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TITLE SELF-CONSISTENT ELECTRONIC STRUCTURE OF ALPHA-PHASE HUME ROTHERY
ELECTRON COMPOUND ALLOYS $\text{Cu}_{1-c}\text{Zn}_c$, $\text{Cu}_{1-c}\text{Ga}_c$, AND $\text{Cu}_{1-c}\text{Ge}_c$

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SELF-CONSISTENT ELECTRONIC STRUCTURE OF α -PHASE HUME-ROTHERY ELECTRON

COMPOUND ALLOYS $\text{Cu}_0\text{Zn}_{1-c}$, $\text{Cu}_0\text{Ga}_{1-c}$, and $\text{Cu}_0\text{Ge}_{1-c}$ ^{*}

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Summary

We have performed charge self-consistent electronic structure calculations for the α -phase Hume-Rothery electron compound alloys $\text{Cu}_0\text{Zn}_{1-c}$, $\text{Cu}_0\text{Ga}_{1-c}$, and $\text{Cu}_0\text{Ge}_{1-c}$ having electron to atom ratios 1:1, 1:2, and 1:3 for each alloy series. The calculations are based on the self-consistent-field Korringa-Kohn-Rostoker coherent-potential approximation (KKR-CPA). We show results for the densities of states and Fermi surface of these alloys; the behavior of these quantities is quite different from that predicted on the basis of the rigid band model. We also show results for the ground state properties of the $\text{Cu}_0\text{Zn}_{1-c}$ alloys that were obtained on the basis of a

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recent generalization of the density functional theory to random alloys. The theory provides a basis for understanding the concentration variation of the lattice parameter (Vegard's Law) of $\text{Cu}_0\text{Zn}_{1-0}$ alloys at the microscopic quantum mechanical level.

Introduction

It is now more than fifty years since Hume-Rothery (1) observed that in a certain class of alloys (primarily the noble metals alloyed with the simple metals to their right in the periodic table) the phase boundaries tend to occur at fairly definite electron to atom ratios (e/a). In the intervening years a great deal of experimental effort has been expended trying to uncover the nature of the underlying electronic structure of these alloys and relating it through simple theoretical models to their structural stability [see reviews by Massalski and Mitzutani (2), by Massalski (3), and by Pettifor (4)].

Prior to the mid-1970s much of the discussion of the electronic structure of Hume-Rothery phases was in terms of the rigid band model (RBM) of Mott (5). In the rigid band model the pure metals and their alloys are assumed to have a common density-of-states curve (often some effective mass-modified free-electron density of states) the extent to which it is occupied being determined by the particular e/a of the alloy. Though able to offer qualitative explanations of much experimental data, by the 1970s it had become clear that the RBM and related techniques failed even qualitatively to explain certain spectroscopic data and quantitatively failed to explain a great deal more.

Of central importance in the development of models of phase stability in the Hume-Rothery alloys is the model of Jones (6), first formulated to describe the α - β (fcc-bcc) phase transition in $\text{Cu}_0\text{Zn}_{1-0}$ alloys. The argument, which is predicated on the RBM, goes as follows: the band structure contribution to the total energy, E_B , is related to the density of states $n(\epsilon)$ at the energy ϵ through $E_B = \int_{-\infty}^{\epsilon_F} \epsilon n(\epsilon) d\epsilon$. For alloys having low e/a ,

the total energy associated with the fcc-phase, E_B^{α} , is less than that associated with the bcc-phase, E_B^{β} , because of the peak in $n(\epsilon)$ associated with the fcc 111-Brillouin zone contact. As e/a increases, the Fermi surface expands and the 110-peak in $n(\epsilon)$ for the bcc-phase falls below the Fermi energy, ϵ_F , then $E_B^{\beta} < E_B^{\alpha}$ and, ultimately, the β -phase is favored. Later, similar arguments, emphasizing the effects of Fermi surface Brillouin zone contact, were developed for the other Hume-Rothery phases (2). It is now generally accepted that such a simple model is no correct for describing the α - β phase transition. Indeed it has been shown (7) that the phase diagrams of $\text{Cu}_0\text{Zn}_{1-0}$, etc. can be reproduced semi-empirically in terms of thermodynamic phase competition ideas of the type pioneered by the Kaufman school (8) and that to do this, it is not necessary to have structure in the heats of solution associated with Fermi surface Brillouin-zone contact. This notwithstanding, correlations have been established between e/a and the existence of and properties of the complex cubic and hexagonal phases (see Ref. 2). Clearly, as yet no unified picture of the electronic structure of the phases has emerged, much less the relationship between the electronic structure and alloy phase stability.

In recent years the conceptual framework for calculating the electronic structure of random substitutional alloys has undergone a revolution [for reviews see Faulkner (9) and Stocks and Winter (10)]. The modern theory is based on the coherent-potential approximation (CPA). The CPA is

a method for treating the effects of disorder on the electronic structure. When used in conjunction with a realistic description of the random effective electron-ion potential (the muffin-tin Hamiltonian), the method is called the Korringa-Kohn-Rostoker-CPA (KKR-CPA). Based on comparisons of the results of KKR-CPA calculations with results of a number of experimental probes of the electronic structure, for a growing number of systems, it now appears that the KKR-CPA method provides an accurate description of the electronic structure of metallic alloys (9,10).

Recently (11) the KKR-CPA method has been made charge self-consistent within the framework of (local) density functional theory (DFT). Thus it is now possible to calculate the electronic structure of an alloy by specifying only the concentrations of the alloying species, the lattice type, and lattice spacing of the alloy in question. Furthermore, since local DFT provides a method whereby the ground state properties can be calculated and is known to work well for pure metals and ordered alloys [see, for example, Moruzzi et al. (12)], it should be possible also to calculate the ground state properties (equilibrium lattice spacing, heats of mixing, etc.) for random alloys.

In this paper, we present results of electronic structure calculations on the Hume-Rothery α -phase alloys of $\text{Cu}_2\text{Zn}_{1-c}$, $\text{Cu}_2\text{Ga}_{1-c}$, and $\text{Cu}_2\text{Ge}_{1-c}$ based on the self-consistent KKR-CPA method. We also present preliminary results for the concentration variation of the equilibrium lattice spacing of α -phase $\text{Cu}_2\text{Zn}_{1-c}$ alloys based on the new extension of local DFT to the case of random alloys. These calculations can be regarded as the first step towards understanding the electronic structure and the phase stability of the Hume-Rothery phases from the point of view of a completely *ab initio* theory.

Ab Initio Electronic Structure Calculations for Random Substitutional Alloys

There have been several reviews of the KKR-CPA method for calculating the electronic structure of random substitutional alloys; of particular relevance to the metallurgical community is the one by Faulkner (9). The extension of the theory to include charge self-consistency was discussed at an early stage of development in the review by Stocks and Winter (10). The reader is referred to these reviews and to the original literature for details of the theory; we include only a brief outline of the method here.

The underlying model of the effective electron-ion interaction is a generalization of the muffin-tin model commonly used in band theory calculations of the electronic structure of pure metals and ordered alloys (see Ref. 12 for example). The effective potential seen by an electron is assumed to be spherically symmetric within touching spheres centered on the lattice sites and to be constant within the interstitial region. Within the muffin-tin spheres all sites of a given type have the same potential associated with them. The species are supposed to be distributed randomly among the lattice sites according to their respective concentrations. Thus, for an A_cB_{1-c} alloy the probability that a particular site will have a muffin-tin potential $v_A(r)$ associated with it is c_A ($\equiv c$) the concentration of the A-species and likewise for the B-species.

The essence of the CPA is that for the purposes of calculating the configurationally averaged properties of the system, the random distribution of (real) v_A and v_B muffin-tin potentials can be replaced by an ordered array of effective muffin-tin potentials v_C . The effective potential is then adjusted such that it gives the "best" description of the

alloy within the so-called "single site" approximation. Programatically this consists of choosing v_C such that an electron, traveling in an infinite array of v_C 's, undergoes, on average, no further scattering upon replacement of a single v_C potential by the true v_A or v_B potential. Expressed mathematically in terms of a set of coupled integral equations, this is the CPA condition. It uniquely determines v_C , or rather the scattering properties of v_C (usually expressed in terms of the effective scattering t -matrix t_C). Once t_C is known, it is a straightforward matter to calculate many of the electronic properties of the alloy system, e.g., electronic densities of states, charge densities, Bloch spectral densities, and Fermi surface, as well as many observable quantities, e.g., soft X-ray spectra, low temperature specific heat coefficient γ , electrical resistivity, angle-resolved photocurrents, and the 2γ -momentum distributions measured in angular correlation of annihilation radiation (ACAR) positron annihilation experiments.

In the non-charge self-consistent version of the theory, the electron-ion potential is constructed according to some reasonable, but ad-hoc, prescription, e.g., the Mattheiss prescription of overlapping neutral atom charge densities (13). In the charge self-consistent version of the theory, once the CPA equations have been solved, the configurationally averaged charge densities associated with the different atomic species are calculated; from these a new muffin-tin potential is calculated. The process is repeated until the charge density calculated from solving the CPA conditions is the same, to within some tolerance, as that which went into the construction of the muffin-tin potentials. Exchange and correlation effects are included through a local exchange-correlation functional (14). Within the framework of the charge self-consistent theory the only inputs required, apart from a knowledge of the atomic species present and their relative concentrations, are the crystal structure and atomic spacing.

Figure 1 - Upper: Low temperature specific heat coefficient of $\text{Cu}_{0.5}\text{Zn}_{0.5}$ random alloys. $\bullet$ - calculated on basis for KKR-CPA; $\circ$, Δ - experiment. The solid line gives the prediction of the rigid band model. Middle: Bare electronic specific heat coefficient calculated using KKR-CPA. The solid line gives the same for the rigid band model. Lower: Electron-phonon mass enhancement factor extracted from resistivity measurements.

Non-self-consistent KKR-CPA calculations have been performed previously on a number of the copper-based Hume-Rothery phases. Faulkner and Stocks (15), Figure 1, showed that the concentration variation of γ , the coefficient of the term linear in T extracted from low-temperature-specific heat measurements, could be understood in terms of KKR-CPA calculations, the results of which were qualitatively different from those based on the RBM. Key to the understanding of the experimental results is a correct concentration variation of the density of states at the Fermi energy, $n(\epsilon_F)$, and the correct concentration variation of the electron-phonon enhancement factor λ . In Figure 1, the lower panel shows the concentration variation of λ extracted from resistivity measurements. In the middle panel, the bare specific heat coefficient $\gamma = (\pi^2 k_B^2 / 3) n(\epsilon_F)$ calculated using the KKR-CPA is compared with that obtained using the RBM based on the density of states of pure copper. The total $\gamma = \gamma(1 + \lambda)$ calculated using both the KKR-CPA and the RBM is compared with experiment in the upper panel.

In a series of papers, Bansil (16) and his collaborators performed KKR-CPA calculations on both $\text{Cu}_x\text{Zn}_{1-x}$ and $\text{Cu}_x\text{Ge}_{1-x}$ α -phase alloys. For the most part these calculations are based on Mattheiss prescription muffin-tin potentials, though often adjusted to reproduce some particular experimental result, e.g., in the $\text{Cu}_x\text{Zn}_{1-x}$ system, the position of the top of the d -band complex was adjusted to match the position of the first peak in optical absorption spectra. Using these adjusted potentials, other experimental data was then interpreted, e.g., additional structure in optical spectra, UV-photoemission and the concentration variation of Fermi surface dimensions as measured by ACAR experiments.

The overall picture of the electronic structure provided by these earlier non-self-consistent KKR-CPA calculations is sufficiently good to indicate that the self-consistent KKR CPA might provide the basis for a unified description of the properties of the Hume-Rothery phases without recourse to any adjustable parameters.

Electronic Structure: Densities of States

We have calculated the electronic structure of three α -phase alloys for each of $\text{Cu}_x\text{Zn}_{1-x}$, $\text{Cu}_x\text{Ga}_{1-x}$, and $\text{Cu}_x\text{Ge}_{1-x}$. For each alloy system, the calculations were performed for $x/a = 1.1, 1.2$, and 1.3 (counting the valences of Cu, Zn, Ga, and Ge as 1, 2, 3, and 4, respectively). The calculations were performed at the measured room temperature lattice parameters (17) which are given in Table I. The potentials were iterated to self-consistency using the cluster method of solving the CPA equations and by using integration in the complex energy plane (18) to obtain single-site charge densities, etc. necessary in the self-consistent field (SCF) procedure. The exchange-correlation potential used was that of von Barth and Hedin (14). Angular momenta up to $l = 2$ were retained in the calculations.

Table I. Compositions and lattice spacings for which KKR-CPA calculations were performed. All alloys are fcc. M is the minority component.

x/a	M	$l-c$	$a(\text{a.u.})$
1.1	Zn	0.10	6.869
	Ga	0.05	6.858
	Ge	0.033	6.852
1.2	Zn	0.20	6.910
	Ga	0.10	6.884
	Ge	0.067	6.872
1.3	Zn	0.30	6.957
	Ga	0.15	6.911
	Ge	0.10	6.895

In Figure 2 are displayed densities of states for three $\text{Cu}_x\text{Zn}_{1-x}$ alloys having $x = 0.7, 0.8$, and 0.9 (19). In Figure 2, and all subsequent figures of $n(\epsilon)$, ϵ_F is

Figure 2 — Densities of states for three $\text{Cu}_c\text{Zn}_{1-c}$ alloys having $c = 0.7$ ($e/a = 1.3$), $c = 0.8$ ($e/a = 1.2$), and $c = 0.9$ ($e/a = 1.1$). In this and subsequent plots, the energy zero is the Fermi energy.

the energy zero. For each concentration the high energy ($\epsilon = -0.15 + -0.35$ Ry) high density of states structure arises from copper d -states, the low energy ($\epsilon \sim -0.65$ Ry) high density of states structure arises from zinc d -states. With increasing zinc content, the zinc d -band grows at the expense of the copper d -band which in turn loses structure. To a first approximation the positions, with respect to ϵ_F , of both Cu- and Zn-related structures are independent of the concentration. A somewhat more detailed analysis shows that the upper edge of the copper d -band recedes from ϵ_F at the rate of approximately 0.017 eV per atomic percent, in good agreement with the rate of movement of the optical absorption edge of 0.017 eV per atomic percent, which is about half the rate found in the RBM (2). We postpone a final discussion of the position of the absorption edge until we have calculated the Bloch spectral functions and have precisely located the position of the upper L_3 -state with which it is usually associated. In Figure 3, we have reproduced the UV-photoemission results of Norris and Williams (20); the energy distribution curves (EDC's) were obtained using 21.2 eV incident photons. The two major structures in the EDC's arise from the Cu and Zn d -states. The zinc-related structure lies approximately 9.7 eV below ϵ_F for all three concentrations; our calculation gives the center of the zinc band at 8.4 eV. In their calculations of the density of states of single impurities embedded in a copper matrix, Zeller and Dederichs (21) find the zinc (bound) d -state to be 8.2 eV below ϵ_F . Bearing in mind the known difficulties involved in comparing peak positions measured in EDC's with those calculated from band theory, the overall agreement between theory and experiment must be considered good.

Figure 3 — Experimental UV-photoemission spectra for $\text{Cu}_x\text{Zn}_{1-x}$ alloys according to Norris and Williams (19). The incident photon energy was 21.2 eV. The curves are plotted relative to the Fermi energy and are displaced vertically by arbitrary amounts. —→

UPS Spectra for CuZn alloys

In Figure 4 we have taken the calculated density of states for the $\text{Cu}_{0.70}\text{Zn}_{0.30}$ alloy ($e/a = 1.3$) and broken it down into component densities of states both in terms of species and in terms of angular momentum character. Plotting the results this way makes the point that the low-lying peak is almost entirely zinc d -related while the upper peak is copper d -related. Interestingly though, some extra copper-related states are introduced by alloying in the energy region associated with the zinc d -band. The existence of any such states clearly

Figure 4 — Total and component densities of states for $\text{Cu}_{0.70}\text{Zn}_{0.30}$ ($e/a = 1.3$). The total density of states is shown in the foreground. The middle curve gives the density of states associated with a copper site in the alloy, the backmost curve that associated with zinc. The component densities of states are plotted per Cu(Zn) atom. In the curves of component densities of states: solid line— total density of states; dot— s -component; dash— p -component; chain dash— d -component.

invalidates arguments based on the RBM. At the lowest energies the states are of s -character while at the energy of the zinc d -band the copper-related states have a substantial d -character.

In Figure 5 we show density of states curves for $\text{Cu}_c\text{Ga}_{1-c}$ alloys having $c = 0.85, 0.90$, and 0.95 . The overall picture is very similar to that in $\text{Cu}_c\text{Zn}_{1-c}$ except that the gallium d -band is now detached from the bottom of the host band. For the same e/a the extent to which fine structure in the copper density of states is washed out by the alloying is much less in $\text{Cu}_c\text{Ga}_{1-c}$ than $\text{Cu}_c\text{Zn}_{1-c}$, as might be expected if it is determined by the concentration of the minority. The movement of the upper edge of the copper d -band, with respect to ϵ_F , is sufficiently small that it is not possible to correlate it with optical data without calculation of the Bloch spectral function. Norris and Williams (20) find the gallium d -band to be 18.7 eV below ϵ_F for $\text{Cu}_{0.83}\text{Ga}_{0.17}$; we find it to be approximately 16.4 eV below ϵ_F , almost independent of concentration. Zeller and Dederichs (21) find the single impurity gallium d -state at -16.6 eV. In Figure 6 we display the component densities of states for the $\text{Cu}_{0.85}\text{Ga}_{0.15}$ alloy ($e/a = 1.3$). It is interesting to note that the occupied conduction band width is considerably wider than in pure Cu and $\text{Cu}_c\text{Zn}_{1-c}$. We will focus on the reason for this later.

Figure 5 — Densities of states for three $\text{Cu}_c\text{Ga}_{1-c}$ alloys having $c = 0.85$ ($e/a = 1.3$), $c = 0.90$ ($e/a = 1.2$), and $c = 0.95$ ($e/a = 1.1$).

Figure 6 — Total and component densities of states for $\text{Cu}_{0.85}\text{Ga}_{0.15}$ ($e/a = 1.3$). The notation is similar to that used in Figure 4.

The densities of states for $\text{Cu}_c\text{Ge}_{1-c}$ alloys, having $c = 0.90, 0.933,$ and 0.967 , are shown in Figure 7. The structure associated with the germanium d -band is at -26.6 eV relative to ϵ_F ; Norris and Williams find -29.2 for $\text{Cu}_{0.87}\text{Ge}_{0.13}$. For a single germanium atom embedded in copper, Zeller and Dederichs find the impurity d -state 26.6 eV below ϵ_F . Once again the position of the upper edge of the copper d -band changes very little on alloying; again the shift is so small that we are unable to correlate it with movement in the optical absorption edge without a more detailed analysis of the Bloch spectral functions. In Figure 8 we show for $\text{Cu}_{0.90}\text{Ge}_{0.10}$ ($e/a = 1.3$) the Cu and Ge component densities of states resolved into angular momentum components. Continuing the trend, the overall bandwidth is greater for the $\text{Cu}_c\text{Ge}_{1-c}$ alloy than for the other systems. Furthermore, a germanium-related sp -band, as well as a germanium d -band, is split off from the bottom of the copper conduction band.

The sequence of events that occurs in the density of states on changing the minority component can be seen more clearly in Figures 9 and 10. In Figure 9 we have plotted the total density of states for $\text{Cu}_c\text{Zn}_{1-c}$, $\text{Cu}_c\text{Ga}_{1-c}$, and $\text{Cu}_c\text{Ge}_{1-c}$ alloys having $e/a = 1.3$. The relative insensitivity of the position of the copper d -band to solute type, the movement towards greater binding energy of the d -band of the solute, and the gradual widening of the "solvent/solute" sp -band are all seen clearly. In Figure 10 we show the density of states associated with Zn, Ga, and Ge sites (per minority site). In pure copper, the occupied conduction bandwidth is 9.4 eV; for the $\text{Cu}_{0.70}\text{Zn}_{0.30}$ alloy, 11.0 eV; for $\text{Cu}_{0.85}\text{Ga}_{0.15}$, 11.6 eV; and for $\text{Cu}_{0.90}\text{Ge}_{0.10}$, 13.4 eV. As pointed out earlier for $\text{Cu}_{0.70}\text{Zn}_{0.30}$, the

Figure 7 — Densities of states for three $\text{Cu}_c\text{Ge}_{1-c}$ alloys having $c = 0.90$ ($e/a = 1.3$), $c = 0.933$ ($e/a = 1.2$), and $c = 0.967$ ($e/a = 1.1$).

Figure 8 — Total and component densities of states for $\text{Cu}_{0.90}\text{Ge}_{0.10}$ ($e/a = 1.3$). The notation is similar to that used in Figure 4.

Figure 9 — Total densities of states for the $e/a = 1.3$ alloys: $\text{Cu}_{0.70}\text{Zn}_{0.30}$ (background), $\text{Cu}_{0.45}\text{Ga}_{0.15}$ (middle), and $\text{Cu}_{0.90}\text{Ge}_{0.10}$ (foreground).

Figure 10 — The minority species component densities of states (per minority atom) for the same $e/a = 1.3$ alloys shown in Figure 9. For each system: solid—total density of states; dot— s -component; dash— p -component; chain dash— d -component.

zinc d -band is at the bottom of, but overlaps with, the conduction band, while for $\text{Cu}_{0.85}\text{Ga}_{0.15}$ and $\text{Cu}_{0.90}\text{Zn}_{0.10}$ it is detached. For $\text{Cu}_{0.80}\text{Ga}_{0.15}$ there is a high density of states of s -character at the bottom of the conduction band; for $\text{Cu}_{0.90}\text{Ge}_{0.10}$ this incipient s -bound state has become detached and forms a separate, primarily s -character impurity band. All of these effects can be viewed as the finite concentration extension of the picture found by Zeller and Dederichs (20), based on their self-consistent KKR-Greens function calculations, for single substitutional Zn, Ga, and Ge impurities in copper. For gallium they found that a bound s -state was just pulled off from the bottom of the copper d -band. Because of the large concentration of gallium in our alloy, this single level is broadened into a band that is sufficiently wide to overlap with the bottom of the copper sp -band. For the germanium impurity they found a bound s -state about 1 eV below the bottom of the copper sp -band. In the alloy this state is again broadened into a band; however, in this case it is not sufficiently wide to overlap with the original copper sp -band. Clearly, it is the formation of these fairly localized, low energy s - and p -impurity states that invalidates any arguments about the electronic structure of the Hume-Rothery phases that are based on the RBM. In Table II we show, for the case of the $e/a = 1.3$ alloys, total and l -component charges associated with Cu, Zn, Ga, and Ge sites. Here the term "site" has a strict meaning, since for the purposes of the KKR-CPA calculations we divide space into Wigner-Seitz cells all of equal size. Consequently, in a given alloy both species have the same "size." Obviously, from Table II there is little departure from charge neutrality; also neutrality is established through the screening effect provided by occupying the low-lying s - and p -states of the minority. This is a very atomic-like picture of the screening process where the relatively low-lying, tightly bound, valence s - and p -states of the minority (that is compared with the valence s -state of copper) are responsible for screening. That the screening takes place in this way has consequences for the alloy Fermi surfaces.

Table II. Total and component charges for Hume-Rothery alloys having $e/a = 1.3$. The charges refer to the charges enclosed in the Wigner Seitz cell. Q_T is the total charge; Q_s , Q_p , and Q_d are the $l = 0, 1$, and 2 component charges, respectively.

Alloy	Species	Q_T	Q_s	Q_p	Q_d
$\text{Cu}_{0.70}\text{Zn}_{0.30}$	Cu	11.043	0.680	0.767	9.596
	Zn	11.899	0.882	0.994	10.023
$\text{Cu}_{0.85}\text{Ga}_{0.15}$	Cu	11.025	0.675	0.764	9.586
	Ga	12.773	1.168	1.419	10.186
$\text{Cu}_{0.90}\text{Ge}_{0.10}$	Cu	11.028	0.672	0.594	9.594
	Ge	13.749	1.456	2.018	10.274

Electronic Structure: Fermi Surfaces

For random substitutional alloys the notion of a Fermi surface has a nice generalization in terms of a quantity called the Bloch spectral density function, $A(k, \epsilon)$ (10). This quantity can be thought of as the density of states at each point, k , in reciprocal space, thus

$$n(\epsilon) = \frac{1}{\Omega} \int_{BZ} A(\vec{k}, \epsilon) d^3k,$$

where the integral is over the Brillouin zone and Ω is its volume. For a pure metal, $A(\vec{k}, \epsilon)$ is simply given by a sum of δ -function contributions, one at each band energy

$$A(\vec{k}, \epsilon) = \sum_v \delta(\epsilon - \epsilon_{\vec{k}, v}).$$

Here, $\epsilon_{\vec{k}, v}$ is the energy of the v th energy band at the point $\vec{k}$ in reciprocal space. The Fermi surface is defined as the locus in $\vec{k}$ -space of the δ -function peaks of $A(\vec{k}, \epsilon_F)$. The effects of the disorder introduced by forming a random substitutional solid solution are to broaden the δ -function peaks associated with the pure metal and to introduce new peaks associated with the second component. The degree to which the δ -function peaks are broadened in $\vec{k}$ -space measures the degree of disorder. A plot of $A(\vec{k}, \epsilon)$, as a function of $\vec{k}$ at the Fermi energy $\epsilon = \epsilon_F$ for an alloy, shows the extent to which the Fermi surface is preserved. Such plots are shown in Figure 11 for the three $e/a = 1.3$ alloys. In these $A(\vec{k}, \epsilon)$ is plotted along directions in $\vec{k}$ -space emanating from the Brillouin zone center and terminating at the Brillouin zone boundary. The directions are contained in the three major planes in reciprocal space. The alloy "Fermi surface" is defined by the locus of the peaks in these plots. The width of the peaks at half-maximum, Δk , gives a direct measure of the disorder. Indeed, provided the disorder is not too large, $\Delta k \sim \hbar/l_F$ where l_F is the electron mean free path that determines the residual electrical resistivity (22).

Despite the fact that the concentration of the minority component in the three alloys shown in Figure 11 is decreasing in the order Zn, Ga, Ge, the degree to which the Fermi surface is smeared increases. The reason for this is, however, readily understood. For all the alloys, the details of the Fermi surface are dominated by the s - and p -components, in the language of multiple-scattering theory, by the $l = 0$ and $l = 1$ phase shifts. The sharpness of the $\text{Cu}_{0.70}\text{Zn}_{0.30}$ Fermi surface reflects the fact that at ϵ_F the $l = 0$ and $l = 1$ phase shifts for Cu-sites and for Zn-sites are rather similar. For Ga and Ge alloys, on the other hand, because of the low-lying s - and p -states that we commented on in the previous section, the phase shift differences at ϵ_F between Cu and the Ga and Ge minority components are large, resulting in a fairly ill-defined Fermi surface. This is more so for the Ge alloy than for the Ga alloy. However, even for the Ga and Ge alloys, the Fermi surface can still be thought of as being sharp on a scale set by the dimensions of the Brillouin zone, $\Delta k/k_{BZ} \sim 1/20$. For all of the alloys the Fermi surface (111) neck is seen.

In Figure 12 we show Fermi energy Bloch spectral functions for $\text{Cu}_{0.80}\text{Zn}_{0.20}$. The Fermi surface for this alloy is somewhat sharper than for the $\text{Cu}_{0.70}\text{Zn}_{0.30}$ shown in Figure 11. The Fermi surface is also slightly smaller. In the past there have been a number of experimental determinations of Fermi surface dimensions. In the very dilute limit these are based on the de Haas-van Alphen effect, in more concentrated alloys on the results of two-dimensional ACAR measurements. We postpone the detailed analysis of these data in terms of the Fermi surface spectral functions to a future publication.

Figure 11 - Fermi energy Bloch spectral functions $A(\vec{k}, \epsilon_F)$ for the $e/a \approx 1.3$ alloys $\text{Cu}_{0.70}\text{Zn}_{0.30}$ (upper), $\text{Cu}_{0.85}\text{Ga}_{0.15}$ (middle), and $\text{Cu}_{0.90}\text{Ge}_{0.10}$ (lower). For each system, $A(\vec{k}, \epsilon_F)$ is plotted along rays emanating from the Brillouin zone center and terminating at the Brillouin zone boundary. The left frame is for the plane containing the points $\Gamma X W X$ in the fcc Brillouin zone; the right frame is for the planes containing $\Gamma X L$ and $\Gamma L W X$.

Figure 12 — Fermi energy Bloch spectral function for $\text{Cu}_{0.80}\text{Zn}_{0.20}$.

Ground State Properties

Having established that the KKR-CPA is capable of giving a detailed parameter-free description of the electronic structure of the Hume-Rothery phase, it is now worthwhile to attempt to develop a theory of the energetics of alloy formation within the same framework. For pure metals and ordered compounds, the DFT provides a proper formal framework for doing this, and as we have commented earlier, it has been very successful (12). Density functional theory is basically a theory for the ground state properties of a system. For an ordered system once the self-consistent charge density and electronic structure has been calculated, by repeated solution of an effective single particle-like Schrödinger equation, the DFT provides a straightforward way of calculating the total energy and pressure. If calculations are performed at a number of lattice spacings for a given crystal structure, the equilibrium lattice spacing is simply that for which the total energy is a minimum (or alternatively the pressure is zero). The cohesive energy is then the difference in energy between this energy and that of isolated atoms. For pure metals and ordered compounds, the calculation of the ground state properties is now a relatively simple matter. There are two main reasons for this. First, because the effective potential entering the single particle Schrödinger equation is periodic, its solutions can be found fairly easily using modern band structure methods. Second, and more important, there is but a single atomic configuration. For a random substitutional alloy there are many possible configurations. For a binary A_0B_{1-0} alloy containing N -atoms there are $N!/m!(N-m)!$ of them to be precise, where m is the number of B -type atoms. A straightforward application of the techniques of DFT to random alloys would require the self-consistent solution of the effective Schrödinger equation and the calculation of the total energy for each possible configuration. The configurationally averaged energy would then be constructed by averaging these with respect to the probability of occurrence of that configuration. Clearly, an alternate path must be found.

For the calculation of the electronic structure the KKR-CPA provides an alternate path. Some configurationally averaged single-site potentials are specified. From this the configurationally averaged electronic properties are calculated directly on the basis of the CPA. Our self-consistent KKR-CPA then formalizes the relationship between the configurationally averaged single-site charge densities and the single-site potentials. Thus, within the KKR-CPA, the averaging process and the solution of the effective Schrödinger equation are inextricably mixed. Consequently, there is no final averaging process to perform and again the solution of the effective Schrödinger equation is relatively simple.

Recently, an extension of this general approach has been found for calculating the total energy and pressure from the self-consistent KKR-CPA single-site charge densities and potentials [Johnson et al. (23)]. In order to bypass the tricky averaging process the expression for the total energy is obtained by starting from Maxwell's relation

$$N(\mu) = \left. \frac{\partial \Omega}{\partial \mu} \right|_{T, V} \quad (1)$$

between the configurationally averaged grand thermodynamic potential Ω , the chemical potential μ , and the total number of particles N . The latter is related to the density of states through

$$N(\mu) = - \int_{-\infty}^{\infty} d\epsilon n(\epsilon) f(\epsilon - \mu) , \quad (2)$$

where $f(\epsilon)$ is the Fermi-Dirac distribution function. Using the expression of Gyurffy and Stocks (24) for the integrated density of states in the CPA and taking the zero temperature limit, it is possible to show that for the KKR-CPA the total energy is given by

$$E = \int_{-\infty}^{\infty} d\epsilon \epsilon \left\{ \sum_i n_i(\epsilon) + \int_0^{\infty} d\tilde{r} \int_{-\infty}^{\infty} d\nu \left\{ \sum_i \sigma_i \rho_i(r) \frac{\partial \nu_i(\tilde{r})}{\partial \nu} \right\} \right\} , \quad (3)$$

where σ_i , n_i , ρ_i , and ν_i are the concentration, density of states, and charge density and muffin-tin potentials associated with the i th species. The first term on the right of Eq. (3) is the usual band structure contribution to the total energy; the second term gives the so-called double counting corrections. Indeed, for the case of an ordered system it can be shown that this latter term can be manipulated to give the same result as Janak (25).

For the KKR-CPA method Johnson et al. (23) show that if the prescription of Stocks and Winter (11) is used for calculating the single-site potentials ν_i from the configurationally averaged single-site charge densities σ_i , then Eq. (3) for the configurationally averaged total energy reduces to the simple form

$$E = \sum_i \sigma_i E_i^J(\sigma_i, \rho_0) , \quad (4)$$

with a similar expression

$$P = \sum_i c_i P_i'(\rho_i, \rho_0) \quad (5)$$

for the pressure P . In Eqs. (4) and (5), $E'(\rho_i, \rho_0)$ and $P_i'(\rho_i, \rho_0)$ are the expressions obtained by Janak (25) for the total energy and pressure of a pure metal excepting that the single-site muffin tin and interstitial charge densities ρ_i, ρ_0 obtained from the KKR-CPA are to be used in these equations. The interstitial charge density is defined to be

$$\rho_0 = \frac{1}{\Omega_{c.t.}} \sum_i c_i [Z_i - 4\pi \int_0^{r_{MT}} r^2 \rho_i(r) dr] , \quad (6)$$

where $\Omega_{c.t.}$ is the interstitial volume and the remainder of the right of Eq. (6) is simply the configurational average of the charge not included in the muffin-tin spheres.

Despite the very different philosophy behind the derivation of the total energy of Johnson et al. from that of the usual DFT, the resulting total energy expression has a number of necessary features in common with DFT. First, the energy can be decomposed into kinetic and potential energy terms; second, the effective potential $v_i(r)$ associated with the i th species is obtained by taking the functional derivative of the potential energy with respect to $\rho_i(r)$; third, the total energy is a minimum with respect to independent variations in the $\rho_i(r)$. That the total energy expressions of Johnson et al. (23) satisfy all of these conditions is a result of the particular, mean-field choice made by Stocks and Winter (10) for the reconstruction of the muffin-tin potentials from the single-site charge densities and that single-site charge densities are calculated on the basis of the KKR-CPA, which, in turn, is a mean field theory of the electronic structure. Other choices of muffin-tin potential construction or other choices of alloy theory, for example, the average t -matrix approximation (26), would not necessarily result in such a happy union.

In Figure 13 we show the calculated equilibrium lattice spacing of α -phase $\text{Cu}_0\text{Zn}_{1-\phi}$ alloys having $\phi = 1.0, 0.90, 0.80$, and 0.70 . The equilibrium lattice spacing was located by finding that lattice spacing for which the pressure, Eq. (5), was zero. Also shown in Figure 13 are the measured room temperature lattice spacings (17). We have also calculated the equilibrium lattice spacings of $\text{Cu}_{0.5}\text{Zn}_{0.5}$ and of pure zinc for the fcc crystal structure. The line drawn through the calculated points is intended as a guide to the eye. Over the concentration range of the α -phase we obtain an almost precisely linear concentration variation of the lattice spacing. Over the entire concentration range we find a small departure from linearity. The value we calculate for the initial α -phase slope is 0.00450 a.u. (atomic unit) per at. %; the experimental value at room temperature is 0.00423 a.u. per at. %. Taking the experimental atomic value of zinc in the hcp-phase and converting that to an equivalent fcc lattice spacing gives 7.352 a.u., Vegard's rule of assuming the lattice spacing to interpolate linearly between the pure metal end points gives a slope of 0.00543 a.u. per at. %. The negative departure from Vegard's rule seen in the α -phase $\text{Cu}_0\text{Zn}_{1-\phi}$ alloys is well reproduced by the theory.

CONCENTRATION VARIATION OF LATTICE SPACING (fcc-phase)

Figure 13 - Concentration variation of the calculated and measured lattice spacings of α -phase $\text{Cu}_0\text{Zn}_{1-0}$ alloys. Theory - —•—•—, Experiment - —o—o—. The experimental results are those of Owen and Roberts (27) as quoted by Pearson (17).

For the α -phase alloys the measured lattice spacings that are plotted in Figure 13 make the agreement between theory and experiment appear better than it is since they are room temperature values. Using the calculated value of 6.895 a.u. and the measured value of 6.809 a.u. for copper at $T = 0$ K (of 6.832 a.u. at 300 K) for comparison, the error is on the order of 1.3%. The major part of this discrepancy is due to the truncation of the angular momentum summations in our calculations at $l = 2$. For pure copper, inclusion of $l = 3$ and 4 terms gives an equilibrium lattice spacing of 6.767 which is within 0.6% of the experimental value. Presumably inclusion of $l = 3$ and 4 terms within the KKR-CPA will result in a similar residual error. The absolute error notwithstanding, we view the overall agreement between our calculation and experiment as encouraging, being the first *ab initio* calculation of the equilibrium lattice spacing of a random alloy.

Having calculated the equilibrium lattice constant, the zero temperature heat of mixing $\Delta E(a)$ of an A_0B_{1-0} alloy can be readily obtained from

$$\Delta E(a) = E^{AB}(a) - aE^A - (1-a)E^B, \quad (7)$$

where $E_{CPA}^{AB}(a)$ is the total energy of the alloy, and E^A and E^B are the total

energies of the pure metals. We have performed preliminary calculations of the heats of mixing of the α -phase $\text{Cu}_x\text{Zn}_{1-x}$ alloys for $\text{Cu}_{0.8}\text{Zn}_{0.2}$ ($\text{Cu}_{0.5}\text{Zn}_{0.5}$); we obtain -2.3 (-4.7) mRy which has to be compared with the semi-empirical value of -4.5 (-7.6) mRy obtained by Saunders and Miodownik (7) using the CALPHAD approach of Kaufman (8) and the experimental high-temperature result of -4.1 (-7.1) mRy obtained by interpolation from the values quoted by Muttgren (28). While these results are encouraging, they must still be treated with some skepticism because of our truncation of angular momentum sums at $l_{\text{max}} = 2$, since the differences between total energies calculated using $l_{\text{max}} = 2$ and $l_{\text{max}} = 4$ are on the order of $10 + 15$ mRy.

Conclusion

We have presented results of the first self-consistent field calculations of the electronic structure of the α -phase Hume-Rothery alloys of Cu with Zn, Ga, and Ge. Preliminary analysis of the results of these calculations indicates that they will be able to account for many of the experimental measurements of the electronic structure that have been made in the past.

Our calculations of the ground state properties of $\text{Cu}_x\text{Zn}_{1-x}$, based on an extension of local DFT to random alloys, are able to reproduce the measured concentration variation of the equilibrium lattice spacing in the α -phase alloys.

Although our calculations are still far from being able to produce an *ab initio* phase diagram of the Hume-Rothery phases, we believe that they form a proper basis on which to build such a theory. On the one hand they give specific predictions about the electronic structure of the alloys that can be checked against the results of experimental probes. On the other hand they provide a sound basis for discussions of the energetics of alloy phase formation along standard thermodynamic lines.

We are currently engaged in further analysis of the electronic structure results in terms of experimental observations and on the inclusion of $l = 3$ (and higher, if needed) angular momentum components into our total energy calculations in order to produce definitive predictions about heats of mixing, etc. The results of these efforts will be published elsewhere.

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