Although this expression is very simple it nevertheless provides a very good description of the lowest valence band in these crystals. Specifying the width of the band (which is about 3.5-4.0 eV in Si and Ge) determines the band structure to within a few tenths of an eV throughout the Brillouin zone. The largest errors (compared to calculations based on the empirical pseudopotential method (EPM)) occur along the Λ direction and along the Z direction which runs between the symmetry points $X = \frac{2\pi}{a} (1,0,0)$ and $W = (1, \frac{1}{2}, 0)$ of the Brillouin zone. Along this direction the two bands are degenerate (by symmetry) and have no dispersion. The second valence band in the group IV crystals is p-like at Γ and (19) does not therefore provide a valid description for this band. The band structure and density of states associated with the tight-binding s-like bands is shown in Fig. 2. The dip in the density of states occurs near the line $X \rightarrow W$ in the Brillouin zone. For $V_{ss} < 0$ the lower energy band is bonding at Γ and the higher band is antibonding. For $V_{ss} > 0$ the order of the bonding-antibonding states is reversed. For the zincblende crystals (6) gives

$$E = \frac{E_{s0} + E_{s1}}{2} \pm \sqrt{\left[\frac{E_{s0} - E_{s1}}{2} \right]^2 + V_{ss}^2 g_0 g_0^*} \quad (20)$$

whereas as a result of inversion symmetry the two bands were degenerate at X in the diamond structure crystals, a gap of magnitude $|E_{s_0} - E_{s_1}|$ opens up at X for the zincblende crystals. The maximum of the first band and the minimum of the second still occur at X. But unlike the case of the group IV crystals the bands approach X with zero slope and this results in a sharp peak in the density of states (not shown) for states near X. Except for this structure the s-band density of states in the group IV and zincblende crystals are very similar to each other. The band structure and density of states associated with the six p-states of the group IV crystals is shown in Fig. 3 for $V_{xx} = 0$, $V_{xy} = 6.8$ and $E_p = 0$. The sharp rise and fall of the curve near threshold occurs at $\Sigma_1^{\min}$ and is very similar to the $\Sigma_1^{\min}$ edge observed in the density of states of a number of diamond and zincblende crystals.^{3,4,8} As in the case of the s-bands there is no dispersion along the line joining the points X and W of the Brillouin zone and the dip in the density of states corresponds to these states. The overall shape of the curves for the s and p-states are similar in the region near the density of states minimum. For the zincblende crystals the band structure and density of states for the p-states is similar to that of Fig. 3. The maximum of the lower three bands and the minimum of the upper three bands occur at X and are separated by a gap. The zero slope of the bands at X gives rise, as in the case of the s-states, to a sharp structure in the density of states (not shown). Except for this structure the densities of states of the p-bands in the group IV and the zincblende crystals are very similar as may be expected.

Sometimes it is more convenient (e.g.: surface calculations: Ref. 111) to use tight-binding orbitals directed along the bond directions. The parameters which appear in this approach can be easily related to s and p interaction parameters. This can be done by taking the Hamiltonian matrix elements between the following directed orbitals (see Fig. 3).

$$\phi_1 = \frac{1}{2} (s_0 + x_0 + y_0 + z_0) \quad \phi_5 = \frac{1}{2} (s_1 + x_1 + y_1 - z_1) \quad (21)$$

$$\phi_2 = \frac{1}{2} (s_0 + x_0 - y_0 - z_0) \quad \phi_6 = \frac{1}{2} (s_1 + x_1 - y_1 + z_1) \quad (22)$$

$$\phi_3 = \frac{1}{2} (s_0 - x_0 + y_0 - z_0) \quad \phi_7 = \frac{1}{2} (s_1 - x_1 + y_1 + z_1) \quad (23)$$

$$\phi_4 = \frac{1}{2} (s_0 - x_0 - y_0 + z_0) \quad \phi_8 = \frac{1}{2} (s_1 - x_1 - y_1 - z_1) \quad (24)$$

The results for diamond structure crystals in Hirabayashi's¹¹¹ notation are:

$$\gamma_1 = \langle \phi_1 | H | \phi_1 \rangle = \frac{1}{4} (E_s + 3E_p) \quad (25)$$

$$\gamma_2 = \langle \phi_1 | H | \phi_2 \rangle = \frac{1}{4} [E_s - E_p] \quad (26)$$

$$\gamma_3 = \langle \phi_1 | H | \phi_8 \rangle = \frac{1}{16} [V_{ss} - 6V_{sx} - 6V_{sy} - 6V_{sz}] \quad (27)$$

$$\gamma_4 = \langle \phi_2 | H | \phi_8 \rangle = \frac{1}{16} [V_{ss} + V_{sx} + 2V_{sy} - 2V_{sz}] \quad (28)$$

$$\gamma_5 = \langle \phi_2 | H | \phi_5 \rangle = \frac{1}{16} [V_{ss} + V_{sx} - 2V_{sy} + 2V_{sz}] \quad (29)$$

$$\gamma_6 = \langle \phi_2 | H | \phi_7 \rangle = \frac{1}{16} [V_{ss} - 3V_{sx} + 2V_{sy} + 2V_{sz}] \quad (30)$$

The parameter γ_1 appears in the diagonal matrix elements and can be taken equal to zero. The parameters γ_2 and γ_3 are the same as the parameters V_1 and V_2 of Weaire and Thorpe² and from Fig. 4 it can be expected that they represent the most important interactions. The properties of a model Hamiltonian based only on these two types of interactions has been studied in detail by Weaire and Thorpe^{107,114} and has been employed in a number of calculations involving crystalline polytypes of Si and Ge.¹⁰⁸ These calculations show that the two parameter model gives a relatively good description of the lower "s-like" valence bands but gives a poor description of the higher p-like bands which appear as delta functions in the density of states. The inclusion of the other interactions broadens the delta functions and gives a better description of the valence bands.

For zincblende crystals we need three extra parameters to describe the overlaps corresponding to nearest-neighbor s-p interactions. The interaction parameters are:

$$\alpha_1 = \langle \phi_1 | H | \phi_1 \rangle = \frac{1}{4} (E_{s_0} + 3E_{p_0}) \quad (31)$$

$$\beta_1 = \langle \phi_8 | H | \phi_8 \rangle = \frac{1}{4} (E_{s_1} + 3E_{p_1}) \quad (32)$$

$$\alpha_2 = \langle \phi_1 | H | \phi_2 \rangle = \frac{1}{4} (E_{s_0} - E_{p_0}) \quad (33)$$

$$\beta_2 = \langle \phi_7 | H | \phi_8 \rangle = \frac{1}{4} (E_{s_1} - E_{p_1}) \quad (34)$$

$$\alpha_3 = \beta_3 = \langle \phi_1 | H | \phi_8 \rangle = \frac{1}{16} [V_{ss} - 3V_{xx} - 6V_{xy} - 3V_{s_0p} - 3V_{s_1p}] \quad (35)$$

$$\alpha_4 = \langle \phi_2 | H | \phi_8 \rangle = \frac{1}{16} [V_{ss} + V_{xx} + 2V_{xy} - 3V_{s_0p} + V_{s_1p}] \quad (36)$$

$$\beta_4 = \langle \phi_1 | H | \phi_5 \rangle = \frac{1}{16} [V_{ss} + V_{xx} + 2V_{xy} + V_{s_0p} - 3V_{s_1p}] \quad (37)$$

$$\alpha_5 = \langle \phi_2 | H | \phi_5 \rangle = \frac{1}{16} [V_{ss} + V_{xx} - 2V_{xy} + V_{s_0p} + V_{s_1p}] \quad (38)$$

$$\alpha_6 = \langle \phi_2 | H | \phi_7 \rangle = \frac{1}{16} [V_{ss} - 3V_{xx} + 2V_{xy} + V_{s_0p} + V_{s_1p}] \quad (39)$$

The fact that the interactions represented by α_4 and β_4 are different is caused by the lack of inversion symmetry.

It can be shown that independent of the choice of the interaction parameters $\gamma_1, \dots, \gamma_6$ (diamond structures) and $\alpha_1, \dots, \alpha_6, \beta_1, \dots, \beta_4$ (zincblendes), the bands have no dispersion along the symmetry direction Z which goes through the points $X = \frac{2\pi}{a} (1, 0, 0)$ and $W = \frac{2\pi}{a} (1, \frac{1}{2}, 0)$ of the Brillouin zone. Other calculations such as those based on the empirical pseudopotential method (EPM) show³ however a dispersion of about one eV between X and W for the upper two valence bands. This dispersion is reflected in the density of states where each of these points gives rise to a characteristic and well resolved peak. To obtain this result in the tight-binding calculation it is necessary to include at least one second nearest-neighbor interaction. Figures 5 show the density of states of a crystal such as Ge with and without second nearest neighbor interactions. For the nearest-neighbor calculation the parameters used were (in eV): $(E_p - E_s) = 8.41$, $V_{ss} = -6.78$, $V_{xx} = 2.62$, $V_{xy} = 6.82$ and $V_{sp} = 5.31$. The second nearest neighbor interaction we have used (in Fig. 7) arises from the overlap of a p_x orbital at the origin with a p_x orbital separated by a lattice vector of the type $(0, \pm \frac{1}{2}, \pm \frac{1}{2})a$. Its effect is

to change the diagonal matrix elements to $\langle x_1 | H | x_1 \rangle = E_p + U_{xx} \cos k_2 \cos k_3$, etc. for diamond structure crystals. The interaction U_{xx} is denoted by $4E_{xx}(011)$ in Ref. 6. The interaction parameters when both nearest and second nearest interactions were used (Fig. 5) are:

$(E_p - E_s) = 8.41$, $V_{ss} = -6.78$, $V_{xx} = 1.62$, $V_{xy} = 6.82$, $V_{sp} = 5.31$ and $U_{xx} = -1.0$ (eV). The resulting density of states in Fig. 5 shows the separate structures arising from the points X and W. These structures coalesce into a single peak when U_{xx} is set equal to zero. It should be pointed out here that not all second nearest neighbor interactions are useful in broadening the bands along Z. Interactions between two s-states or between s and p states separated by a primitive lattice vector have no effect on the dispersion along Z which is affected mainly by second-nearest neighbor interactions between p-states, the largest one being U_{xx} .

3. Results for C, Si, Ge, GaAs and ZnSe

Since there is not sufficient information on the valence bands of C we have used only nearest-neighbor interactions in our calculations on C. The parameters were obtained by fitting to the results of a variational calculation¹¹⁵ and they are shown in Tables I. The energy eigenvalues are compared to other calculations in Table II and the resulting band structures and densities of states are shown in Fig. 6. Table II shows good agreement between the simple tight-binding calculation and the variational¹¹⁵ calculations for the valence bands of C. The results are also very similar to those obtained from an APW¹¹⁶ calculation. The conduction bands are not well reproduced by the simple

tight-binding method except at Γ where the splittings were fitted.

For Si and Ge we have used one second nearest neighbor interaction in addition to the nearest neighbor interactions in the calculations. The nature of these interactions was discussed in section II. The interaction parameters for Si and Ge are listed in Table I and the eigenvalues at some symmetry points in the Brillouin zone are compared to the EPM^{117,10} values in Table II. The corresponding band structures and densities of states are shown in Figs. 7-8 and compared to those obtained from recent EPM calculations^{117,10} involving non-local (angular momentum dependent) potentials. The agreement in all cases is within a few tenths of an eV for the valence bands but for the conduction bands the method is not as successful. For the sake of completeness we give in Tables III and IV the interaction parameters for C, Si, and Ge if only nearest neighbor interactions are used. These tables show that the strength of nearly every interatomic interaction decreases as we go from C to Si to Ge.

In the case of the zincblende crystals GaAs and ZnSe we have only used nearest neighbor interactions for convenience. A second nearest neighbor interaction between the Ga or Zn p-states similar to the one used for Si and Ge is, however, necessary to broaden the upper two valence bands. The band structures and densities of states for GaAs and ZnSe are shown in Figs. 9-10 and compared to nonlocal (angular momentum dependent) EPM calculations.^{12,118} The interaction parameters are listed in Tables V and VI. The largest error in the band structures occur for the states denoted by $\Sigma_1^{\min}$. The tight-binding results are

actually much closer to older EPM calculations which used local pseudopotentials resulting in upper valence bands which are narrower. Ultraviolet and X-ray photoemission spectra however reveal a larger width for these bands than those indicated by local pseudopotentials and this has been one reason for the use of nonlocal pseudopotentials. The energy eigenvalues at some symmetry points in the Brillouin zone are given in Table VII and compared to the EPM values. For more accurate conduction bands second nearest neighbor interactions, especially those between s and p states, need to be included.

The tight-binding method allows a simple calculation of the s and p character of the valence bands and it is interesting to see how close to ideal sp^3 they are. We have therefore computed the average s and p components of the wavefunctions for the valence bands. We find the top two valence bands to be completely p-like in character in all five crystals. The differences in the s-p characters occur mainly for the first two valence bands and these are shown in Table VIII. The average of the s and p-electrons in the four valence bands of C, Si and Ge are, C: 1.25s, 2.75p; Si: 1.4s, 2.6p and Ge: 1.5s, 2.5p. The ratio of the number of s to p electrons is 0.45 for C, 0.54 for Si and 0.6 for Ge. Carbon is therefore as expected the closest to the ideal ratio of 0.333. In GaAs and ZnSe the first valence band is s-like around As and Se. The second valence band is mainly s-like around Ga and Zn and p-like around As and Se.

In the simple model of Weaire and Thorpe¹⁰⁷ in which only two interaction parameters (equivalent to γ_2 and γ_3) are used the bonding and antibonding π states give rise to two δ -functions, each of weight two, in the density of states. The delta functions correspond to doubly degenerate bands which are flat throughout the Brillouin zone. The addition of extra interactions obviously broadens these bands and the δ -functions. It is interesting to see which interactions are most important in producing this broadening of the bands. In the s-p interaction picture, it can be shown that if we set $V_{xx} = V_{xy}$ then we immediately obtain, for both diamond and zincblende crystals, two sets of bands which are doubly degenerate and flat throughout the Brillouin zone independent of the magnitude of the other nearest neighbor interactions. In the directed-orbital representation Eqs. (29) & (30), and Eqs. (38) & (39) show that $V_{xx} = V_{xy}$ corresponds to $\gamma_5 = \gamma_6$ (diamond structures) or $\alpha_5 = \alpha_6$ (zincblendes). Therefore independent of the other interactions between the orbitals if $\gamma_5 = \gamma_6$ or $\alpha_5 = \alpha_6$ we will have flat p bands in the entire Brillouin zone. The broadening of the p bands can be expected to be related to $V_{xx} - V_{xy}$. In fact if we take second nearest neighbor interactions to be zero then in diamond structure crystals the width of the doubly degenerate valence bands is exactly equal to $|V_{xx} - V_{xy}|$ or $4|\gamma_5 - \gamma_6|$ with the top of the bands at Γ and the bottom at X. It is obviously not a good approximation to take $V_{xx} = V_{xy}$ or $\gamma_5 = \gamma_6$. In fact we expect the interaction V_{xy} to be stronger than V_{xx} because the overlap between the orbitals x_0, y_1 is larger than the overlap between the orbitals x_0 and x_1 . This is born out in Tables I, III, and V.

In order to calculate the interaction parameters we used the dependence of the energy gaps at a few points in the Brillouin zone on the potentials. Along some symmetry directions and at some symmetry points the dependence of the energies on the potentials can be obtained in closed form. Here we list some of these relations a number of which were first obtained in Ref. (2).

For the diamond structure crystals we have:

$$E(\Gamma_1) = E_s + V_{ss}$$

$$E(\Gamma_2) = E_s - V_{ss}$$

$$E(\Gamma_{25'}) = E_s + (E_p - E_s) + U_{xx} - V_{xx}$$

$$E(\Gamma_{15}) = E_s + (E_p - E_s) + U_{xx} + V_{xx}$$

At L the doubly degenerate eigenvalues are given by

$$E(L_{3'}) = E_s + (E_p - E_s) \pm \frac{1}{2} (V_{xx} + V_{xy})$$

and the four non-degenerate states are:

$$E(L) = E_s + \left(\frac{E_p - E_s}{2} \right) \pm \frac{1}{4} (V_{ss} - V_{xx} + 2V_{xy})$$

$$\pm \frac{1}{2} \sqrt{\left\{ \frac{V_{ss} + V_{xx} - 2V_{xy}}{2} \mp (E_p - E_s) \right\}^2 + 3V_{sp}^2}$$

(There is a slight error in Ref. (2) for this expression, i.e., V_{ss} outside the square root is replaced by V_{sp} .) At X the energy of the

doubly degenerate roots are given by

$$E(X_4) = E_s + (E_p - E_s) - U_{xx} \pm V_{xy}$$

$$E(X_1) = E_s + \frac{E_p - E_s + U_{xx}}{2} \pm \frac{1}{2} \sqrt{(E_p - E_s + U_{xx})^2 + (2V_{sp})^2}.$$

When U_{xx} is set equal to zero the energy of the bands for $k = \frac{2\pi}{a} (1, k, 0)$

are equal to the energies at X. Along the symmetry direction

$\Delta = \frac{2\pi}{a} (k, k, k)$ only the energy of the doubly degenerate bands can be obtained in closed form:

$$E(A_3) = E_p + U_{xx} \cos^2 \pi k \pm |V_{xx} g_0 - V_{xy} g_1|$$

$$= E_p + U_{xx} \cos^2 \pi k$$

$$\pm \sqrt{(V_{xx} \cos^3 \pi \frac{k}{2} + V_{xy} \sin^2 \pi \frac{k}{2} \cos \pi \frac{k}{2})^2 + (V_{xx} \sin^3 \pi \frac{k}{2} + V_{xy} \cos^2 \pi \frac{k}{2} \sin \pi \frac{k}{2})^2}.$$

Along the symmetry direction $\Delta = \frac{2\pi}{a} (k, 0, 0)$, the singly degenerate eigenvalues are given by

$$E(k) = E_s + \frac{E_p - E_s + U_{xx} \pm (V_{ss} + V_{xx}) \cos \pi \frac{k}{2}}{2}$$

$$\pm \frac{1}{2} \sqrt{(E_p - E_s + U_{xx} \pm (V_{xx} - V_{ss}) \cos \pi \frac{k}{2})^2 + (2V_{sp} \sin \pi \frac{k}{2})^2}.$$

The doubly degenerate eigenvalues along Δ are given by

$$E = E_s + (E_p - E_s) + U_{xx} \cos \pi k \pm \sqrt{(V_{xx} \cos \pi \frac{k}{2})^2 + (V_{xy} \sin \pi \frac{k}{2})^2}$$

Along the symmetry direction $\Sigma = \frac{2}{a} (k, k, 0)$, the energy of the fourth valence band is given by

$$E(k) = E_s + (E_p - E_s) + U_{xx} \cos \pi k - (V_{xx} \cos^2 \pi k + V_{xy} \sin^2 \pi k) .$$

Changing the sign of V_{xx} and V_{xy} gives the result for one of the conduction bands.

The tight binding expressions sometimes give equalities between energies at different points in the Brillouin zone, e.g. $E_4(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) = E_4(\frac{1}{2}, \frac{1}{2}, 0) = E_p - \frac{1}{2} (V_{xx} + V_{xy})$, where the subscripts refer to the band index. This equality holds only when a few parameters are used and as it stands it is incompatible with the results of EPM calculations^{116,117} which show a difference of 0.1-0.2 eV between the two states. The interaction parameters can be determined by using the following eigenvalues $E(\Gamma_1)$, $E(\Gamma_{25'})$, $E(\Gamma_{15})$, $E(\Gamma_2)$, $E(X_1)$, $E(X_4)$, and $E(L_1) - E(L_2)$.

For the zincblende crystals the eigenvalues at the symmetry points Γ , X and L are given by

$$E(\Gamma_1) = \frac{E_{s0} + E_{s1}}{2} \pm \sqrt{\left(\frac{E_{s0} - E_{s1}}{2}\right)^2 + V_{ss}^2}$$

$$E(\Gamma_{15}) = \frac{E_{p0} + E_{p1}}{2} \pm \sqrt{\left(\frac{E_{p0} - E_{p1}}{2}\right)^2 + V_{xx}^2} \quad (\text{triply degenerate})$$

$$E(X_1) = \frac{E_{s_0} + E_{p_1}}{2} \pm \sqrt{\left(\frac{E_{p_0} - E_{p_1}}{2}\right)^2 + v_{s_0}^2 p^2}$$

$$E(X_3) = \frac{E_{s_1} + E_{p_0}}{2} \pm \sqrt{\left(\frac{E_{s_1} - E_{p_0}}{2}\right)^2 + v_{s_1}^2 p^2}$$

$$E(X_5) = \frac{E_{p_0} + E_{p_1}}{2} \pm \sqrt{\left(\frac{E_{p_0} - E_{p_1}}{2}\right)^2 + v_{xy}^2}$$

$$E(L_3) = \frac{E_{p_0} + E_{p_1}}{2} \pm \frac{1}{2} \sqrt{\left(\frac{E_{p_0} - E_{p_1}}{2}\right)^2 + (v_{xx} + v_{xy})^2}$$

The energies of the bands for $k = \frac{2\pi}{a} (1, k, 0)$ is equal to the energies at X when only the nearest neighbor interactions listed above are used.

Table I. Tight-binding interaction parameters (in eV) for C, Si and Ge. The parameter U_{xx} represent a second nearest neighbor interaction. The parameter E_s determines the zero of energy and is arbitrary.

	E_s	$(E_p - E_s)$	V_{ss}	V_{sp}	V_{xx}	V_{xy}	U_{xx}
C	--	7.40	-15.2	10.25	3.0	8.30	--
Si	--	7.20	-8.13	5.88	1.71	7.51	-1.46
Ge	--	8.41	-6.78	5.31	1.62	6.82	-1.0

Table II. Comparison of the energy eigenvalues of C, Si and Ge at some symmetry points in the Brillouin zone. The energies in (eV) are measured relative to the top of the valence bands at $\Gamma_{25'}$.

State	C		Si		Ge	
	Tight-Binding	DVM ^a	Tight-Binding	EPM ^b	Tight-Binding	EPM ^c
$\Gamma_{25'}$	0	0	0	0	0	0
Γ_1	-19.6	-19.6	-12.16	-12.16	-12.57	-12.57
Γ_{15}	6.0	6.0	3.42	3.42	3.24	3.24
Γ_2	10.8	10.8	4.10	4.10	0.99	0.99
L_2	-15.2	-14.5	-9.44	9.57	-10.30	-10.30
L_1	-9.8	-11.7	-7.11	-6.98	-7.52	-7.52
L_3	-2.6	-2.4	-1.44	-1.23	-1.60	-1.44
X_1	-11.6	-11.6	-7.70	-7.70	-8.60	-8.56
X_4	-5.3	-5.3	-2.87	-2.87	-3.20	-3.20
$\Sigma(0.5,0.5,0)$	-2.35	--	-3.84	-3.74	-3.80	-3.80
$\Sigma(0.7,0.7,0)$	-1.83	--	-4.32	-4.46	-4.29	-4.29

a. Ref. 115.

b. Ref. 117.

c. Ref. 10.

Table III. Interaction parameters (in eV) appropriate for C, Si and Ge when second nearest neighbor interactions are ignored. The parameter E_s is arbitrary.

	E_s	$(E_p - E_s)$	V_{ss}	V_{sp}	V_{xx}	V_{xy}
C	--	7.40	-15.2	10.25	3.0	8.3
Si	--	7.20	-8.13	5.88	3.17	7.51
Ge	--	8.41	-6.78	5.31	2.62	6.82

Table IV. Interaction parameters (in eV) between directed orbitals for C, Si and Ge. These parameters are related to those in Table III through the equations given in Sec. II. The parameter γ_1 can be chosen arbitrarily.

	γ_1	γ_2	γ_3	γ_4	γ_5	γ_6
C	--	-1.85	-8.47	-1.01	-0.52	0.81
Si	--	-1.80	-6.13	-0.11	-0.51	0.57
Ge	--	-2.10	-5.46	-0.07	-0.45	0.60

Table V. Interaction parameters (in eV) for GaAs and ZnSe. The four intra-atomic parameters E_{s_0} , E_{s_1} , E_{p_0} and E_{p_1} give information only on the relative energy differences between the tight-binding s and p functions. The subscripts 0 and 1 refer to As (or Se) and Ga (or Zn) respectively.

	E_{s_0}	E_{s_1}	E_{p_0}	E_{p_1}	V_{ss}	V_{s_0p}	V_{s_1p}	V_{xx}	V_{xy}
GaAs	-6.01	-4.79	0.19	4.59	-7.00	7.28	3.70	0.93	4.72
ZnSe	-0.92	-0.28	0.12	7.42	-6.14	5.47	4.73	0.96	4.33

Table VI. Tight-binding parameters (in eV) between directed orbitals for GaAs and ZnSe. These parameters are related to those in Table V through the relations given in Sec. II.

	α_1	β_1	α_2	β_2	$\alpha_3 = \beta_3$	α_4	β_4	α_5	α_6
GaAs	-1.36	2.25	-1.55	-2.35	-4.44	-0.92	-0.03	-0.28	0.66
ZnSe	-2.14	5.57	-2.26	-1.93	-4.12	-0.51	-0.32	-0.23	0.62

Table VII. Comparison of the energy eigenvalues of GaAs and ZnSe at some symmetry points in the Brillouin zone. The energies in (eV) are measured relative to the top of the valence bands at Γ_{15} .

GaAs			ZnSe	
State	Tight-binding	EPM ^a	Tight-binding	EPM ^b
Γ_{15v}	0	0	0	0
Γ_{1v}	-12.4	-12.4	-12.1	-12.1
Γ_{1c}	1.6	1.6	2.9	2.9
Γ_{15c}	4.8	4.8	7.5	7.5
L_{1v}	-10.7	-10.5	-11.0	-10.9
L_{2v}	-6.2	-6.7	-4.7	-4.9
L_{3v}	-1.2	-1.2	-0.75	-0.75
L_{1c}	1.7	1.6	3.9	4.1
L_{3c}	6.0	4.8	8.3	7.9
X_{1v}	-9.7	-9.7	-10.6	-10.6
X_{3v}	-6.8	-6.8	-4.8	-4.8
X_{5v}	-2.8	-2.8	-1.9	-1.9
X_{1c}	2.2	2.2	4.7	4.7
X_1^{min}	-3.1	-4.1	-2.1	-3.2

a. Ref. 12.

b. Ref. 18.

Table VIII. The average *s* and *p* characters for the valence bands of C, Si, Ge, GaAs and ZnSe.

	Band 1 s,p	Band 2 s,p	Bands 3,4 s,p
C	0.84,0.16	0.39,0.61	~0,1
Si	0.9,0.1	0.45,0.55	~0,1
Ge	0.9,0.1	0.57,0.43	~0,1
GaAs	0.88,0.12	0.61,0.39	~0,1
ZnSe	0.94,0.06	0.42,0.58	~0,1

Figure Captions

- Fig. 1. Tight-binding *s*-orbitals on a tetrahedron.
- Fig. 2. Band structure and density of states of *s*-states for diamond structure crystals.
- Fig. 3. Band structure and density of states of *p*-states for diamond structure crystals.
- Fig. 4. Directed sp^3 orbitals on two adjacent tetrahedrons. The different possible interactions of the orbitals on the nearest neighbor atoms are given in Sec. 2.
- Fig. 5. The density of states of Ge with and without second nearest neighbor interaction. The second nearest neighbor interaction splits the energies at X and W and gives rise to extra structure in the density of states.
- Fig. 6. Band structure and density of states of diamond.
- Fig. 7. Tight-binding band structure and density of states of Si as compared to the results obtained from empirical pseudopotential calculations. (Ref. 117)
- Fig. 8. Tight-binding band structure and density of states of Ge as compared to the results obtained from empirical pseudopotential calculations. (Ref. 12)
- Fig. 9. Tight-binding band structure and density of states of GaAs compared to the results of EPM calculations. (Ref. 12)
- Fig. 10. Tight-binding band structure and density of states of ZnSe compared to the results of EPM calculations. (Ref. 118)

XBL 748-7011

Fig. 1.

Fig. 2.

XBL 748-7007

XHL 748-7004

Fig. 3.

XBL 748-7012

Fig. 4.

Fig. 5.

XII. 748-7006

Fig. 6.

XBL 748-7054

Fig. 7.

XBL 748-7002

Fig. 8.

XBL 748-7009

XBL 748-7005

Fig. 10.

XRL 748-7003

B. Intrinsic (111) Surface States of Ge, GaAs and ZnSe

Abstract

In this section we study the intrinsic (111) surface states of Ge, GaAs and ZnSe using the tight-binding method. The local density of states of atoms on different layers are calculated and the various types of surface states are discussed. The effects of relaxation on the surface states are examined for Ge.

1. Introduction

The tight-binding (TB) method is very useful in providing a practical and relatively simple way of studying the electronic surface states of semiconductors. By using a small number of interaction parameters it is possible to obtain good results for both bulk²⁴ and surface states of diamond^{25,26,119} and zincblende type^{25,26} compounds. The (TB) parameters appropriate for Ge, GaAs and ZnSe were obtained in section A. In this section we wish to describe in more detail the (111) surface states of Ge, GaAs and ZnSe. Similar calculations on the (110) surface of diamond and zincblende semiconductors have also been recently done.¹²⁰ Surface reconstruction is not considered in our calculation, however, the effects of surface relaxation are studied for Ge. The local density of states (LDS) for surface atoms and atoms close to the surface layer are calculated. The character and degree of localization of the charge density associated with the various surface states are also calculated.

This paper is organized in the following way. In section 2 we briefly discuss some aspects of the calculation and give the interaction

parameters we have used. The surface states of Ge with and without relaxation effects are studied in section 3. The (111) and ($\bar{1}\bar{1}\bar{1}$) surfaces of GaAs and ZnSe are discussed in section 4.

2. Calculation

The calculation of surface states by the TB method for group IV materials has been discussed by Hirabayashi¹¹¹ and we have extended the method to zincblende compounds. In the calculation of surface states we have taken a system consisting of a finite number, N , of atomic layers. To distinguish surface states from bulk states without ambiguity we have taken $N = 16$. For GaAs or ZnSe the atomic layers are composed only of one type of atom which alternate between the Ga-type and As-type atoms.

The interaction parameters for Ge, GaAs and ZnSe are the same as those determined in section A.

To simulate the effects of surface relaxation for Ge we have assumed that the surface layer moves inward¹²¹ by 0.3 Å and we have changed the interatomic interaction parameters at the surface according to¹¹⁹

$$H_{ij} = H_{ij}^0 \exp(\beta \Delta R)$$

where H_{ij}^0 is the matrix elements given above and ΔR is the change in the nearest-neighbor distance. This approximation works well in the case of Si.¹¹⁹ We have used $\beta = 10.4/a$ where a is the cubic lattice constant. The intra-atomic interaction parameter γ_2 was also changed (as in Ref. 122) to account for the change in the s - p character of the orbitals resulting from relaxation.

We have calculated the local density of states $N_k(E)$ of atoms on different layers for Ge, GaAs and ZnSe. To do this the expression

$$N_k(E) = \sum_i \sum_{k,n} \delta(E - E_n(k)) |\langle \psi_{k,n} | \phi_1 \rangle|^2$$

was used where $\psi_{k,n}$ is the total wavefunction corresponding to the n th eigenvalue, and the sum i is over the orbitals of the atoms on a particular layer. All the densities of states curves discussed in the next section have been normalized to the bulk (or crystalline) density of states to facilitate comparison between them.

3. Results

a. Ge: Unrelaxed Surface. In Fig. 1 we show the total density of states of 16 layers together with the LDS of the surface layer. Figures 2 and 3 show the LDS of a layer just below the surface (denoted by $(Ge)_2$) and the LDS of atoms four layers below the surface $(Ge)_5$. The total density of states of 16 layers (Fig. 1) is very similar to the bulk (or crystalline) density of states shown in Fig. 3, except for structure arising from the two surfaces. In particular the structures S_1 and T_1 are associated with localized surface states and can be seen to become weaker as we go away from the surface. The peak denoted S_1 is seen in energy loss spectroscopy;¹²³ it has an integrated weight equal to one electron per surface atom. It has a width of about 1 eV and lies 0.4 eV above the top of the bulk valence bands E_v . Over 70% of the charge density associated with this peak is localized in the first two layers at the surface: 52% at the surface layer and 20% on the layer below. The Fermi energy E_F lies about 0.6 eV

above E_v inside the S_1 peak. The energy E_s in Fig. 1 gives the energy at which the integrated LDS of surface atoms equals the number of surface atoms (so that the surface is neutral); it is less than 0.1 eV away from E_F in the unrelaxed surface configuration.

The contribution to the S_1 peak comes mainly from the dangling bond states and also from the back-bonding states of the atoms on the layer below the surface. As seen in Figs. 1-3 these states become progressively weaker as we go away from the surface and virtually disappears within four to five layers below the surface.

The T_1 peak in Fig. 1 corresponds to back-bonding surface states. Only certain wavevectors in the region near the point K (corner of the hexagonal Brillouin zone) contribute to this peak. At K the charge density associated with T_1 has a concentration of 80% on the surface layer. The average contribution over the Brillouin zone is however much smaller and the integrated weight of the structure is equivalent to 0.25 electrons per surface atom.

The structures R_1 and R_2 (Fig. 1) are resonant states also associated with back-bonding states. The wavefunctions associated with these states have a charge density of about 0.15 electrons per atom at the surface layer. The D_1 structure (Fig. 1) is not associated with any surface states but apparently results from the use of a finite number of layers; the states involved have a small dispersion throughout the Brillouin zone.

The Figs. 1-3 show that the LDS of atoms on the surface layer and on layers near the surface are remarkably similar to the total density of states (of 16 layers) or to the bulk density of states (except, of course, for the presence of surface structure). Most of the small step-like structures evident in these figures result from the use of a finite number of planes in the calculations and they gradually disappear as more planes are used. We have smoothed out the step-like structures and the noise in the densities of states by using Gaussian functions 0.15 eV wide at half-maximum.

The structures we have obtained for the (111) surface of Ge are very similar to those for a (110) surface⁴ except for the T_1 peak which is absent for the (110) surface. The existence of the T_1 structure is however very sensitive to the value of the structure factor describing the relative positions of the atoms on the surface.

b. Ge: Relaxed Surface. The effect of surface relaxation on the LDS of the atoms on the surface layer is shown in Fig. 4. As can be seen relaxation results in the appearance of new surface states denoted by S_2 and S_3 and a weakening of the S_1 and T_1 states. There is a broadening of about 0.4 eV in the top valence bands for states near the surface. The energy E_s which corresponds to the neutrality level for the surface layer is 2.0 eV below ϵ_F . This shift in E_s (relative to the unrelaxed case) would result in an excess charge density of 0.07 electrons per surface atom but this is unlikely since band bending near the surface would cause a redistribution of the surface charge.

The integrated weight of the S_1 peak in the total density of states (Fig. 5) is still equivalent to one electron per surface atom. But the charge density associated with this peak is not strongly concentrated on the surface layer but extends over the first four layers at the surface.

The S_2 and S_3 surface states result from surface relaxation and correspond to back-bonding orbitals of the first two atomic layers. At the K point of the zone the charge associated with the S_2 structure is completely localized on the first two layers. The localization is however much smaller (about 10%) for most of the other points in the zone. The S_3 structure has a weight of 0.35 electrons per surface atom over an energy range of about 3 eV. The T_1 structure is strongly damped by relaxation and this may explain why it has not been observed experimentally. A comparison of Figs. 1-4 shows that relaxation effects are very important in the description of surface states. Although we have treated surface relaxation only approximately here the results give an indication of the type of changes that occur as a result of relaxation.

4. Surface States of GaAs and ZnSe

The (111) surface is not a cleavage plane for zincblende crystals, however it has recently become possible to prepare such surfaces by Ar^+ bombardment and annealing under ultra high vacuum conditions^{124,125} and photoemission¹²⁴ and energy loss¹²⁵ experiments have been done on GaAs and GaP samples. The (111) surfaces are polar, i.e., the layers alternate between Ga-type and As-type atoms.

In Figs. 5-9 we show the results of our calculations on a system consisting of 16 layers. The notation used in these figures is as follows. The various layers are numbered consecutively so that $[Ga]_1$ refers to the gallium and $(As)_1$ to the arsenic surface layers respectively. Layers near the Ga surface are denoted by brackets and those near the As surface by parenthesis. Thus $[As]_2$ refers to the arsenic layer just below the Ga surface layer and $(Ga)_2$ to the gallium layer next to the As surface layer. A similar procedure is also used for identifying the Zn and Se layers in ZnSe.

Let us now examine the detailed structure in the densities of states. A comparison of Figs. 5 and 8 shows the structures in GaAs and ZnSe to be very similar. The only differences between the two are in the width of the surface peaks and the degree of charge localization in each peak. We will discuss these in detail later in this paper. For the moment we will give a general description of the surface states and concentrate on GaAs.

Figure 5a shows the LDS of the gallium surface layer $[Ga]_1$, the LDS of the arsenic layer below it $[As]_2$, together with the total density of states for 16 layers. The LDS of the As surface layer, $(As)_1$ and the gallium layer next to it, $(Ga)_2$ are shown in Fig. 5b. The structure A_0 corresponds to the first conduction band in the zincblende phase (see also Fig. 7). The peaks $A_1, \dots, A_4$ are however associated with the various surface states. The peaks A_1 corresponds to a mixture of dangling bond Ga states together with back-bonding As states. The peak A_2 however is almost totally an As dangling bond state. It is interesting to note that nearly all the contribution

to the A_1 (A_2) peak comes from atoms near the Ga (As) surface layer. There is, for example, practically no contribution to the A_2 (As-dangling bond state) from As atoms near the Ga surface layer; only As atoms near the As surface contribute to this peak.

The A_3 structure corresponds to Ga surface states which overlap with the bulk valence bands. These surface states are associated with Ga back-bonding orbitals. Gallium atoms on both the Ga-rich and As-rich sides contribute to the A_3 peak. The localization of the charge density at the surface layer is less for this state than for the A_1 and A_2 peaks. Our calculation also shows As surface states overlapping with bulk bands at -3 eV, near the region that corresponds to the $\Sigma_1^{\min}$ edge for the zincblende case. (The zero of energy in Figs. 5-9 has been chosen at the top of the bulk valence bands. This also happens to be (see Fig. 7) the energy for the top As (Se) surface states.) The A_4 structure corresponds to As back-bonding states and the major contribution to it comes from the As surface layer. There is no contribution to A_4 arising from As or Ga atoms near the Ga rich surface.

We will now examine the character and degree of localization of the various peaks in GaAs and ZnSe. The A_1 structure in GaAs (ZnSe) has an integrated weight of one electron per Ga (Zn) surface atom and the Fermi energy lies in the middle of this peak. The Ga (Zn) dangling orbitals contribute 0.32 (0.55) electrons to the whole peak while the As (Se) back-bonding states next to the surface layer contribute 0.47 (0.33) electrons. About 80% of charge density

associated with A_1 is therefore seen to be localized within the first two surface layers with a stronger localization in the case of the more ionic ZnSe.

The integrated weight of the A_2 structure is one electron per As (Se) surface atom. The As (Se) dangling bond orbitals contribute 0.71 (0.82) electrons to this structure. The Ga (Zn) atoms next to the surface layer make no contribution to this peak but other As (Se) layers near the surface make smaller contributions to A_2 as can be seen from Figs. 5-9.

In the A_3 structure surface states begin near the edge of the band and extend over an energy range of about 1 eV. The localization at the surface of the states associated with A_3 are on the average smaller than those for A_1 and A_2 . The A_3 peak is very interesting in that Ga (Zn) and As (Se) atoms near both the Ga (Zn) rich and As (Se) rich surfaces contribute to it as can be seen from Figs. 5 and 8. The major contribution in GaAs is from Ga back-bonding orbitals located at the Ga surface layer or on Ga atoms on the layer below the As surface. The contribution of As back-bonding orbitals on both the Ga and As side of the surface is about half as large as that coming from the Ga orbitals. In ZnSe the Zn and Se atoms contribute almost equally to the A_3 structure.

The As (Se) back-bonding orbitals on both the As (Se) surface and on atoms next to the Ga (Zn) surface layer also give rise to surface states which are very similar to A_3 . These states occur at ~ 3 (-2) eV in GaAs (ZnSe) for wavevectors near K.

The A_4 states are very strongly localized on the As (Se) surface atoms. Figure 4 shows the A_4 structure to have a very small overlap with the bulk states. The integrated weight of A_4 is equivalent to 1 electron per As (Se) surface atom. The As (Se) back-bonding surface orbitals contribute about 0.36 (0.78) electrons and the Ga back-bonding orbitals next to the As surface atoms contribute 0.11 (0.10) electrons.

Figure Captions

- Fig. 1. Total density of states (solid line) of Ge for a system consisting of 16 layers. The local density of states (dashed line) of surface atoms has been normalized to the total density of states for a better comparison between the two.
- Fig. 2. Local density of states (LDS) of Ge atoms on the layer below the surface. Surface states are labelled in Fig. 1.
- Fig. 3. Local density of states of Ge atoms four layers below the surface (solid line) and the bulk (or crystalline) density of states (dashed line).
- Fig. 4. Total density of states (solid line) of Ge for a system consisting of 16 layers and for a relaxed surface. The local density of states of surface atoms is also shown.
- Fig. 5. Total density of states (solid line) of GaAs for a system of sixteen layers (a) and (b). The local densities of states (LDS) of Ga surface atoms denoted by $[Ga]_1$ and the LDS of the As layer $[As]_2$ next to the $[Ga]_1$ are also shown in (a). The corresponding LDS for the As surface are shown in (b).
- Fig. 6. The LDS of Ga atoms $[Ga]_5$ on a plane four layers below the $[Ga]_1$ surface (solid line) and the LDS of $[As]_6$ atoms five layers below the surface (dashed line) are shown in (a). The corresponding features for atoms below the As surface are shown in (b).

Fig. 7. The total density of states of GaAs for a system consisting of 16 layers (solid line) as compared to the bulk crystalline density of states calculated using the same interaction parameters. The dotted zincblende curve refers to the bulk.

Fig. 8. The LDS of $[Zn]_1$, $(As)_1$ surface atoms and the LDS of $[Se]_2$ and $(Zn)_2$ atoms next to the surface layers. See also caption for Fig. 5.

Fig. 9. See caption for Fig. 6.

Fig. 1.

XBL 748-7024

XBL 748-7026

Fig. 2.

Fig. 3.

NBL 74B-7015

Fig. 4.

XBL 748-7020

XBL 748-7027

Fig. 5.

XBL 748-7029

Fig. 6.

XBL 748-7025

Fig. 7.

NBL 748-7025

Fig. 8.

XBL 748-7017

Fig. 9.

ACKNOWLEDGEMENTS

I am deeply grateful to my thesis advisor Professor Marvin L. Cohen for his guidance and encouragement throughout the course of my research. I also would like to thank him for giving me the opportunity to work with him, at the University of Paris, during his sabattical leave in the 1972-73 academic year.

I would like to thank Professors Charles Kittel, Leo Falicov, Ron Shen, Yves Petroff, Ching Fong and David Shirley for many valuable discussions. I also wish to thank Professors Minko Balkanski, Sebennie, Yves Petroff and Gerard Martinez for their help and hospitality at the University of Paris.

I like to thank many friends and colleagues at Berkeley and elsewhere. I owe special thanks in particular: to John Walter for his help during the initial stage of my research; to Carmen Varea de Alvarez, John Joannopoulos, Jim Chelikowsky, Steve Louie, Drs. Michael Schlüter, Gerard Martinez and Felix Yndurain for numerous occasions of lively and stimulating discussions; to Dr. Roger Pollak, Dr. Lothar Ley, Steve Kowalczyk, and Read McFeely for the discussion of the experimental x-ray photoemission results; and to Drs. Dean Eastman and Warren Grobman for the discussion of the experimental ultraviolet photoemission spectra.

I like to thank: Mrs. Madeline Moore and Mrs. Carol Tung for their efficiency and skill in the typing of manuscripts; and Ms. Alice Ramirez and Mrs. Shirley Ashley for the excellent job they have done in typing my thesis.

Finally I thank my parents for their support and encouragement during all these years.

This work was done under the auspices of the U. S. Atomic Energy Commission.

REFERENCES

1. M. L. Cohen and V. Heine, Solid State Physics 24, 37 (1970).
2. J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).
3. J. R. Chelikowsky, D. J. Chadi, and M. L. Cohen, Phys. Rev. B8, 2786 (1973).
4. L. Ley, et al., Phys. Rev. Lett. 29, 1088 (1972); 29, 1103 (1972); and Phys. Rev. B9, 600 (1974).
5. R. A. Pollak, L. Ley, S. Kowalczyk, D. A. Shirley, J. D. Joannopoulos, D. J. Chadi, and M. L. Cohen, Phys. Rev. Letters 29, 1103 (1972).
6. S. P. Kowalczyk, P. R. McFeely, L. Ley, R. A. Pollak, and D. A. Shirley, Phys. Rev. B9, 3573 (1974).
7. W. D. Grobman and D. E. Eastman, Phys. Rev. Lett. 29, 1508 (1972).
8. D. E. Eastman, W. D. Grobman, J. L. Freeouf, and M. Erbudak, Phys. Rev. B9, 3473 (1974).
9. J. C. Phillips and K. C. Pandey, Phys. Rev. Lett. 30, 787 (1973).
10. J. R. Chelikowsky and M. L. Cohen, Phys. Rev. Lett. 31, 1582 (1973).
11. K. C. Pandey and J. C. Phillips, Phys. Rev. B9, 1552 (1974).
12. J. R. Chelikowsky and M. L. Cohen, Phys. Rev. Lett. 32, 674 (1974).
13. W. D. Grobman, D. E. Eastman, and M. L. Cohen, Phys. Letters 43A, 49 (1973).
14. D. J. Chadi, M. L. Cohen, and W. D. Grobman, Phys. Rev. B8, 5587 (1973).
15. D. J. Chadi, J. P. Walter and M. L. Cohen, Phys. Rev. B5, 3058 (1972).
16. D. J. Chadi and M. L. Cohen, Phys. Rev. B7, 692 (1973).
17. A. Baldereschi, Phys. Rev. B7, 5212 (1973).
18. D. J. Chadi and M. L. Cohen, Phys. Rev. B8, 5747 (1973).

19. D. J. Chadi and M. L. Cohen, *Solid State Comm.* 13, 1007 (1973).
20. D. J. Chadi and M. L. Cohen (unpublished).
21. D. J. Chadi and M. L. Cohen, *Phys. Stat. Solidi (b)* 62, 235 (1974).
22. D. J. Chadi and M. L. Cohen (unpublished).
23. D. J. Chadi and M. L. Cohen, *Phys. Rev.* B10, 496 (1974).
24. D. J. Chadi and M. L. Cohen, (to be published).
25. D. J. Chadi and M. L. Cohen, *Solid State Comm.* (in press).
26. D. J. Chadi and M. L. Cohen (to be published).
27. W. E. Spicer, in *Proc. 3rd Int. Mat. Res. Symp., Electronic Density of States*, Nat. Bur. Stand. (U.S.), Spec. Pub. 323 (1971), p. 139.
28. D. E. Eastman, in *Electron Spectroscopy*, ed. by D. A. Shirley (North-Holland Publishing Co., Amsterdam and London, 1972) p. 487.
29. N. Smith, *CRC Critical Reviews in Solid State Sciences* 2, 45 (1971).
30. K. Siegbahn, et al., *Electron Spectroscopy for Chemical Analysis* (Almqvist and Wiksells AB, Stockholm, Sweden, 1967).
31. C. S. Fadley and D. A. Shirley, *J. Nat. Bur. Stand.* 74A, 543 (1970).
32. S. B. Hagström, in *Electron Spectroscopy*, ed. D. A. Shirley (North-Holland Publishing Co., Amsterdam and London, 1972) p. 215.
33. M. L. Cohen and T. K. Bergstresser, *Phys. Rev.* 141, 789 (1966).
34. R. L. Zucca, J. P. Walter, Y. R. Shen, and M. L. Cohen, *Solid State Comm.* 8, 627 (1970).
35. J. P. Walter and M. L. Cohen, *Phys. Rev.* B1, 2661 (1970).
36. M. Appapillai and V. Heine, Technical Report No. 5 (July 1972), Solid State Theory Group, Cavendish Laboratory, Cambridge, England.
37. G. Weisz, *Phys. Rev.* 149, 504 (1966).
38. S. Bloom and T. K. Bergstresser, *Solid State Comm.* 6, 465 (1968).

39. J. P. Walter, M. L. Cohen, Y. Petroff and M. Balkanski, Phys. Rev. B1, 2661 (1970).
40. F. Herman and S. Skillman, Atomic Structure Calculations, (Prentice Hall, Inc., Englewood Cliffs, N. J., 1963).
41. G. Gilat and L. J. Raubenheimer, Phys. Rev. 144, 390 (1966).
42. J. C. Phillips, Rev. Mod. Phys. 42, 317 (1970).
43. J. A. Van Vechten, Phys. Rev. 182, 891 (1969).
44. P. O. Löwdin, J. Chem. Phys. 19, 1396 (1951).
45. C. Y. Fong and M. L. Cohen, Phys. Rev. Lett. 21, 22 (1968).
46. Data for InSb, GaAs, GaP, and CdTe were obtained by D. E. Eastman, W. D. Grobman, J. Freeouf and M. Erbudak (Ref. 8). Data for ZnSe and another value for GaAs were obtained by R. A. Pollack and D. A. Shirley (unpublished). Data for KI, KBr, KCl, NaBr, NaI were obtained from R. Pollak, Ph.D. thesis (unpublished), University of California, Berkeley, California 94720, and from Ref. 7. Data for RbCl were supplied by C. Vesely and D. Langer.
47. S. Bloom and T. K. Bergstresser, Phys. Status Solidi 42, 191 (1970).
48. D. Brust, Phys. Rev. 134, A1337 (1964).
49. D. G. Thomas, J. Appl. Phys. Suppl. 32, 2298 (1961).
50. M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967).
51. M. Cardona and D. L. Greenaway, Phys. Rev. 131, 98 (1963).
52. D. T. F. Marple and H. Zirnreich, Phys. Rev. Letters 8, 87 (1962).
53. J. L. Shay, W. E. Spicer, and F. Herman, Phys. Rev. Letters 18, 649 (1967).

54. J. L. Shay and W. E. Spicer, Phys. Rev. 161, 799 (1967).
55. S. Groves and W. Paul, in Proceedings of the Seventh International Conference on Semiconductors, Paris, 1964 (Academic, New York, 1965) p. 141.
56. S. H. Groves, R. N. Brown, and C. R. Pidgeon, Phys. Rev. 161, 779 (1967).
57. C. R. Pidgeon and S. H. Groves, Proceedings of the 1967 International Conference on Physics of II-VI Semiconductors, edited by D. G. Thomas (Benjamin, New York, 1967), p. 1080.
58. W. J. Scouler and G. B. Wright, Phys. Rev. 133, A736 (1964).
59. B. Velicky and J. Sak, Phys. Stat. Solidi 16, 147 (1966).
60. J. C. Phillips, Phys. Rev. 136, A1705 (1964).
61. C. B. Duke and B. Segall, Phys. Rev. Letters 17, 19 (1966).
62. Y. Toyozawa et al., J. Phys. Soc. Japan 21, 133 (1966).
63. J. Hermanson, Phys. Rev. 166, 893 (1968).
64. E. O. Kane, Phys. Rev. 180, 852 (1969).
65. Y. Petroff and M. Balkanski, Phys. Rev. B3, 3299 (1971).
66. W. D. Lawson, S. Nielson, E. H. Putley, and A. S. Young, J. Phys. Chem. Solids 9, 325 (1959).
67. J. L. Schmit and C. J. Speerschnneider, Infrared Phys. 8, 247 (1968).
68. D. Long, in Energy Bands in Semiconductors (John Wiley & Sons, Inc., New York, 1968), pp. 156-159.
69. L. Melingailis and A. J. Strauss, Appl. Phys. Lett. 8, 179 (1966).
70. M. W. Scott, J. Appl. Phys. 40, 4077 (1969).
71. W. G. Spitzer and C. A. Mead, J. Phys. Chem. Solids 25, 443 (1964).

72. D. Long and J. L. Schmidt, Semimetals and Semiconductors, ed. R. K. Willardson and A. C. Beer (Academic Press, New York, 1970), Vol. 5, Chap. 5.
73. J. P. Walter and M. L. Cohen, Phys. Rev. B4, 1877 (1971).
74. J. C. Woolley and B. Ray, J. Phys. Chem. Solids 13, 151 (1960).
75. J. L. Schmit and E. L. Steiner, J. Appl. Phys. 40, 4865 (1969).
76. S. H. Groves, T. C. Harman, and C. R. Pidgeon, Solid State Comm. 9, 451 (1971).
77. C. Vérié, Proceedings of the 1967 International Conference on II-VI Semiconducting Compounds, D. G. Thomas, ed. (Benjamin, N. J., 1967), p. 1124.
78. E. O. Kane, J. Phys. Chem. Solids 1, 249 (1957).
79. W. Kohn, Phys. Rev. 115, 809 (1959).
80. E. I. Blount, in Advances in Solid State Physics, eds. F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1962), Vol. 13, p. 305.
81. J. D. Joannopoulos and M. L. Cohen, J. Phys. C6, 1572 (1973).
82. D. J. Chadi and M. L. Cohen (unpublished).
83. C. Y. Fong and M. L. Cohen, Phys. Rev. Letters 32, 720 (1974).
84. J. D. Joannopoulos and M. L. Cohen, Phys. Rev. (to be published); and J. D. Joannopoulos, Ph.D. thesis, University of California (unpublished).
85. I. Ch. Schüter and M. Schlüter. Phys. Rev. B9, 1652 (1974).
86. L. Kleinman and J. C. Phillips, Phys. Rev. 116, 880 (1959).
87. E. O. Kane, J. Phys. Chem. Solids 1, 249 (1957).
88. J. P. Walter and M. L. Cohen (unpublished).

89. W. Paul in Proceedings of the Colloquiums on the Physical Properties of Solids under Pressure, Grenoble, 1969 (Centre National de la Recherche Scientifique, Grenoble, 1970), p. 199.
90. Carmen Varea de Alvarez and M. L. Cohen, Solid State Comm. 14, 317 (1974).
91. T. H. Geballe, et al., Physics 2, 293 (1966).
92. L. F. Mattheiss, Phys. Rev. B5, 315 (1972).
93. K. Schwarz, Monatsh. für Chem. 102, 1400 (1971).
94. C. Y. Fong and M. L. Cohen, Phys. Rev. B6, 3633 (1972).
95. J. B. Conklin, Jr., et al. Supplement, Journal de Physique 33, C3-213 (1972).
96. L. A. Hemstreet, C. Y. Fong and M. L. Cohen, Phys. Rev. 2, 2054 (1970).
97. L. Ramqvist et al., J. Phys. Chem. Solids 32, 149 (1971).
98. J. E. Holliday, The Electron Microprobe (edited by T. D. McKinley, K. S. J. Heinrich and D. B. Wittry) p. 3 John Wiley, N. Y., 1966.
99. We became aware of these experimental results after the completion of our calculation.
100. J. B. Conklin and D. J. Silversmith, Int. J. Quantum Chem. Symp. 1967, No. 2, 243.
101. V. Ern and A. C. Switendick, Phys. Rev. 137, A1927 (1965).
102. M. L. Cohen, Science 179, 1189 (1973).
103. H. G. Smith, in Superconductivity in d- and f-Band Metals, AIP Conference Proceedings No. 4, edited by D. H. Douglass (American Institute of Physics, New York, 1972).

104. H. G. Smith and W. Glaser, Phys. Rev. Letters 25, 1611 (1970);
29, 353 (1972).
105. W. Weber, H. Bilz, and U. Schröder, Phys. Rev. Lett. 28, 600 (1972).
106. G. G. Hall, Phil. Mag. 43, 338 (1952), *ibid.*, 3, 429 (1958).
107. D. Weaire and M. F. Thorpe, Phys. Rev. B4, 2508 (1971); M. F. Thorpe,
D. Weaire, and R. Alben, Phys. Rev. B7, 3777 (1973).
108. J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B7, 2644 (1973).
109. N. J. Shevchik, J. Tejeda, and M. Cardona, Phys. Rev. B9, 2627
(1974).
110. W. A. Harrison and S. Ciraci (to be published), S. Ciraci and
S. T. Pantelides (to be published).
111. K. Hirabayashi, J. Phys. Soc. Japan 27, 1475 (1969).
112. J. D. Joannopoulos, Ph.D. thesis, University of California
(unpublished).
113. *By nearest neighbor interactions we mean interactions of orbitals
on nearest neighbor atoms.*
114. M. F. Thorpe and D. Weaire, Phys. Rev. B4, 3518 (1971).
115. G. S. Painter, D. E. Ellis and A. R. Lubinsky, Phys. Rev. B4,
3610 (1971).
116. R. Keown, Phys. Rev. 150, 568 (1966). This paper gives many
references to earlier theoretical and experimental work on C.
117. J. R. Chelikowsky and M. L. Cohen (to be published).
118. J. R. Chelikowsky and M. L. Cohen, Physics Lett. 47A, 7 (1974).
119. K. C. Pandey and J. C. Phillips, Phys. Rev. Lett. 32, 1433 (1974).
120. J. D. Joannopoulos and M. L. Cohen, (to be published).
121. J. A. Appelbaum and D. R. Hamann, Phys. Rev. Letters 31, 106 (1973).
122. K. C. Pandey and J. C. Phillips, Solid State Comm. 14, 439 (1974).

123. J. E. Rowe and H. Ibach, Phys. Rev. Lett. 31, 102 (1973); 32, 421 (1974).
124. W. Ranke and K. Jacobi, Solid State Comm. 13, 705 (1973);
K. Jacobi and W. Ranke, Proc. of the 12th Int. Conf. on the
Phys. of Semic., Stuttgart (1974) (to be published).
125. R. Ludeke and L. Esaki (to be published).