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Electronic Band Structure and Optical Properties
Of The Cubic Sc, Y And La Hydride Systems

by

Douglas Jay Peterman

Ph.D Thesis submitted to Iowa State University

Ames Laboratory, DOE

Iowa State University

Ames, Iowa 50011

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by

Douglas Jay Peterman

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Electronic band structure and optical properties
of the cubic Sc, Y and La hydride systems^{*}

Douglas Jay Peterman

Under the supervision of David W. Lynch
From the Department of Physics
Iowa State University

Electronic band structure calculations are used to interpret the optical spectra of the cubic Sc, Y and La hydride systems. Self-consistent band calculations of ScH_2 and YH_2 are carried out using the Korringa-Kohn-Rostoker method. The respective joint densities of states are computed and compared to the dielectric functions determined from the optical measurements of Weaver, Rosei and Peterson. Additional calculations are performed in which the Fermi level or band gap energies are rigidly shifted by a small energy increment. These calculations are then used to simulate the derivative structure in thermomodulation spectra and relate the origin of experimental interband features to the calculated energy bands. While good systematic agreement is obtained for several spectral features, the origin of low-energy interband transitions in YH_2 cannot be explained by these calculated bands. A lattice-size-dependent premature occupation of octahedral sites by hydrogen atoms in the fcc metal lattice is suggested to account for this discrepancy. Various non-self-consistent calculations are used to examine the effect of such a premature occupation. Measurements of the optical absorptivity of LaH_x

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with $1.6 < x < 2.9$ are presented which, as expected, indicate a "more premature" occupation of the octahedral sites in the larger LaH_2 lattice. These experimental results also suggest that, in contrast to recent calculations, LaH_3 is a small-band-gap semiconductor.

I. INTRODUCTION

A. Preliminary Remarks

When hydrogen, the simplest of elements, is combined with a metal to form a solid, an alloy of increasing technological and scientific importance is obtained - a metal hydride. The technological importance of these materials is seen in their use for hydrogen storage, as components of nuclear reactors and in a host of other applications (1). The role of hydrogen in the superconductivity of PdH and in the hydrogen embrittlement of metals is the subject of much research. In taking a scientific approach to the study of materials, an attempt is made to understand basic physical properties and develop a theory with which these properties can be correlated. While this approach does not directly address practical problems, their systematic resolution is facilitated by a better understanding of these fundamental properties.

B. History

Interest in metal hydrides has grown considerably since 1866 when Graham discovered that palladium could absorb large amounts of hydrogen (2). This interest has been sparked by a technological demand for understanding as well as by the scientific curiosity aroused by some surprising characteristics of metal hydrides. As materials technology developed, an increased demand to understand the process of hydrogen embrittlement followed. In some steels, one part per million (ppm) of hydrogen can cause embrittlement whereas in titanium, several hundred ppm can be absorbed without serious effects (3). With the growth of

nuclear technology the need arose for materials that would possess the characteristics of high strength, stability and machinability while being able to interact strongly with neutrons. Metal hydrides are now used extensively in reactor components. As discussions of a possible hydrogen economy continue, methods of hydrogen storage become more and more important. Several metal hydrides contain hydrogen in a volume less than half that required by hydrogen in the liquid form. In recent years, however, the big impetus to the more basic metal hydride research was due to the discovery of hydrogen-concentration-dependent superconductivity in palladium hydrides.

Prior to 1972 and the discovery of superconductivity in PdH by Skoskiewicz (4), relatively little theoretical work concerning the electronic structure of metal hydrides had been done. Switendick pioneered the work in applying first-principles energy band calculations to the understanding of hydrogen in metals, publishing his first results in 1970 (5). In the course of his studies he considered the effect of hydrogen when alloyed with Y, Er, Pr, Ti, V, Cr, Sc, Nb, Mo, Pd, and Ta (5,6,7,8). Unfortunately there were little or no experimental data available to lend support to this wealth of theoretical information and the older "protonic" and "anionic" models continued to be discussed. These models attempted to explain experimental results by assuming that the electronic states contributed by the hydrogen atom were either above or below the Fermi energy. Since each hydrogen contributes two states but only one electron, the hydrogen, following this model, would either lose its electron to the metal states (protonic model) or gain an electron from the metal states (anionic model) (9).

After the discovery of superconductivity (4) and an inverse isotope effect (10) in the Pd-H(D) system, experimental and theoretical work increased quite rapidly. Perhaps the difference between hydrogen and deuterium which is ignored in the standard band structure formalism was important. While hydrogen is the simplest of elements, its interactions in a metal lattice are complicated by its small mass. The first and easiest comparisons between experiment and one-electron band theory dealt largely with Fermi-surface-sensitive probes, testing only the calculated states at the Fermi surface. Some of these results have been discussed by Switendick (11) and Cotts (12). A large amount of work was carried out on the Pd-H system using a variety of theoretical (13, 14, 15, 16) and experimental (17, 18, 19) techniques. Papaconstantopoulos and colleagues obtained agreement with experiment when they showed that their calculated density of states versus H/Pd ratio varied in accordance with T_c as expected using the McMillan formalism (15). Agreement was also obtained with the earlier photoemission results of Eastman et al. (17). The optical experiments begun by Weaver and co-workers allowed a more detailed comparison with theory. In their early work with the Sc-H (20) and the Nb-H and Ta-H (21) systems only limited theoretical information was available from previous calculations. Their study of the Y-H system, a system studied in detail by Switendick (6), was the first optical test of the energy bands of a metal hydride. Their initial results (22) could not be explained using Switendick's calculations, prompting this study in which band structure calculations and experimental measurements are used to understand the electronic structure of the cubic Sc-H, Y-H and La-H systems.

C. Electronic Structure Calculations

In the process of calculating the electronic structure of a solid, many approximations must be made in order to make the problem tractable by present standards of computational speed and storage memory size. One desires information that can be compared with certain experimentally derived properties so that a test of the theoretical formulation and the accompanying approximations can be made. In this work, the calculated quantities of interest include the energy bands, the density of states (DOS) and the joint density of states (JDOS). The connection of these computed results with measured properties is discussed in later sections.

There are several simplifications to the Hamiltonian that are common in the band theory of solids (23). If one considers all interactions between atoms in a solid one obtains three important contributions to the Hamiltonian: one due to the electrons, another due to the nuclei and the third due to the nucleus-electron interactions.

$$H = H_{\text{nuclei}} + H_{\text{electron}} + H_{\text{electron-nuclei}}$$

where

$$H_{\text{nuclei}} = \sum_I \frac{p_I^2}{2M_I} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|},$$

$$H_{\text{electron}} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

and

$$H_{\text{electron-nuclei}} = - \sum_{I,i} \frac{z_I e^2}{|\vec{R}_I - \vec{r}_i|} .$$

Upper case letters are used to represent nuclear variables while lower case letters are for electron variables. This formulation already ignores relativistic effects (which could be included) and other possible interactions. The Born-Oppenheimer approximation allows one to separate the problem and consider only the electron part of the Hamiltonian defined by

$$H = H_{\text{electron}} + H_{\text{electron-nuclei}} \quad (1.1)$$

This may be a significant approximation with hydrides because it involves an expansion in terms of the ratio of nuclear vibrational displacement to internuclear distance. This expansion parameter can be shown to vary as the fourth root of the electron to nucleus mass ratio (24). In the case of hydrogen this ratio is 0.153, for deuterium 0.129 and for scandium 0.059. Miller and Satterthwaite suggested that the inverse isotope effect in PdH(D) was due to a difference in the electronic structure arising from the difference in zero-point motion between H and D (25). However, the electronic energy is of zero order and the vibrational energy of second order in this parameter.

The Hamiltonian in Eq. (1.1) represents a complicated many-body problem which is simplified through the use of the Hartree-Fock approximation (26,27). Using this formulation, a one electron picture emerges in which the electron responds to a potential which depends on its own wavefunction. This is still quite complicated however because the

exchange part of the potential in the Hartree-Fock Hamiltonian is a nonlocal, integral operator. Many methods to reduce this mathematical difficulty have been discussed which involve a local density approximation (28,29,30). Using Slater's approach, the new potential in the one-electron approximation becomes

$$V(\vec{r}) = - \sum_I \frac{Z_I e^2}{|\vec{r} - \vec{R}_I|} + e^2 \int \frac{\rho(\vec{r}_1)}{|\vec{r} - \vec{r}_1|} d\vec{r}_1 - 3e^2 \alpha \left[\frac{3}{8\pi} \rho(\vec{r}) \right]^{1/3} . \quad (1.2)$$

The first two terms constitute the Coulomb contribution. The adjustable parameter, α , varies between 2/3 and 1 for different elements to account for exchange and correlation (28). The Schrödinger equation to be solved is given by

$$\left[- \frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \right] \psi_n(\vec{k}, \vec{r}) = E_n(\vec{k}) \psi_n(\vec{k}, \vec{r}) . \quad (1.3)$$

Since $V(\vec{r})$ depends on $\rho(\vec{r})$ where

$$\rho(\vec{r}) = \sum_{\text{occupied}} |\psi_n(\vec{k}, \vec{r})|^2 ,$$

a self-consistent approach to solving the Schrödinger equation entails using an initial charge density to calculate a trial wavefunction, then using this wavefunction to generate a new charge density at which point the procedure may be repeated until appropriate convergence criteria are met. Equation (1.3) represents the basic band approximation equation and various methods of obtaining solutions to it have been employed. Switendick (6) used the non-self-consistent augmented plane wave (APW)

method (31) in his calculations of the YH_2 energy bands. Using this method, one expands the crystal states in terms of a complete set of functions which are solutions of the Schrödinger equation within a unit cell. The coefficients of the expansion are then determined by satisfying appropriate boundary conditions. A similar method of calculation is that given by Korringa (32) and by Kohn and Rostoker (33). Both this method (the KKR method) and the APW method use the so-called muffin-tin approximation to the actual crystal potential $V(\vec{r})$. The potential is assumed to be spherically symmetric inside spheres centered at the atomic sites and constant outside these spheres. This approximation has been shown to give meaningful results for quite a variety of materials and can be expanded, as is discussed in a later section, to overcome some of its shortcomings.

The KKR method for band structure calculation is an accurate and relatively fast method for computing energy eigenvalues. The choice of a particular method is often dependent on the availability of existing computer codes which are quite complex. In this case, these programs were developed under Dr. S. H. Liu at Iowa State University with contributions to various phases from many co-workers. The final formulas including many references and credits were given by Myron (34) and the method of calculating the muffin-tin potential was elucidated by Marchiando (35). Therefore, only a few general highlights of this method will be discussed here.

The KKR method is based on a Green's function approach to solving the Schrödinger equation. One starts with an integral equation for the

wavefunction in a potential $V(\vec{r})$. By incorporating the muffin-tin approximation and the conditions imposed by periodicity one obtains, following Ziman (36),

$$\psi_{\vec{K}}(\vec{r}) = \frac{-1}{4\pi} \int G(k, \vec{K}; \vec{r} - \vec{r}_1) v(\vec{r}_1) \psi_{\vec{K}}(\vec{r}_1) d\vec{r}_1, \quad (1.4)$$

$$G(k, \vec{K}; \vec{r} - \vec{r}_1) \equiv \sum_{\vec{\ell}} \frac{\exp(ik|\vec{r} - \vec{r}_1 + \vec{\ell}|)}{|\vec{r} - \vec{r}_1 + \vec{\ell}|} e^{i\vec{K} \cdot \vec{\ell}}$$

and

$$k^2 = E.$$

These equations are for a wavefunction, $\psi(\vec{r})$, which is self-consistently scattered into itself, the scattered waves from all unit cells combining with appropriate phase factors to give ψ again. The function $G(k, \vec{K}; \vec{r} - \vec{r}_1)$ is the structural Green's function which describes the effect at $\vec{r}$ due to waves scattered from $\vec{r}_1$. Equation (1.4) can be solved using a variational procedure. A trial wavefunction of the form

$$\psi_{\vec{K}}(\vec{r}) = \sum_{\ell, m} C_{\ell m} R_{\ell}(\vec{r}) Y_{\ell m}(\theta, \phi)$$

leads to a quadratic function in the $C_{\ell m}$'s,

$$\Lambda = \sum_{\ell m, \ell' m'} \Lambda_{\ell m, \ell' m'} C_{\ell m} C_{\ell' m'}^*,$$

on which the variational condition imposes a set of linear equations whose determinant, $|\Lambda_{\ell m, \ell' m'}|$, must vanish. The roots of the determinant give the energy dispersion relationships, $E(\vec{K})$, while the wavefunctions

are determined by the respective eigenvectors of the $\Lambda_{\ell m, \ell' m'}$ matrix.

With the energy dispersion relationships or energy bands determined, the remaining quantities of interest, the DOS and JDOS, may be found.

The DOS is defined by

$$N(E) = \frac{2}{(2\pi)^3} \sum_n \int \delta[E_n(\vec{k}) - E] d\vec{k} \quad (1.5)$$

where n is the band index. This integral can be transformed to an integral over a surface of constant energy so that

$$N(E) = \frac{2}{(2\pi)^3} \sum_n \int_{E(\vec{k})=E} \frac{dS}{|\nabla_{\vec{k}} E|}$$

and the integral replaced by a sum over small tetrahedra

$$N(E) \approx \frac{2}{(2\pi)^3} \sum_{n,i} \frac{S_n(E, \vec{k}_i)}{|\nabla_{\vec{k}} E_n(\vec{k})|_{\vec{k}_i}}$$

where $S_n(E, \vec{k}_i)$ is the area of an appropriately chosen constant energy plane of energy E inside the i -th tetrahedron containing the point $\vec{k}_i$.

A procedure for carrying out this calculation known as the linear energy tetrahedron method (37,38) is used here and was discussed by Oh (39). Its accuracy depends upon the accuracy in the parametrization of the energy bands obtained from the KKR calculation as well as on the size chosen for the little tetrahedra.

The JDOS can be calculated using the same method of approach. The JDOS is defined by

$$J(E) = \frac{2}{(2\pi)^3} \sum_{m < n} \int \delta(E_n(\vec{k}) - E_m(\vec{k}) - E) f_{m\vec{k}} (1 - f_{n\vec{k}}) d\vec{k} \quad (1.6)$$

which, again, can be put in terms of a sum over small tetrahedra,

$$J(E) = \frac{2}{(2\pi)^3} \sum_{\substack{m < n \\ i}} \frac{S_{m,n}(E, \vec{k}_i)}{|\nabla_k (E_n(\vec{k}) - E_m(\vec{k}))|_{\vec{k}_i}} \quad (1.7)$$

$S_{m,n}(E, \vec{k}_i)$ is the area of the constant energy plane determined by the energy difference between the occupied state of energy $E_m(\vec{k}_i)$ and the unoccupied state of energy $E_n(\vec{k}_i)$, within the i -th tetrahedra. The calculated JDOS may be compared with the results of optical experiments.

D. Optical Properties

In a quantum-mechanical treatment of the interaction of light with matter, the joint density of states as defined by Eq. (1.6) can be related, after an approximation is made, to the complex dielectric function, $\tilde{\epsilon}(\omega)$. This in turn is related to measured optical quantities. Two such quantities are the reflectance, R , and the thermally modulated reflectance $\Delta R/R$.

An electron belonging to the occupied valence band of a solid may be excited into a state of higher energy in the empty conduction bands. A quantum-mechanical description of this excitation involves a perturbation brought about by the interaction of the electron with the radiation field. If the vector potential is given by

$$\vec{A} = \frac{1}{2} \hat{a}(\vec{A}_0 \exp[i(\vec{k} \cdot \vec{r} - \omega t)] + \vec{A}_0^* \exp[-i(\vec{k} \cdot \vec{r} - \omega t)]) \quad , (1.8)$$

to first order the perturbation is

$$H_p = \frac{e}{2m} \sum_j (\vec{A}(\vec{r}_j) \cdot \vec{p}_j + \vec{p}_j \cdot \vec{A}(\vec{r}_j)) ,$$

where j denotes the j -th electron. Then, using Fermi's golden rule (24), the transition probability between the valence and conduction band is given by

$$P_{\vec{C}\vec{K}', \vec{V}\vec{K}} = \frac{\pi}{2\hbar} \frac{e^2}{m^2} \tilde{A}_0 \tilde{A}_0^* |\langle \vec{C}\vec{K}' | e^{i\vec{k} \cdot \vec{r}} \hat{a} \cdot \vec{p} | \vec{V}\vec{K} \rangle|^2 \delta[E_C(\vec{K}') - E_V(\vec{K}) - \hbar\omega] \quad (1.9)$$

where $|\vec{C}\vec{K}'\rangle$ and $|\vec{V}\vec{K}\rangle$ represent, respectively, the conduction and valence band Bloch states and $\hat{a}$ is a unit vector parallel to $\vec{A}$. This transition probability may be related to ϵ_2 , the imaginary part of the complex dielectric function, through the ratio of the energy absorption rate (W) to the magnitude of the Poynting vector ($|\vec{S}|$):

$$\epsilon_2(\omega) = \frac{nc}{\omega} \frac{W}{|\vec{S}|} ,$$

where

$$W(\omega) \equiv \hbar\omega \sum_{V,C} \int_{\vec{K}, \vec{K}'} P_{\vec{C}\vec{K}', \vec{V}\vec{K}}(\omega)$$

and from Eq. (1.8) for $\vec{A}$,

$$|\vec{S}| = \frac{1}{2} nc \epsilon_0 \omega^2 \tilde{A}_0 \tilde{A}_0^* .$$

As a consequence of the periodicity of the lattice and the sum over $\vec{K}$ and $\vec{K}'$ in Eq. (1.9), a selection rule, $\vec{k} + \vec{K} - \vec{K}' = 0$ is obtained (40).

Since $\vec{k}$, the radiation wavevector, is small compared to reciprocal lattice dimensions, $\vec{K} = \vec{K}'$. Then

$$\epsilon_2(\omega) = \frac{2\pi}{\epsilon_0} \frac{e^2}{m^2} |\langle C | \hat{a} \cdot \vec{p} | V \rangle|^2 \frac{1}{\omega^2} \int_K \delta[E_C(\vec{K}) - E_V(\vec{K}) - \hbar\omega]$$

where an average dipole matrix element over the Brillouin zone is assumed. Of course, the matrix element is a function of $\vec{K}$ and even vanishes at certain places of high symmetry in the Brillouin zone. Nevertheless, it is assumed to be slowly varying compared to structure in the remaining integral and comparison with Eq. (1.6) shows that

$$\epsilon_2(\hbar\omega) = CM^2 J(\hbar\omega)/\omega^2 \quad (1.10)$$

where M denotes the matrix element average and J is the familiar joint density of states.

The connection between the measured reflectance, R, and the complex dielectric function $\tilde{\epsilon}$ is made through the use of Kramers-Kronig relations. R, which is usually measured at normal incidence, can be written in terms of the complex reflectivity, $\tilde{r}$, as

$$R = \tilde{r} \tilde{r}^* \quad (1.11)$$

and

$$\tilde{r} = re^{i\theta} \quad (1.12)$$

where θ represents the phase change due to reflection. Thus, in the complex plane, two variables are needed to describe fully the interaction

of light with matter. Other more convenient variables than r and θ are n and k , the real and imaginary parts of the complex refractive index, and ϵ_1 and ϵ_2 . These are related by the following definitions

$$\tilde{r} = \frac{\tilde{N} - 1}{\tilde{N} + 1}$$

$$\tilde{N} = n + ik$$

and

$$\tilde{\epsilon} = \epsilon_1 + i\epsilon_2 = \tilde{N}^2.$$

As expected from Eq. (1.10), the quantity of most interest here is ϵ_2 , the imaginary part of the dielectric function. From Eqs. (1.11) and (1.12) it is clear that in order to find ϵ_1 and ϵ_2 both r and θ must be known, but only r is measured directly. However, the response of a medium to an electric field imposes conditions arising from causality known as Kramers-Kronig relations which connect r and θ (and similarly n and k , and ϵ_1 and ϵ_2) (41). One form of the relation between r and θ is given by

$$\theta(\omega) = \frac{2\omega}{\pi} P \int_0^\infty \frac{\ln[r(\omega')]}{\omega'^2 - \omega^2} d\omega' \quad (1.13)$$

Thus by measuring R ($R = r^2$), r and θ may be found and related to ϵ_1 and ϵ_2 . Equation (1.13) reveals, however, that r must be known over an infinite frequency range. Careful extrapolation techniques must then be used to obtain valid results when performing this integration. In the low energy regime, where data are difficult to obtain, the physics

of low-energy excitations must be examined in order to make the appropriate extrapolations.

For low-energy excitations Eq. (1.10), in which $\epsilon_2(\omega)$ is derived from interband or band-to-band transitions, is not a sufficient description of the photoexcitations. At low energies, intraband transitions are the dominant physical processes determining ϵ_2 in metals and one is led to expand Eq. (1.10) to account for them. These processes are due to electrons scattering through a variety of mechanisms. In the Drude theory for metals various impurities, crystal imperfections and phonons may lead to random collisions or scattering events. In the presence of a temporally periodic electric field, random collisions can be shown (42) to give the following contributions to the dielectric function, which must be added to the interband terms:

$$\begin{aligned}\epsilon_{1\text{Free}} &= 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} \\ \epsilon_{2\text{Free}} &= \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)}\end{aligned}\tag{1.14}$$

and

$$\omega_p^2 = \frac{4\pi N e^2}{M}.$$

In this model τ is the mean free time between collisions, N is the free electron density and ω_p is known as the plasma frequency. In practice, these parameters are chosen to match the measured optical properties in

the low energy regime and the parameters adjusted in a self-consistent fashion to give the best fit to ϵ_1 and ϵ_2 . Although this treatment is often adequate for metals, in semiconductors the absorption coefficient, α ($\alpha = \omega\epsilon_2/nc$), has been shown to vary as $\lambda^{1.5}$ for scattering by acoustic phonons, as $\lambda^{2.5}$ for scattering by optical phonons and as $\lambda^{3.0-3.5}$ for scattering by ionized impurities (43). While the Y-H and Sc-H systems are good metallic systems, the La-H system displays non-Drude-like behavior at high hydrogen concentrations and the problem of choosing a realistic low energy approximation is more difficult.

At high energies, different approximations must be made to carry out the integral of Eq. (1.13). Since the comparison between theory and experiment is only over a range of less than 5 eV, a limit imposed by experimental considerations here, the use of experimental reflectance to 20 eV and a power law dependence above is quite adequate. Various power law expansions are discussed by Stern (41).

Another experimentally measured quantity which provides a very sensitive test of the energy bands is the normal-incidence thermorefectance, $\Delta R/R$. Using a modulated temperature wave, the change in reflectance, ΔR , due to a change in temperature, ΔT , is synchronously detected using phase sensitive techniques. While the experimental details can be found elsewhere (40,44), of immediate interest is the connection between $\Delta R/R$ and the JDOS.

For a metal, among the various consequences of increasing the temperature (45), the largest optical effects in the energy range of interest are due to a change in the Fermi distribution function, changes

in scattering arising from an increase in phonon population, and changes in transition energies due to shifting or warping of the energy bands induced by thermal expansion. The effects of a change in the Fermi distribution function, $f_{\vec{k}}$, or in the band gap energy, $(E_n - E_m)$, can be understood in terms of changes in the JDOS since these terms explicitly appear in Eq. (1.6). Experimentally, optical spectra are classified as to whether or not they involve the Fermi surface. Lineshape analysis leads to this classification, the analysis being based on phenomenological models for the JDOS employing appropriate modulated parameters (40,44). Characteristic lineshapes for $\Delta\epsilon_1$ and $\Delta\epsilon_2$ based on Δ JDOS can be compared with the experimentally-obtained lineshapes of $\Delta\epsilon_1$ and $\Delta\epsilon_2$ which are found using Kramers-Kronig relations involving the measured quantity $\Delta R/R$. While the structure due to Fermi surface modulation is difficult to model without detailed knowledge of the JDOS, great success has been made with parametrizing critical-point transitions in terms of band gap energy and lifetime broadening.

Critical-point transitions are transitions occurring at a point in reciprocal space where there is a van Hove singularity in the JDOS. These are points where $\nabla_{\vec{k}}[E_n(\vec{k}) - E_m(\vec{k})]$ vanishes in Eq. (1.7). While one might expect that these critical points would be quite evident in experimental spectra such as ϵ_2 , in practice they are not, because the discontinuities are not infinite. However, their derivatives are infinite and this is what makes derivative spectroscopy such a powerful experimental tool. A realistic model for $\Delta\epsilon_2$, however, involves replacing the delta function in Eq. (1.6) by a Lorentzian function to account for

the finite lifetime of an excited state. By expanding the JDOS in a Taylor series about the critical point and keeping terms to second order in energy, the various types of singularities can be defined by the signs of the effective mass terms. A Kramers-Kronig integral relates $\Delta\epsilon_2$ to $\Delta\epsilon_1$ and it can be shown that, for a three dimensional critical point, (46)

$$\frac{d\tilde{\epsilon}(\omega)}{d\omega_g} = i \frac{d\tilde{\epsilon}(\omega)}{d\Gamma} = -i^{r-3} c M^2 (\omega - \omega_g + i\Gamma)^{-1/2} \quad (1.15)$$

where $\hbar\omega_g$ is the band gap energy, Γ is the Lorentzian broadening parameter, M is the matrix element (assumed to be temperature independent) and r is 0, 1, 2, or 3, depending on the particular type of critical point.

The functions $\tilde{\epsilon}$ and $\Delta\tilde{\epsilon}$, found from the measured quantities R and $\Delta R/R$, may be used to compare experiment and theory. From Eq. (1.10), the calculated JDOS should resemble ϵ_2 when scaled by ω^2 . It is to be noted that at low energy the Drude terms, Eqs. (1.14), become important. Furthermore, the constant matrix element approximation ignores dipole selection rules. For experimentally derived $\Delta\tilde{\epsilon}$ spectra, lineshape analysis using Eq. (1.15) allows the identification of the type and energy position of a critical point. Since the type of critical point is directly related to the geometry of the energy bands, such identification provides a strict test of the bands.

E. Group IIIB FCC Metal Hydrides

The face centered cubic (fcc), group IIIB metal hydride systems display a wide range in lattice parameter. The lattice constants reported for the dihydride phases are: $\text{ScH}_2 - 4.783\text{\AA}$, $\text{YH}_2 - 5.204\text{\AA}$ and $\text{LaH}_2 - 5.661\text{\AA}$. Only La allows an fcc metal trihydride phase and its measured lattice constant is $5.604\text{\AA}$. These and other physical properties of metal hydrides are reviewed by Mueller *et al.* (1). The crystal structure of the dihydride is CaF_2 with the hydrogen atoms occupying the tetrahedral sites, one quarter of the distance along the body diagonal as shown in Fig. 1. For LaH_3 the structure is BiF_3 with the octahedral sites (one half of the distance along the body diagonal and between the metal atoms along the cube edge) also being filled. Although experimental information concerning phase stability is lacking or unclear, especially at low temperatures, the reported single-phase regions exist in the composition ranges $1.8 < x < 1.98$ for ScH_x (47), $1.9 < x < 2.2$ for YH_x (48), and $1.8 < x < 3.0$ for LaH_x (1,48). Unlike Sc, which does not accept more than 2 hydrogen atoms, Y forms a trihydride after undergoing a phase transition to a hexagonal close packed lattice. The correlation of these composition effects with the dihydride lattice parameter should be noted.

The stoichiometry of the La-H system has received much more attention than the other two because of its wide composition range and the attendant electronic changes. Fischer *et al.* (49) reported that there was evidence for a small displacement of the octahedral D atoms in neutron diffraction studies of LaD_3 . The La-D system is thought to be quite similar to the Ce-D system because the lattice parameter of CeH_2 ,

- METAL
- OCTAHEDRAL HYDROGEN
- TETRAHEDRAL HYDROGEN

Figure 1. fcc metal lattice with hydrogen located at all interstitial sites (MH_3). The solid hydrogen spheres are at the octahedral sites and are not present in a CaF_2 -structured dihydride which has only tetrahedral site occupation

5.572Å⁰, is close to that of LaH₂. (The difference between the hydride and deuteride is negligible.) In the Ce-D system a similar lattice distortion has been discussed (50), as has a composition-dependent metal-semiconductor phase transition (51). Stalinski reported conductivity measurements which he interpreted as indicating the presence of a metal-semiconductor transition for $2.7 < x < 2.86$ in LaH_x (52). One must, however, question the influence of impurities, especially in the older work. Schreiber and Cotts, in their NMR studies, attributed the presence of prematurely filled octahedral sites to the inaccessibility of tetrahedral sites due to the effect of impurities or crystal imperfections (53).

F. Purpose

The purpose of this work is to understand the electronic structure of the group IIIB metal hydrides, answering the question posed by Weaver (22): Why does the optical spectrum for YH₂ disagree with Switendick's (6) calculated results? In addressing this question, Weaver's optical work is first compared, in the following chapter, to band structure calculations of YH₂ and ScH₂. A cloudy picture still remains and in subsequent chapters three directions are taken in which further calculations of the Y-H system, an improved calculation of ScH₂ and an experimental investigation of the La-H system are presented. This work is interspersed with the collaborating experimental results of Weaver and co-workers as this mystery is unraveled.

II. ENERGY BANDS OF CaF_2 -STRUCTURED ScH_2 AND YH_2

A. Introduction

The first step in comparing theory with experiment for YH_2 was to perform non-self-consistent (NSC) calculations to check the validity of Switendick's results (6). Good agreement was found between the respective calculations but not with the optical experiments of Weaver (22). Figure 2 shows some of the early work of Weaver for YH_2 . The structure near 0.3 eV can only be attributed to interband transitions. In Fig. 3, Switendick's NSC results for YH_2 are reproduced and one can see that the smallest direct interband transition expected is at 1.9 eV along the symmetry direction Q (between L and W), much larger than is experimentally observed. Since NSC calculations did not agree with experiment, self-consistent (SC) calculations were performed. As will be seen later, it became necessary to take advantage of the systematics, both in calculation and experiment, of ScH_2 and YH_2 in order to understand the electronic structure of the trivalent metal dihydride system. Thus, SC calculations were compared to the ongoing experiments of Weaver and co-workers, experiments providing valuable input and direction to this study. In the following, calculational details for both SC and NSC energy bands are discussed and the results of this work are compared in detail to optical experiments.

B. Calculational Details

In computing energy bands some parameters are chosen according to an acceptable error tolerance while others are chosen simply to bring

Figure 2. Optical absorptivity ($A = 1 - R$, where R is the reflectance) of YH_2 at 4.2K (Ref. 22). The two lowest-energy features near 0.3 and 1.2 eV are due to interband transitions well below the interband onset predicted by the energy bands in Fig. 3

Figure 3. Non-self-consistent energy bands for CaF_2 -structured YH_2 calculated by Switendick (Ref. 6). The onset of direct interband transitions is calculated to occur between L and W with an energy of 1.9 eV

agreement with experiments. Other factors, such as the exchange parameter (α in Eq. (1.2)) are chosen to be as physically reasonable as possible in the hope that good experimental agreement will be obtained.

The first parameters chosen dealt with error criteria. The number of nearest neighbor interactions to include was chosen by finding the potential due to a certain number of shells of neighbors and then determining whether or not it would be changed significantly by adding another shell. For YH_2 , four shells of neighbors were found to be sufficient. That is, the charge overlap included Y contributions involving the fourth shell of Y atoms (and, of course, H contributions within this fourth shell distance). From programming considerations this same fourth shell Y-Y distance was used in the ScH_2 calculation and since the ScH_2 lattice is smaller than that of YH_2 , the ScH_2 calculation included five shells of Sc atoms. In the self-consistent work the convergence criteria included an energy eigenvalue variation of less than 1 mRy with the final iteration. Other parameters were chosen with this criterion in mind. For example, in the KKR scheme, the angular momentum expansion for each type of atom was taken through $\ell = 3$ and $\ell = 1$ for the metal and hydrogen atoms, respectively. Increasing ℓ by 1 was found to fit the above criteria of negligible energy eigenvalue variation.

The first calculations which were performed were non-self-consistent with parameters chosen following Switendick (6). Although the methods of calculation differ, the APW method has been shown to yield the same results as the KKR method if the same parameters are employed

(36). The muffin-tin radii were such that the sphere surrounding the metal atom extended 65% of the distance to the hydrogen atom. Full Slater exchange, $\alpha = 1$, was used and the NSC potential obtained in the usual fashion using overlapping atomic charge densities. For this step, Switendick used the s^1d^2 atomic configuration for the metal atoms (6). In the present study both the s^1d^2 and s^2d^1 configurations were used but neither resulting potential provided a mechanism for the observed low-energy interband transitions. In this energy range, both the APW and KKR calculations were in excellent agreement, although some of the high-energy bands disagreed. This disagreement was later attributed to the lack of a complete set of basis functions in the APW calculation (54). Since neither YH_2 NSC energy band calculation agreed with experiment, SC calculations were performed.

For the self-consistent energy band calculations a few parameters were chosen to obtain better theoretical approximations. The use of full Slater exchange typically overestimates the effects of exchange and correlation in SC calculations and, if α is to be kept constant, is reduced to a value between 1 and 2/3. Rather than taking this approach, the Hedin-Lundqvist formalism was adopted in which α (in Eq. (1.2)) is no longer treated as a constant but is a function of the charge density (30). This method has been used quite successfully to calculate the SC electronic structure of the paramagnetic 3d and 4d transition metals (55). All relativistic effects, except for spin-orbit coupling, were included, though these effects are small (56). The convergence criteria were such that the eigenenergies and the total charge within the

muffin-tin spheres changed by less than 0.001 Ry and 0.001 electron, respectively, upon final iteration. The core states of the metal were recalculated during each iteration. The 'special point' scheme of Chadi and Cohen (57) was used to obtain a suitable set of $\vec{k}$ -points in the irreducible 1/48th of the Brillouin zone at which the first-principles energy eigenvalues were computed. The 60 points so chosen allowed accurate calculations of the Brillouin-zone-averaged charge density. The final iteration included 24 additional points of high symmetry. An interpolation scheme, fitting 45 symmetrized plane waves to these 84 points, was then used to obtain band energies at the corners of 2048 tetrahedra which filled the irreducible wedge of the Brillouin zone. The DOS and JDOS were then computed using the lowest five parametrized bands (which had a typical rms fitting error of less than 1 mRy) following the linear energy tetrahedron method discussed in the last chapter (37,38).

C. Computational Results

The self-consistent energy bands for ScH_2 and YH_2 are shown in Figs. 4 and 5. The dotted lines (bands 1 and 2, numbered from lowest energy) show the position, relative to the Fermi level, and shape of the two lowest bands in the $s^1 d^2$ NSC calculation. The major differences accompanying these new calculations are in the band width ($\Gamma'_2 - \Gamma_1$) and in the position of the first two bands. These bands contain hydrogen s-character and significant metal s-, p- and d-character. The wavefunctions at Γ_1 are largely covalent, having both hydrogen s-

Figure 4. Self-consistent energy bands of ScH_2 calculated with Hedin-Lundqvist exchange parameters. The lower two bands are hydrogen-derived and are termed the bonding bands in the text. The dotted lines indicate the positions of the non-self-consistent ($\alpha = 1$) bonding bands. The bands at E_F (except for the pocket around Γ) are d-derived and are referred to as the d-like or metal-like bands

Figure 5. Self-consistent energy bands of YH_2 (see caption to Fig. 4). For YH_2 , the bonding bands are completely below E_F . The inter-band onset along Q has increased to 2.3 eV from the non-self-consistent value from the bands in Fig. 3

and metal s-character. The Γ'_2 wavefunctions are nearly pure hydrogen s-character (80% of the charge for this state is inside the relatively small hydrogen muffin-tin spheres) with a small admixture of metal f-character, and have been described as Bloch sums of antibonding 1s orbitals between the two hydrogen atoms in the unit cell (6). The changes in these bands are due primarily to the use of the Hedin-Lundqvist exchange formalism rather than to the effect of self-consistency. The partially-occupied third band and higher bands are derived from the metal d-states and have appreciable hybridization with the hydrogen states, especially below the Fermi level along Q, W-K and Σ . In Table 1, the band energies at various high-symmetry points are given, highlighting the differences between the various NSC and SC calculations. Of course, it was hoped that a mechanism explaining the low-energy interband transitions would appear in the new calculation of YH_2 . The energy bands in Fig. 5 reveal, however, that the calculated onset of direct interband transitions is 2.3 eV, much higher than the observed onset, and one is led to question the validity of the calculational scheme. With this wealth of theoretical information now available, a more critical examination of the calculational results can be undertaken in which the charge transfer, DOS and JDOS are compared with experimental results.

The amount and direction of charge transfer is useful in understanding the nature of the metal-hydrogen bond. A precise definition of charge transfer is difficult to formulate, especially if one wants to specify a magnitude, because it is somewhat dependent on the choice

Table 1. Energy of selected symmetry points from non-self-consistent (both $d^1 s^2$ and $d^2 s^1$ configurations) and self-consistent (SC) calculations. Energy is given in eV relative to the Fermi level

Symmetry Point	Configuration					
	ScH ₂			YH ₂		
	$3d^1 4s^2$	$3d^2 4s^1$	SC	$4d^1 5s^2$	$4d^2 5s^1$	SC
Γ_{12}	2.33	3.40	2.93	3.23	3.81	4.12
Γ_{25}'	1.04	1.71	1.37	1.29	1.68	1.83
Γ_2'	-0.42	-1.72	0.50	-2.01	-2.43	-0.98
Γ_1	-8.71	-5.46	-8.65	-7.96	-8.18	-7.74
L_3	1.02	1.64	1.32	1.23	1.60	1.71
L_2'	-4.53	-5.48	-4.11	-4.26	-4.49	-3.44
W_1	1.84	2.36	2.12	2.13	2.41	2.37
W_2'	-1.03	-1.23	-1.22	-1.11	-1.00	-1.10
W_3	-4.68	-5.56	-4.22	-4.83	-5.04	-4.04

of muffin-tin radii. The results given in Table 2 define the meaning of charge transfer here. The entry labeled 'atomic charge' represents the number of electrons of an isolated atom contained within a sphere of radius equal to the muffin-tin radius. If these atoms are positioned at the appropriate lattice sites the charge within each muffin-tin sphere increases due to the overlapping charge of neighboring atoms. Table 2 shows that this effect adds to much of the screening of the proton since the charge within the hydrogen spheres is increased by more than 30%. The iterations to self-consistency result in a transfer of 0.14 electrons to the hydrogen sphere, a value quite close to the 0.125 value found for PdH (15).

Experimentally, evidence for charge transfer away from metal sites in CaF_2 -structured dihydrides has been found for ScH_2 (58) and $\text{ZrH}_{1.65}$ (59) using x-ray photoemission techniques and in DyH_2 using Mössbauer spectroscopy (60). These experiments agree with the direction of charge flow calculated here and contradict the simple protonic model for hydrogen in metals. This type of agreement does not lend nearly as much support to the calculated bands as would agreement with optical measurements and further discussion of charge transfer is postponed until Chapter IV.

The calculated densities of states for the first five bands of ScH_2 and YH_2 are shown in Figs. 6 and 7. The most apparent difference between the two figures is that YH_2 displays two prominent peaks associated with the bonding bands while ScH_2 shows only one. This difference is related to the energies of the states at K_1 , K_3 and L_2 .

Table 2. Lattice constants and charge transfers for ScH_2 and YH_2

Charge inside muffin-tin sphere	ScH_2 $a = 4.783 \text{ \AA}$			YH_2 $a = 5.204 \text{ \AA}$		
	Sc	H	interstitial	Y	H	interstitial
Atomic charge	19.019	0.536	-	36.793	0.578	-
Overlapping atoms	19.531	0.707	2.055	37.283	0.756	2.205
Charge after final iteration	19.323	0.844	1.989	37.116	0.896	2.093

Figure 6. The electronic density of states (DOS) for the self-consistent energy bands of ScH_2 . Only the lowest five bands have been included. The peak at -4.1 eV arises from the flat band from L_2' to K_3 in Fig. 4

Figure 7. The electronic density of states (DOS) for the self-consistent energy bands of YH_2 . Only the lowest five bands have been included. For YH_2 there is greater dispersion in the bonding bands along L-W-K (see Fig. 5) which is reflected by the appearance of two peaks near -4.0 eV

relative to W_3 and is detectable, as will be discussed later, using photoemission techniques.

The joint densities of states for the first five bands of ScH_2 and YH_2 are shown in Figs. 8 and 9. The difference in the onsets of the JDOS should be observed experimentally as a difference in the onsets of interband transitions. As mentioned earlier, the calculated onset in YH_2 is at 2.3 eV from band 3 to band 4 along Q. In ScH_2 , however, the calculated onset is at 1.4 eV from band 2 to band 3 along Δ and Λ . Since such interband transitions occur in a small volume of $\vec{k}$ -space and would result in a charge transfer from a state of very high hydrogen s-character to one of very high metal d-character, it is expected to be of small probability, i.e., the electric dipole matrix element and the JDOS both should be small. Rather, an experimentally detectable onset is more likely to occur, as with YH_2 , along Q at 1.7 eV. This onset is seen theoretically as a change in slope in the JDOS of Fig. 8. This trend in onset energy along Q, within a d-like band complex, is consistent with pure metal results which show the d bands in 3d transition metals to be narrower than the d bands of corresponding 4d metals. Recalling Eq. (1.10) and the earlier discussions on reflectance and thermorefectance measurements, the optical results of Weaver et al. (61), can be compared critically to these calculated results.

D. Comparison With Optical Results

The experimental results of Weaver et al. (61) shown in Fig. 10 were difficult to understand in light of the calculated energy bands.

Figure 8. The joint density of states (JDOS) for the first five bands of ScH₂. The weak onset at 1.4 eV indicates direct inter-band transitions from states near Γ . The stronger onset at 1.7 eV reflects the onset from the 3rd and 4th bands along Q

Figure 9. The joint density of states (JDOS) for the first five bands of YH_2 . The predicted onset of interband transitions at 2.3 eV is from band 3 (along Q at E_F) to band 4

Figure 10. Optical absorptivity of ScH_x , YH_x and LuH_x from Ref. 61 showing the x -dependence of the optical features. This dependence is relatively small for ScH_x but for YH_x there appears to be less and less agreement with the calculations as the stoichiometric concentration, $x = 2$, is approached

While the bands indicated that the onset of interband transitions would increase in going from ScH_2 to YH_2 (and by inference) to LuH_2 , features attributable to interband transitions were evident in the optical spectra of $\text{YH}_{1.96}$ and $\text{LuH}_{1.98}$ at much lower photon energy than in $\text{ScH}_{1.98}$. The Y-H and Lu-H systems displayed hydrogen-concentration-dependent low-energy features which strengthened as the dihydride concentration was approached. One would expect that in deviating from stoichiometry, spectral features would perhaps weaken and broaden. Should not the $\text{YH}_{1.98}$ spectrum be most like that expected from the calculations which, of course, were for the perfect CaF_2 -structured dihydride? To answer this question, the JDOS and other computed functions were compared to the results of reflectance and thermorefectance measurements.

The reflectance measurements led to the determination of the dielectric function spectra for $\text{ScH}_{1.61}$, $\text{YH}_{1.73}$ and $\text{LuH}_{1.83}$ shown in Fig. 11 (61). Recall from Fig. 10 that these spectra are obtained from samples that showed no low-energy transitions. In ϵ_2 one observes Drude behavior at low energies with interband onsets at approximately 1.2, 1.6 and 1.9 eV for $\text{ScH}_{1.61}$, $\text{YH}_{1.73}$ and $\text{LuH}_{1.83}$, respectively. This trend agrees with the calculated trend, the onset along Q occurring at 1.7 and 2.3 eV for ScH_2 and YH_2 , respectively. Again, this trend can be understood as arising from the widening of the d bands in going from 3d to 4d transition metals. Although this agreement in systematics is encouraging, there is little else that can be identified. The ϵ_2 spectra, when scaled by ω^2 , should be proportional to the JDOS.

(see Eq. (1.10)) if the dipole matrix element average is a good approximation. As can be seen by comparing Figs. 8 and 9 with Fig. 11, however, there is little agreement. Comparing experimental with theoretical onsets shows that the calculated d-band complex along Q, W-K and Σ is too wide by 0.4 and 0.6 eV in ScH_2 and YH_2 , respectively. To proceed further an examination of thermorefectance results, whose interpretation is less sensitive to matrix element effects, is made.

Thermorefectance measurements performed on the same low hydrogen samples were analyzed to yield the $\Delta\tilde{\epsilon}$ spectra shown in Fig. 12 (61). These spectra reveal a few more identifiable features that may be compared more critically with the energy bands. Specifically, the structures in $\Delta\epsilon_1$ and $\Delta\epsilon_2$ centered about 2.95, 3.10 and 3.15 eV in $\text{ScH}_{1.61}$, $\text{YH}_{1.73}$ and $\text{LuH}_{1.87}$, respectively, show a systematic increase in energy consistent with the widening of the d-like complex calculated for the energy bands along Q, W-K and Σ . As discussed earlier, the main contributions to $\Delta\tilde{\epsilon}$ spectra arise from critical-point transitions and from transitions originating at, or terminating on, the Fermi surface (40,44). In order to investigate these transitions in more detail, various joint density of states calculations were employed.

To examine the effect that modulation might have on critical-point transitions, the functions defined by

$$\Delta_G \text{JDOS}(\omega) \equiv \frac{1}{2} [\text{JDOS}^+(\omega) + \text{JDOS}^-(\omega)] - \text{JDOS}(\omega) \quad (2.1)$$

were computed, where $\text{JDOS}^\pm(\omega)$ denotes the joint density of states

Figure 11. The dielectric functions for $\text{ScH}_{1.61}$, $\text{YH}_{1.73}$ and $\text{LuH}_{1.83}$ as derived by Weaver et al. from the results of Fig. 10 (Ref. 61). Below 1.5 eV the Drude, or free electron, absorption dominates while at higher energy, interband effects determine the spectra. The high energy portion of the ϵ_2 spectra may be compared to the JDOS calculations. The dashed lines for $\text{ScH}_{1.61}$ sketch the interband onset

Figure 12. Thermomodulation spectra for $\text{ScH}_{1.61}$, $\text{YH}_{1.73}$ and $\text{LuH}_{1.83}$ from Ref. 61. The portion of the spectra dominated by interband effects may be compared to the ΔJDOS calculations

calculated after rigidly shifting one particular band either up (+) or down (-) by a small energy increment. These functions, which simulate the effects of a band gap shift, are valuable in identifying regions in $\vec{k}$ -space, usually at critical points, where the JDOS is sensitive to changes in the nature of the bands. From Eq. (1.10) it follows that

$$\Delta\epsilon_2(\omega) = C M^2 \Delta J(\omega)/\omega^2$$

if the matrix elements are temperature independent. Since critical points in the bands occur most frequently at positions of high symmetry, some of the structures computed using Eq. (2.1) will not be seen in $\Delta\epsilon_2$ due to dipole selection rules. Nevertheless, $\Delta_G \text{JDOS}$ reveals the sensitive areas in the bands where the effects of band shifting or lifetime broadening with temperature are likely to appear experimentally in $\Delta\epsilon_2$.

The theoretical functions $\Delta_G \text{JDOS}$, scaled by ω^2 to compare with $\Delta\epsilon_2$, and for which the 4th band was rigidly shifted up and down by 5 mRy are shown in Figs. 13 and 14 for ScH_2 and YH_2 . As expected, much more structure is seen in these figures than is seen in the $\Delta\epsilon_2$ spectra. The large feature in $\Delta_G \text{JDOS}$ for ScH_2 at 1.7 eV and the analogous smaller structure at 2.3 eV in $\Delta_G \text{JDOS}$ for YH_2 are due to the onsets along Q involving the Fermi surface and will be discussed later. The most notable feature is seen at 3.5 eV in Fig. 14 for YH_2 ; its smaller analog in ScH_2 is apparent at 3.3 eV. By examining the energy bands, the $\vec{k}$ -space origin of this structure can be identified as involving bands 3 and 4 at the symmetry point W - a critical point. By using

Figure 13. Calculated change in the JDOS of ScH_2 due to a rigid shift by 5 mRy of the 4th energy band. The calculated spectrum simulates changes in the JDOS due to modulation of the band gap energy and is compared to the thermoreflectance results in Fig. 12. The first derivative-like structure reflects modulation of transitions along Q at E_F while the feature near 3.3 eV corresponds to the M_2 -type critical point transition, $W_2' \rightarrow W_1$ (see Fig. 4)

Figure 14. Calculated change in the JDOS of YH_2 due to a rigid shift by 5 mRy of the 4th band. See caption to Fig. 13

the plane-wave fits of the energy bands, this W'_2-W_1 critical point is identified as being of type M_2 . That is, due to the geometry of the bands, r in Eq. (1.15) is equal to 2 for this transition.

Knowing the type of critical point involved, the experimental spectra may be searched for the expected lineshape using Eq. (1.15). Figure 15 shows the predicted lineshape for changes in the dielectric function due to broadening ($d\tilde{\epsilon}/d\Gamma$) and to band gap modulation ($d\tilde{\epsilon}/d\omega_g$) for an M_2 -type critical-point transition. The sum of these two effects, $\Delta\tilde{\epsilon}(\omega_g, \Gamma)$, yields a lineshape consistent with that seen experimentally in Fig. 12. That is, the calculated features at 3.3 and 3.5 eV are identified experimentally at 2.95 and 3.10 eV for ScH_2 and YH_2 , respectively. As with the interband onsets, these transitions show that the d-like complex is too wide by 0.4 eV. With these experimental lineshapes identified, the remaining significant optical features are below 2.5 eV and, if they are to agree with the calculated bands, they must be due to Fermi surface transitions.

To examine the effect that modulation might have on transitions involving the Fermi surface the functions defined by

$$\Delta_F \text{JDOS}(\omega) \equiv \frac{1}{2} [\text{JDOS}(\omega, E_F + \delta) + \text{JDOS}(\omega, E_F - \delta)] - \text{JDOS}(\omega, E_F) \quad (2.2)$$

were computed, where δ denotes a small energy shift of the Fermi energy, in this case 10 mRy. When scaled by ω^2 this function should approximate the lineshape expected in $\Delta\epsilon_2$ due to the temperature dependence of the Fermi function. This result is due to the nature of the Fermi function as is demonstrated in Fig. 16.

Figure 15. Predicted lineshape for the changes in the dielectric function due to broadening ($d\tilde{\epsilon}/d\Gamma$) and to gap modulation ($d\tilde{\epsilon}/d\omega_g$) of an M_2 -type critical point transition. This lineshape is seen in Fig. 12 at 2.95 eV for ScH_2 and 3.10 eV for YH_2 (see Refs. 40, 46)

Figure 16. Change in the Fermi function, Δf , due to an increase in temperature compared to the effective change, Δf_e , implied through the use of the term $1/2[\text{JDOS}(\omega, E_F + \delta) + \text{JDOS}(\omega, E_F - \delta)]$ in Eq. (2.2). The sharp corners in the approximation are smoothed in the calculation

The calculated function $\Delta_F \text{JDOS}$ for ScH_2 is shown in Fig. 17 scaled by ω^2 . Again, a large amount of structure evident in this curve may not appear experimentally due to matrix element effects. Three features have been numbered in the figure. The first can be identified with states near Γ which, as mentioned earlier, are thought to involve small transition matrix elements. The second feature is from states between bands 3 and 4 along Q - the same states giving rise to the 1.7 eV structure in Fig. 13. One may well expect to see such a signal experimentally. The third feature arises from transitions along Σ and Δ and is appreciably smaller than the second one.

Examining the experimental spectra of $\Delta\epsilon_2$ in Fig. 12 for similar lineshapes indicates possible agreement near 1.3 eV. Unfortunately, at low energy the effect of the free electron or Drude terms becomes dominant and masks the interband contributions. Furthermore, in this energy range the spectra of $\text{ScH}_{1.61}$ and $\text{YH}_{1.73}$ show complicated lineshapes in $\Delta\epsilon$, presumably due to transitions in different parts of the Brillouin zone, but at nearly the same energy, prohibiting any definite identification of their origins. The experimental lineshapes for $\Delta\epsilon_1$ and $\Delta\epsilon_2$ near 1.3 and 1.7 eV in $\text{ScH}_{1.61}$ and $\text{YH}_{1.73}$ are consistent with those expected for transitions at the Fermi surface (44) and agree reasonably with the interband onsets seen in ϵ_2 . Therefore, a tentative assignment of these interband features to energy bands 3 and 4 along Q is made.

Comparisons of the JDOS calculations with the reflectance and thermorefectance results yield agreement between the interband onsets

Figure 17. Calculated change in the JDOS for Sch_2 arising from shifting the Fermi level by 10 mRy. As discussed in relation to Fig. 16, this spectrum simulates the effect of thermo-modulation on interband transitions to or from the Fermi surface. Structures labeled 1-3 can be related to transitions near Γ , along Q and along Δ and Σ , respectively

and between the critical-point transitions at W. While, not surprisingly, features in ϵ_2 could not be identified with anything in the calculated JDOS, the main features in $\Delta\epsilon_2$ were well accounted for using the calculational results. However, this agreement is with the substoichiometric samples $\text{ScH}_{1.61}$ and $\text{YH}_{1.73}$. Though the experimental spectrum of $\text{ScH}_{1.98}$ is not significantly different, that of $\text{YH}_{1.98}$ is, and the puzzle of the low-energy interband transitions remains for further study.

E. Discussion

The low-energy interband transitions in YH_2 cannot be explained using the self-consistent energy bands. While the comparisons with optical spectra (61) presented in the preceding section showed disturbing discrepancies in the energy locations of identifiable spectral features, the systematics shored up any doubt about their identification. One naturally questions the interpretation of experimental spectra derived from two-phase samples, both $\text{ScH}_{1.61}$ and $\text{YH}_{1.73}$ being outside the reported single-phase regions. However, the optical spectrum of $\text{ScH}_{1.98}$ differs only slightly from that of $\text{ScH}_{1.61}$. Furthermore, adjusting the energy bands of YH_2 to account for the low-energy transitions would require a severe, non-physical modification of the bands and would destroy the agreement we do have. In addition, any scheme of doing so would have the same effect on the ScH_2 bands, yet no corresponding low-energy transitions are observed experimentally. A sample-related phenomenon is thus postulated in which a gradual filling of the

octahedral sites occurs in YH_2 before all tetrahedral sites are filled (see Fig. 1).

There is considerable indirect evidence that octahedral sites may indeed be occupied. As discussed in the introduction, scandium does not accommodate more than two hydrogen atoms, while lanthanum, with its larger metal lattice, forms a trihydride, the hydrogen atoms occupying octahedral sites. YH_2 has an intermediate-sized lattice which reportedly can take up to 2.2 hydrogen atoms while keeping the fcc metal phase (48). Although Weaver did not obtain any specimens with greater than 2.0 hydrogen atoms per yttrium atom, the low-energy features of a $\text{YH}_{1.89}$ sample were shown to depend on the method of cooling after hydrogen charging at high temperatures (61). That is, when the sample was reheated then quenched in ice water the low-energy features grew, suggesting an increase in either octahedral site occupation or some other type of disorder.

Support for the idea of premature occupation of octahedral sites can be found in several of the lanthanide (Ln) hydrides. Recent studies of DyH_2 using Mössbauer spectroscopy gave results indicating such premature occupation (60). Inelastic neutron scattering on $\text{CeH}_{1.98}$ showed a small isolated peak attributed to hydrogen occupying a few percent of the octahedral sites (62). However, similar measurements on $\text{CeD}_{2.0}$ reported the perfect CaF_2 structure (50) so that questions of isotope effects and sample preparation arise. In early NMR studies of LaH_x , Schreiber and Cotts suggested that the concentration-dependent line narrowing for $x > 1.92$ was due to the filling of octahedral sites (53).

They surmised that this effect was due to tetrahedral sites being unavailable for occupancy, again raising questions of sample preparation. Clearly more work, both theoretical and experimental, is needed in order to confirm the hypothesized occupation and understand its effect on the electronic structure.

There are three important questions that can be considered here for further investigation of the group IIIB metal dihydride band structure. First, what is the mechanism for these low-energy transitions and can they be understood within a band theoretical model? Second, if ScH_2 has no such octahedral site occupation affecting the optical spectra what is the reason for the energy discrepancies in the calculation? Finally, if this is indeed octahedral site occupation which is affected by lattice size, shouldn't similar low-energy features be observable in the La-H system? These three questions are addressed, in turn, in the following three chapters.

III. NON-SELF-CONSISTENT CALCULATIONS OF CUBIC YH_2 AND YH_3

A. Introduction

When the self-consistent band structure calculations (63) for CaF_2 -structured YH_2 could not provide a mechanism for the experimentally observed low-energy interband features in $\text{YH}_{1.97}$ (61), it was postulated that the premature occupation of octahedral sites might provide the needed mechanism. The occupation of a few percent of the octahedral sites in YH_2 has since been confirmed through the NMR, neutron scattering and ESR results of, respectively, Anderson et al. (64), Khatamian et al. (65), and Venturini and Richards (66). Since most of the hydrogen sites are tetrahedrally coordinated, theoretical approaches such as the coherent potential approximation used by Faulkner for PdH_x (13) would be the most helpful in trying to understand non-stoichiometric electronic properties. Nevertheless, the band structure programs used here, while being limited to a relatively small number of atoms per unit cell, may provide valuable insight into the effect of octahedral site occupation on the electronic structure and optical properties of YH_2 .

Two non-self-consistent calculations were performed using the KKR method. The first, suggested and actually begun by D. L. Johnson, was for YH_2 with the zincblende, rather than the CaF_2 , fluorite structure (67). With this structure, all octahedral, but only half of the tetrahedral, sites are filled, giving the octahedral hydrogen atom 4 nearest-neighbor hydrogen atoms. It was thought that the

hydrogen-hydrogen distance was the important quantity and that, since the octahedral-tetrahedral distance in YH_2 is close to the tetrahedral-tetrahedral distance in ScH_2 , the energetics of the system might favor this symmetry. For this calculation, the d^1s^2 outer electron configuration was used and the muffin-tin radius for the octahedral sphere was taken to be as large as possible without changing the size of the other two spheres from the values used in the previous calculations. As will be shown in the next section, the needed low-energy mechanism was not found.

The second non-self-consistent calculation performed was for cubic YH_3 in which all tetrahedral and octahedral sites are filled (see Fig. 1). This study was motivated by the negative results of the previous calculation and by the earlier work of Switendick (6) in which he suggested that the octahedral site would not fill unless the neighboring tetrahedral sites were already occupied. His calculation showed that YH_3 was a semiconductor and, as such, had no low-energy mechanism for the observed interband transitions. However, due to program limitations, the potential at the octahedral site was taken to be the same as that at the tetrahedral site. Since the environment of an octahedral hydrogen atom is quite different from that of a tetrahedral hydrogen atom, a new calculation was performed treating the potentials properly. The lattice constant used was, of course, the same as that used for the dihydride.

While cubic YH_3 is not stable at standard pressures, cubic LaH_3 does exist and the band structure of YH_3 should be somewhat similar to that of LaH_3 . Thus, besides providing a possible mechanism for low-energy interband transitions in YH_2 , the YH_3 calculation will help understand LaH_3 . The Hedin-Lundqvist formalism for handling exchange and correlation (30) was used even though this was a NSC calculation. There are two reasons for this. First, from Switendick's work it was evident that a greater bonding bandwidth was desirable to provide the low-energy mechanism and previous experience indicated that the effect of this treatment would be consistent with this goal. Second, in the SC work with ScH_2 and YH_2 the results of the first iteration using the Hedin-Lundqvist parameters were closer to the SC results than were the NSC results when full Slater exchange was used. Other calculational details are essentially the same as for the previous work described in Chapter II. As will be shown in the next section, this calculation did indeed provide a mechanism for the low-energy optical transitions.

B. Results and Conclusions

The non-self-consistent energy bands of zincblende-structured YH_2 are shown in Figure 18. The symmetries are labeled for the appropriate structure following Parmenter (68). As can be seen, the interband onset for this structure is 1.4eV along Q, much greater than is needed.

The non-self-consistent energy bands of BiF_3 -structured YH_3

Figure 18. Non-self-consistent energy bands for zincblende-structured YH_2 . The interband onset is at 1.2 eV and does not provide a mechanism for the observed low-energy interband transitions

are shown in Figure 19. As opposed to Switendick's results, YH_3 here is a metal and the energy of the interband onset near Γ is of the order of a few tenths of an electron volt. Thus, the needed mechanism for low-energy interband transitions is obtained, further suggesting that these transitions are indeed effects of octahedral site occupation.

This trihydride band structure may also be used as a guide to understanding the electronic structure of LaH_3 but one must be cautious for several reasons. The lattice parameter of LaH_3 is significantly smaller than that of LaH_2 , $5.604\text{\AA}$ vs. $5.661\text{\AA}$ (1). Recall that the lattice constant was unchanged in this trihydride calculation. That difference notwithstanding, the various SC and NSC calculations indicated that these hydrogen-induced bands, the lowest three bands in this case, are sensitive to calculational parameters. For example, changes in the muffin-tin radii or the method of approximating exchange and correlation might well yield a semimetal or semiconductor rather than a metal.

With these cautions in mind, several predictions regarding the x -dependent properties of LaH_x may be made. As in YH_2 , when $x \approx 2$, low-energy interband transitions should be evident in the optical spectra. As x rises above 2.0, rapid changes in the low energy portion of the optical spectrum are expected to occur. For the dihydride, the optical transitions (except those due to the octahedral site occupation) occur within the d-like complex along Q, W-K and Σ (see Fig. 5). This complex disappears as x approaches three and we may expect anything from a metal to a semiconductor to result. One of

Figure 19. Non-self-consistent energy bands for BiF₃-structured YH₃. The interband onset near Γ is at a few tenths of an electron volt and provides a mechanism for the observed low-energy interband transitions

the largest changes in the band structure concerns the position of the center of the occupied bands relative to the Fermi level. As is evident by comparing Figures 5 and 19, the center of occupied bands drops by ~ 2 eV - a difference that is quite dramatic when comparing the DOS and which should be seen in photoemission experiments. These predictions will be examined in detail in Chapters V and VI in relation to the experimental results for the LaH_x system.

The YH_3 band structure calculation has indicated that the occupation of octahedral sites in YH_2 does indeed provide a mechanism for the observed low-energy interband transitions, thus answering the first question posed at the end of the previous chapter. Additionally, with a few cautions in mind, this calculation will be helpful in understanding the experimental results for LaH_x to be presented in Chapter V. In the following chapter the electronic structure of ScH_2 is reexamined in order to answer the second question remaining from Chapter II. That is, if there is no octahedral site occupation in ScH_2 (and no 'anomalous' low-energy optical features are observed experimentally (61)) what is the reason for the energy discrepancies between the self-consistent calculation and the optical results?

IV. IMPROVED SELF-CONSISTENT CALCULATION OF ScH_2

A. Introduction

In Chapter II the self-consistent band structures of ScH_2 and YH_2 (63) were shown to demonstrate good systematic agreement with the optical measurements of Weaver et al. (61) but the theoretical transitions occurred at higher energies. In the previous chapter it was shown that the premature occupation of octahedral sites could account for some of the anomalies in the interband features of YH_2 . As discussed in Chapter II, however, there is no evidence for other than tetrahedral site occupation in ScH_2 and one is led to question the calculational approximations rather than any structural differences to explain the remaining energy discrepancies between experiment and theory. Additional experimental information regarding the density of occupied states provided by Weaver et al. (69) using photoemission spectroscopy indicated that the bonding bands were too close to the Fermi level in the SC calculations. Specifically, for ScH_2 a peak in the emission intensity occurred at 5.1 eV below E_F while the calculations placed this peak in the DOS at 4.2 eV below E_F (see Fig. 6).

In this chapter the calculational details and results of an improved self-consistent calculation are discussed. This improvement is made by including an additional muffin-tin sphere at the octahedral site. The results show much better agreement with the experiments. The discussion of charge transfer begun in Chapter II is continued in greater detail.

B. Computational Details and Results

The new band structure calculation for ScH_2 included an interstitial muffin-tin sphere at the octahedral site (see Fig. 1). Recall that in the previous calculation, where this was not done, the sphere surrounding the metal site extended 65% of the way to the hydrogen position. With this arrangement, only 47% of the unit-cell volume was included within the muffin-tin spheres. In the muffin-tin approximation the remaining interstitial volume is one of constant potential. In the new configuration, the metal and tetrahedral hydrogen spheres remained unchanged in size and the largest possible octahedral sphere was added. The resulting spheres contained 74% of the unit-cell volume - a significant increase. The radii of the metal, tetrahedral and octahedral spheres were, respectively, 2.47, 1.41, and 1.93 a.u., where the fcc lattice constant was 9.038 a.u. (4.78 Å). This large octahedral sphere, while it contained no nucleus, was large enough to include 0.80 electrons due to the initial charge overlap, compared to the 0.71 electrons within the smaller hydrogen spheres. By including the interstitial sphere, the charge within its large volume was treated on the same footing as that in the other muffin-tin spheres.

The band structure calculation was performed using the standard KKR method as discussed in Chapter II. The resulting self-consistent energy bands for ScH_2 are shown in Fig. 20. Hereinafter the new calculation is labeled $\text{ScH}_2^\square$ with the $\square$ denoting the interstitial sphere. In comparison with the ScH_2 bands in Fig. 4, the hydrogen-derived bonding bands are generally lower in energy with respect to the Fermi

Figure 20. Self-consistent energy bands of $\text{ScH}_2\Box$ calculated with Hedin-Lundqvist exchange parameters and including an interstitial muffin-tin sphere (denoted by the $\Box$) at the unoccupied octahedral site. The changes from the previous calculation shown in Fig. 4 are discussed in the text

level and the d-like complex at E_F along Q, W-K and Σ is narrower. The effect of these differences on the densities of states is compared in Fig. 21.

The new results compared much more favorably with both optical (61) and photoemission (69) experiments. The experimentally-identified M_2 -type critical point, a $W_2' \rightarrow W_1$ transition at ~ 2.95 eV (see Figs. 12 and 15), was calculated to occur at 3.30 eV for ScH_2 but at 2.85 eV in $ScH_2^\square$. The small underestimation of 0.10 eV is reasonable since self-energy corrections have not been included in evaluating these transition energies (30). The calculated interband onset along Q is reduced from 1.7 to 1.4 eV in the new calculation. The thermoreflectance results (61) shown in Fig. 12 indicated that interband transitions involving the Fermi surface occurred near 1.3 eV. The corresponding onset was also seen experimentally in the ϵ_2 spectrum shown in Fig. 11. The excellent agreement with the optical experiments results from the narrowing of the splitting between bands 3 and 4 along Q, W-K and Σ .

Comparison with the photoemission experiments (69) is made in Fig. 22. The peak near -4.5 eV has lowered by -0.4 eV from the previous SC calculation into better agreement with experiment. Furthermore, the first peak in the DOS below E_F which is due to the d-like bands has narrowed and also agrees better with these experiments. The remaining discrepancy of 0.6 eV in the position of the large peak in the DOS is not serious. As discussed by Papaconstantopoulos *et al.* in relation to PdH (15), the position of the hydrogen-derived bands is much more sensitive to the choice of muffin-tin radii than are the d-like bands. Thus,

Figure 21. The electronic density of states (DOS) for the first five self-consistent energy bands of ScH_2 (solid line from Fig. 6) compared to those of $\text{ScH}_2^\square$ (dashed line). The effect of including the new sphere is to lower the hydrogen-derived bonding bands and to narrow the d-like complex near E_F

Figure 22. The ScH₂□ DOS convolved with 0.5 eV Gaussian is compared to a photoelectron energy distribution (PED) curve from Ref. 69. The PED is shown with arbitrary units and the DOS curve is offset for clarity

perhaps such a change is all that is needed to improve the agreement. However, effects such as the hydrogen vibration in the lattice, relaxation or a non-spherical potential within the Sc sphere might be important.

C. Charge Transfer

As noted in Chapter II, in the course of obtaining self-consistency, charge is transferred out of the metal sphere and into the hydrogen sphere. In addition to the previously-cited experiments supporting this direction for charge flow (58,59,60) the recent photoemission results obtained by Weaver et al. (70,71) on many different hydride systems show the commensurate core level shifts to higher binding energies expected for such transfer. Charge transfer to the hydrogen site has also been reported in the self-consistent electronic structure calculations of PdH (15), Pd₆H (72) and Zr₄H (73).

The charge redistribution in ScH₂ is illustrated in Figs. 23 and 24 where the valence electron charge density is plotted along the [100] and [111] directions. In these figures the initial charge distribution, shown as a solid line, was obtained by overlapping the 4s² and 3d¹ atomic charge densities of the neutral Sc atoms with the 1s¹ hydrogen charge densities. The final charge distributions resulting from the self-consistent calculation of the solid are shown by the dashed curves. The most apparent trends are for charge transfer to the hydrogen site and for an increase in anisotropy of the metal d-like charge. The charge transfer to the hydrogen site shown in Fig. 23 is

Figure 23. Charge density in the [100] direction from overlapping the atomic electrons ($3d^1 4s^2$ and $1s^1$) and from the self-consistent band charge

Figure 24. Charge density in the [111] direction from overlapping atomic electrons ($3d^1 4s^2$ and $1s^1$) and from the self-consistent band charge

very similar to that for hydrogen in the Zr_4H calculation of Jena et al. (73). Nearest to the metal site, in the solid curves in either of Figs. 23 or 24, is a peak due to the 4s electrons, followed by a broader peak from the 3d electrons. In the SC calculation of the solid, the peak due to the 4s electrons is no longer apparent because of the p-character present in the band wavefunctions. In the [100] direction the d-peak near 0.7 a.u. increases as a result of solid state effects, while in the [111] direction it decreases.

These changes in charge distribution are due to the interactions between atoms and provide insight into the character of the bonding. The changes indicate a lack of d-bonding along the [100] direction but a degree of covalent bonding between the hydrogen and the metal d-like states with wavefunctions directed along the [111] direction. As in the previous calculation, charge is transferred to the hydrogen sphere. As summarized in Table 3, the hydrogen sphere gains 0.11 electrons while the metal sphere loses 0.19 electrons. This ionicity coupled with the covalency indicates that the effect of hydrogen in this metal lattice is an appreciable perturbation and is the reason these compounds are so stable.

D. Conclusions

The trends and conclusions derived from the improved energy band calculation of ScH_2 may be applied to YH_2 and other CaF_2 -structured metal hydrides. In the second chapter it was shown that two experimentally-identified features in the optical spectra of both ScH_2 and

Table 3. Charge inside muffin-tin spheres for the new and old calculation of ScH_2

ScH_2 $a = 4.783 \text{ \AA}$							
Charge inside muffin-tin sphere	NEW				OLD		
	Sc	H	Octahedral	Interstitial	Sc	H	Interstitial
Atomic charge	19.019	0.536	0.0	0.0	19.019	0.536	0.0
Overlapping atoms	19.532	0.707	0.798	1.256	19.532	0.707	2.055
Charge after final iteration	19.336	0.820	0.613	1.411	19.323	0.844	1.989

YH_2 , an interband onset and an M_2 -type critical-point transition, can be identified with features in the calculated bands. It was the systematics in both the experiments and calculations that hinted at this identification because the computed energy locations were too large by several tenths of an electron volt. The improved calculation of ScH_2 shows excellent agreement with experiment and confirms the original interpretation placing the interband onset along Q and the M_2 -type critical point at W. One may safely assume that a self-consistent calculation of $\text{YH}_2^\square$ would also yield such good agreement with the optical experiments.

In the last three chapters, band structure calculations have been used to understand the optical properties of ScH_x and YH_x as measured by Weaver et al. (61). In the last two of these chapters, explanations for the anomalous low-energy interband transitions in YH_2 and for the systematic energy discrepancies between experiment and theory for both ScH_2 and YH_2 were presented. The optical properties of ScH_2 are well understood using the self-consistent $\text{ScH}_2^\square$ energy bands. For YH_2 , which has a lattice parameter 9% larger than that of ScH_2 , one must consider not only the CaF_2 -structured dihydride but also the effect of the hydrogen occupation of octahedral sites in order to understand the optical properties.

In the following chapter, optical properties of another member of the group IIIB metal hydrides are discussed in an experimental study of LaH_x . If the premature occupation of octahedral sites is affected by lattice size, as suggested in the second chapter, low-energy interband transitions similar to those in YH_2 should be observed.

V. OPTICAL PROPERTIES OF THE La-H SYSTEM

A. Introduction

After having considered the electronic structure and optical properties of ScH_2 and YH_2 , we now examine another group IIIB metal hydride system, LaH_x . In the previous chapters it was shown that one-electron band theory is quite successful in understanding the experimental optical results for ScH_2 and YH_2 . In order to understand the optical spectra of YH_2 , however, the premature occupation of octahedral sites was postulated. This deviation from the ideal fluorite structure is thought to be related to lattice size, the deviation growing with increasing lattice parameter. With LaH_2 , low-energy interband transitions similar to those observed optically in YH_2 should then be evident.

Another motivation for this optical study is due to the interesting concentration-dependent properties at high hydrogen concentration. For LaH_x with $2 < x < 3$, the metal lattice retains its face-centered-cubic symmetry and the electronic structure depends on the hydrogen content. Metal-semiconductor and metal-semimetal transitions at $x > 2.7$ have been discussed (52,74).

In this chapter the results of optical absorptivity measurements of LaH_x with $1.6 < x < 2.9$ are presented. These measurements are made at 4.2K with a photon energy between 0.16 and 4.5 eV. Systematics in the optical spectra are related to those previously noted for the other group IIIB metal dihydrides. The results indicate a "more

premature" octahedral site occupation in LaH_x and suggest that LaH_3 is a semiconductor.

B. Experimental Details

The experimental techniques employed for both sample preparation and optical measurement are essentially the same as those employed by Weaver et al. (61) for ScH_2 and YH_2 . The lanthanum hydride optical data were taken over a much wider composition range which dictated the use of additional steps in the hydrogen-charging process. Furthermore, the La-H system is more reactive to air, and sample degradation was a more serious problem.

All of the samples used in this study were prepared in bulk form under the supervision of D. T. Peterson. The starting material was high-purity polycrystalline lanthanum obtained from the Ames Laboratory. The use of bulk samples has the advantage of ensuring a more uniform hydrogen concentration than can be obtained with powders. The starting metal typically contained less than 20 atomic ppm of any metallic impurity with 300, 100 and 200 ppm of O, C and F, respectively. The metal was electropolished in a solution of 6% perchloric acid in methanol at $\sim 200\text{K}$. The sample was then wrapped in tantalum foil and heated under vacuum in the hydrogen-charging apparatus to 850°C to outgas the metal and increase its surface permeability to hydrogen. The tantalum foil served to preclude contamination by the quartz or stainless steel furnace tubes by reacting with carbon or oxygen, while allowing hydrogen or helium to pass through. A mixture

of hydrogen and helium gases was used for the low-pressure charging runs, the helium serving to moderate the reaction and thus assure sample integrity. The hydrogen and helium used were high-purity tank gases. The temperatures, pressures and times were controlled to yield the appropriate hydrogen concentration. For samples with a hydrogen-to-metal ratio greater than 2.6, high-pressure charging was employed. In this process, a previously-prepared di- or higher hydride was transferred to the high-pressure apparatus where the sample was first outgassed at a temperature of 850°C then cooled to about 800°C before adding special-purity tank hydrogen up to a pressure of ~100 atmospheres.

The samples were hydrogen-analyzed using a hot vacuum-extraction method. A small portion of the prepared sample was cut from the bulk and weighed. The hydrogen from this weighed piece was driven off at 1225°C and pumped into a calibrated volume. The accuracy of this method is about two relative percent. These hydrides are extremely brittle and breakage would sometimes occur between the sample weighing and hydrogen extracting stages, causing the hydrogen concentration to be underestimated. For this reason, several composition determinations per sample often were made.

The optical surfaces were prepared by grinding with abrasives under alcohol in stages ending with Linde A (0.3 micron alumina) on a rotating wax wheel. The smooth samples revealed little structural damage and some displayed rather large (1 mm x 1 mm) grain sizes when examined by optical metallography. Early optical experiments on

lanthanum hydrides showed that broadening of spectral features occurred if the samples were electropolished, thus sample preparation ended with the mechanical polish.

After polishing, the samples were ultrasonically cleaned in alcohol, dried using tank nitrogen, and immediately transferred for optical measurement to the calorimeter which was then evacuated. The samples typically were exposed to air for ~12 minutes before the fore-pump was engaged. The samples were highly reactive and, for the typical size of 8 mm x 12 mm x 2 mm, would decompose into a fine white powder within 24 hours if not stored under a vacuum. Examination of the samples before and after the experiments revealed a slight discoloration or cloudiness, an effect depending on air-exposure time. As will be discussed, however, the effect of sample loading time on the optical spectra is believed to be small for the typical 12-minute exposure time.

The optical experiments were conducted using a calorimetric technique described by Bos (75). A Leiss double-prism monochromator passes light to a mirror box which directs it to the sample as is shown in Fig. 25. The experimental chamber is surrounded by liquid helium and the sample temperature is near 4.2K. Figure 26 gives a more detailed view of the optical detection system. Monochromatic light impinging on the sample at near normal incidence is either absorbed or reflected. The reflected light travels to the gold-black-coated absorber which absorbs essentially all of the light. The radiation shields are also gold-black-coated to eliminate problems due to scattered light. The

Figure 25. Details of light path and dewar system

Figure 26. Detailed view of the optical detection system

absorbed or reflected light is detected via induced temperature changes.

The temperatures of both the absorber and sample are monitored by thermometer resistors, 47-ohm Allen-Bradley resistors with large temperature coefficients of resistance. Temperature increases of millidegrees due to the absorbed radiation are then duplicated, with the light blocked off, by passing current through matched 1000-ohm metal film heater resistors. The heater and thermometer resistors are mounted side by side and attached thermally to copper blocks, one block attached to the gold-black-coated absorber and the other to the sample. The copper blocks are thermally insulated from the apparatus with copper leads serving as heat leaks. The lengths and diameters of these leads were such that acceptable thermal time constants were obtained for the measurements. For an incident light intensity, I_0 , the ratio of the absorbed intensity, AI_0 , to the reflected intensity, $RI_0 = (1 - A)I_0$, is $A/(1 - A)$. When light is blocked off, current is passed through the heater resistors to match the temperature rise observed when the light was present. Then this absorptivity ratio can be related to the ratio of currents passing through the matched heater resistors:

$$A = \frac{1}{1 + \frac{I_A^2}{I_S^2}}$$

where I_A and I_S are, respectively, the currents through the absorber

and sample heater resistors. Electrical leads to the resistors pass through the bottom flange, through a stainless steel tube (not shown in the figure), out of the helium bath and out of a Torr-Seal joint in the tube. The electronics associated with these measurements remain as outlined by Bos (75).

This calorimetric method of obtaining the absorptivity is quite accurate. Comparison to other methods of data collection for metals and alloys reveals that this is a comparatively sensitive method in this energy range (see for example Refs. 76 and 77 and references therein). The quality of the gold black is an important factor in these measurements and the procedure used to make it is described by Bos (75) and Weaver (78). With each new coating, spectra were taken of well-characterized samples to assure good quality. Additional details relating to sensitivity and resolution may be found elsewhere (75,79).

For these measurements, the most serious uncertainty is due to sample degradation rather than any systematic error associated with the experimental apparatus. As mentioned earlier, the samples had a cloudy appearance with increasing exposure to air. The first absorptivity measurements of LaH_x were aimed at determining the effect of exposure to air. Spectra of $\text{LaH}_{1.6}$ with exposure times of 12 min, 1 hr and 1 3/4 hr were compared. The changes ranged from 0 to 10% of A with the magnitude of A decreasing with exposure time. The spectral features did not change significantly except at very low energies and, as will be discussed in the following section, show no structure other

than that expected based on the previous work with the group IIIB metal hydrides. Although the spectra of the low-x samples were not very sensitive to reasonable air-exposure times, the same was not true of the high-x samples. In particular, the $\text{LaH}_{2.87}$ specimen was quite sensitive to air and exposure times greater than 45 minutes caused drastic spectral changes. As will be seen, however, the interpretation of these results is supported by recent NMR and resistivity experiments.

C. Experimental Results and Conclusions

Optical spectra of LaH_x were obtained for the concentrations $x = 1.6, 2.04, 2.15, 2.36, 2.51, 2.63, 2.67$ and 2.87 . In Figs. 27 and 28, representative absorptivity spectra of several of these samples are shown. In the following paragraphs the low-x concentrations are first examined in light of the present understanding of the dihydride-based electronic structure. The high-x optical spectra are then interpreted using available di- and trihydride band structure calculations.

Figure 27 shows the optical absorptivity of $\text{LaH}_{1.6}$ and $\text{LaH}_{2.04}$. In spite of the rather large difference in hydrogen concentration, relatively little change is seen in the optical structure. The feature near 0.4 eV is due to octahedral site occupation and is much like that observed in YH_2 and LuH_2 (61). Comparing this figure with Fig. 10 shows that, of the three group IIIB metal dihydrides, LaH_2 has the "most premature" octahedral site occupation. With ScH_x no evidence of octahedral site occupation was found, even at $x = 1.98$. In YH_x , with a dihydride lattice constant 9% larger than that of ScH_2 , octahedral site occupation was evident in YH_2 but not in $\text{YH}_{1.73}$ (61). Finally, with

Figure 27. Optical absorptivity spectra of LaH_x

Figure 28. Optical absorptivity spectra of LaH_x . The results are offset by $A = 0.2$ for clarity

LaH_x which has a dihydride lattice constant 9% larger than that of YH_2 , evidence for octahedral site occupation is apparent even at $x = 1.6$. This deviation from the ideal CaF_2 structure does indeed appear to be a function of lattice size as suggested in the second chapter.

The optical features in the absorptivity spectrum of $\text{LaH}_{2.04}$ may be compared to those of ScH_2 and YH_2 . This comparison is more meaningful after performing the Kramers-Kronig integrals to determine the dielectric functions as discussed in Chapter I. The low-energy extrapolation for the integration included a Drude term which provided a fairly good fit to the absorptivity data. From 4.5 to 25 eV reflectance data for ScH_2 were shifted to match the $\text{LaH}_{2.04}$ results (80). Above 25 eV, a power law function was used. The error introduced by these extrapolations is difficult to quantify. In the energy region of interest, $0.3 < h\nu < 4.5$ eV, the most sensitive region is the high-energy region since the Drude fit is quite good and small variations were observed to make little difference. At high energy, the use of the ScH_2 optical data is not as good an extrapolation. Nevertheless, even a poor approximation would tend to modify amplitudes rather than positions of optical features and it is the positions that are of most interest. Furthermore, even in the well-understood optical spectra of ScH_2 , the only feature in ϵ_2 that could be related to the bands with any confidence was the interband onset near 1.4 eV. This feature is sufficiently far in energy from the extrapolated regions as to remain relatively insensitive to the approximations.

The results of the Kramers-Kronig integration are shown in Figs. 29 and 30. In Fig. 29 the real and imaginary parts of the complex

Figure 29. The dielectric functions of $\text{LaH}_{2.04}$ derived from the absorptivity spectrum in Fig. 28.

Figure 30. The loss function, $\text{Im}(-1/\tilde{\epsilon})$, for $\text{LaH}_{2.04}$ calculated from the absorptivity spectrum

dielectric function are shown and can be compared to the ScH_2 and YH_2 results of Weaver *et al.* (61) shown in Fig. 11. In Fig. 29 an interband onset near 1.2 eV is evident. The increase in ϵ_2 on the low-energy side of this onset appears to be the characteristic Drude or free-electron-like behavior. However, as is evident in the absorptivity spectrum (Fig. 27) there are interband contributions at lower energy due to octahedral site occupation. With ScH_2 and YH_2 , Weaver *et al.* (61) were able to eliminate this contribution by using substoichiometric samples to be representative of the ideal dihydrides, that is, dihydrides with the CaF_2 structure. With LaH_x , however, this effect could not be eliminated. Therefore, the assignment of this interband onset to the dihydride bands near E_F along Q (see Figs. 4 or 5) is not as certain as in the ScH_2 or YH_2 case. Nevertheless, the ϵ_2 spectrum is quite similar to those shown in Fig. 11.

Perhaps the most surprising difference concerns the position of the broad peak in ϵ_2 . In Fig. 11, in going from ScH_2 and YH_2 this peak moves to higher energy and was related to the increase in the width of the band complex along Q, W-K and Σ (see Fig. 4 and 5). The width of this complex is related to the metal d-band width which increases in going from 3d to 4d elemental metals. Of course, this width is a function of the lattice size and a comparison of the changes in the metal lattice to the dihydride lattice provides additional insight to the changes in electronic structure. One measure of the change in lattice size is the change in atomic concentration. From the reported lattice parameters for the dihydrides (1), the decrease in atomic

concentration is 29% in going from ScH_2 to YH_2 and 29% in going from YH_2 to LaH_2 . For the elemental metal this change is 29% in going from Sc to Y but only 11% in going from Y to La (81). Thus the dihydride lattice is significantly larger in LaH_2 than would be anticipated by considering changes in the metal lattice. It is not so surprising then that the d-complex is narrower in LaH_2 and that the broad peak in ϵ_2 is at a lower energy. Indeed, recent band calculations by Kulikov et al. (74,82) indicate that the $W_1 - W_2'$ separation is less in LaH_2 than in ScH_2 . While his calculated eigenvalues lead to band separations which disagree substantially with both the optical measurements and calculations, the systematics for this complex agree.

The peak in the absorptivity of $\text{LaH}_{2.04}$ near 1.2 eV is related to a plasmon. Figure 30 shows the volume loss function, $\text{Im}(-1/\tilde{\epsilon})$, which is a measure of the probability that a propagating high-energy electron will excite a volume plasmon. The position of this peak is lower in energy than that observed in ScH_2 and YH_2 . The effect of interband transitions on the position of this peak is such that one cannot make any meaningful conclusions regarding the free-electron parameters. That is, since the peak occurs in a region where both intraband (see Eqs. (1.14)) and interband (see Eq. (1.10)) transitions are important, as shown in Fig. 31, one cannot consider only the free-electron or intraband parameters. Indeed, for ScH_2 , changes in the peak position with hydrogen concentration were reportedly opposite from that expected from only free-electron considerations (61).

Figure 31. Optical functions for an ideal Drude metal, labeled A, and for the same metal to which a single Lorentzian oscillator has been added to represent interband transitions. In B the oscillator is 0.5 eV below the free-electron plasmon energy of 2 eV and in C it is 0.5 eV above. While the peak in the loss function, $\text{Im}(-1/\tilde{\epsilon})$, is at the free-electron plasmon energy in A its position and shape are strongly affected by the presence of the oscillator in B and C

This study of the low- x lanthanum hydrides indicates that the octahedral site occupation is "more premature" than in the yttrium hydrides, supporting the suggestion in Chapter II that this effect is related to lattice size. Furthermore, in comparison to the results for ScH_2 and YH_2 , these experiments suggest that the band complex near E_F along Q, W-K and Σ in the dihydride energy bands (see Figs. 4 and 5) is narrower for LaH_2 , an effect related to the large increase in lattice size. In the remaining paragraphs the high- x optical spectra of Fig. 28 are examined.

The concentration-dependent absorptivity spectra of LaH_x obtained in the course of these experiments could be classed in three types according to the x -value. In Fig. 28 the similarity of the $x = 2.04$ and $x = 2.36$ spectra is quite apparent. However, those with $x = 2.63$ and $x = 2.87$ are very different from each other and from the low- x spectra. Other samples between $x = 2.51$ and $x = 2.67$ displayed optical features quite similar to those of $x = 2.63$. The presence of three distinct types of samples also seemed to be evident in the hydriding process. That is, it was relatively easy to obtain concentrations of $x = 2.0$, 2.6 and 2.9 and it was more difficult to obtain concentrations between these values. With increasing x , one expects that the electronic structure, and thus the optical features, will change from dihydride-like to trihydride-like. The low- x absorptivity spectra are well-understood in terms of the dihydride electronic structure plus a contribution due to premature octahedral site occupation. The high- x samples were less reflective and at $x = 2.87$ data

could be obtained only up to a photon energy of 3.5 eV because of the small amount of light reaching the absorber. However, it is the low-energy range of the spectrum that is of most interest as it appears to be more characteristic of a semiconductor than a metal (43). In order to compare experiment with theory, the dielectric functions of these spectra were obtained by Kramers-Kronig analysis.

The low-energy extrapolations for the Kramers-Kronig integral were not as good for the high-x samples. A good Drude fit could not be obtained to the $x = 2.63$ sample. For $x = 2.87$ the absorptivity is decidedly not Drude or free-electron-like. With the $x = 2.87$ sample two drastically different extrapolations, one a constant $A = 0.8$ and the other a smooth decrease to $A = 0$, were used. The resulting difference in the dielectric functions obtained was not serious but precluded the identification of the small band gap energy. The same high-energy extrapolation method was used for these samples as was discussed for $\text{LaH}_{2.04}$.

The dielectric functions for LaH_x are shown in Figs. 32 and 33 for $x = 2.63$ and $x = 2.87$, respectively. For $x = 2.63$, ϵ_2 shows an onset of interband transitions near 2.4 eV with interband contributions significant at lowest energies. At $x = 2.87$ there is a peak near 1.7 eV and a sharp minimum near 2.3 eV followed by an onset. While the $x = 2.63$ results are difficult to understand apart from regarding them as a combination of the low-x and high-x results, the $x = 2.87$ spectrum may be understood in terms of the trihydride band structure (see Fig. 19).

Figure 32. The dielectric functions of $\text{LaH}_{2.63}$ derived from the absorptivity spectrum in Fig. 28

Figure 33. The dielectric functions of $\text{LaH}_{2.87}$ derived from the absorptivity spectrum in Fig. 28

In the trihydride, the band complex that was present in the dihydride bands near Q, W-K and Σ is absent. It was that complex which led to the optical spectrum in LaH_2 . For the trihydride the interband onset is near Γ and is expected to be of relatively low strength due to the small densities of states involved. Of course, since these results suggest that $\text{LaH}_{2.87}$ is a semiconductor, Γ_1 lies below Γ_{25}' in energy by less than 0.14 eV. The onset near 2.5 eV can most likely be identified with the $L_2' - L_3$ energy separation.

Recalling Eq. (1.10), the joint densities of states (JDOS) for the lanthanum hydrides may be compared. Figure 34 shows that below 2.5 eV the JDOS decreases with increasing hydrogen concentration assuming that matrix elements remain constant. This is related to the disappearance of the Q, W-K, Σ , dihydride band complex. The low-energy portion of the $x = 2.04$ curve is related to the occupation of octahedral sites. The structure at less than 2 eV in the $x = 2.87$ curve arises from transitions between bands near Γ .

The concentration-dependent electronic structure of LaH_x is thus well-understood in terms of the dihydride and trihydride band features shown in the calculations. The low- x results are similar to those of YH_2 but have a "more premature" octahedral site occupation. The high- x results are understood in terms of the trihydride band structure presented in Chapter III. The identification of semiconducting behavior is not certain but it does agree with the NMR results presented by Barnes (83), reporting a band gap of about 0.1 eV. As

Figure 34. The imaginary part of the dielectric function, ϵ_2 , scaled by $(h\nu)^2$ to approximate the joint density of states. The results for LaH_x derived from the absorptivity spectra of Fig. 28 are compared

will be discussed in the following chapter, this conclusion is further supported by the results of photoemission experiments.

VI. CONCLUSION

The optical properties of the cubic Sc-H, Y-H and La-H systems are now well-understood in terms of one-electron band theory. The original difficulty in interpreting the optical spectra of YH_2 was due to the unexpected premature occupation of octahedral sites, an effect which led to the presence of low-energy interband transitions.

The electronic structure of the group IIIB metal dihydrides is better understood at this point than that of lanthanum trihydride. ScH_2 has the smallest lattice parameter and the optical spectra have been related to the portion of the calculated energy bands near E_F along Q, W-K and Σ (see Fig. 20). Optical studies of ScH_2 have revealed no features that could not be related to these energy bands. Such is not the case with YH_2 which has a larger lattice parameter. The low-energy interband transitions could not be explained even by the self-consistent energy bands shown in Fig. 5. Only the optical transitions in the yttrium hydrides with a low hydrogen content could be understood as arising from the same portion of the bands as discussed for ScH_2 . It was then postulated that the anomalous low-energy transitions were due to a premature occupation of octahedral sites. This effect was thought to be due to the larger dihydride lattice. The band calculation of YH_3 showed that it was reasonable to expect that such octahedral site occupation would lead to low-energy excitations. Optical studies of LaH_x then confirmed the lattice size effect by showing that even the samples with a low hydrogen concentra-

tion displayed the spectral evidence of octahedral site occupation.

Since the beginning of this study, several other experiments have supported both the calculated bands and the postulated site occupancy. Photoemission experiments (69) displayed the differences in the hydrogen-induced bonding bands which were expected from the calculated densities of states shown in Figs. 6 and 7. ESR (66), NMR (64) and neutron scattering (65) results have shown the presence of prematurely-occupied octahedral sites in YH_2 .

The optical properties of LaH_3 have also been explained using the energy bands. There are no good calculations available for making as detailed a comparison with the optical results; however, the spectra indicate that it is a small-band-gap semiconductor. This result agrees with the preliminary results of NMR (83) and resistivity (84) measurements. Recent photoemission studies of the La-H system (85,86) also show a drastic decrease in the occupied states at E_F as is shown in Fig. 35. In these studies the Fermi level of $\text{LaH}_{2.89}$ could not be identified - a characteristic of semiconducting behavior.

Although the optical properties of cubic ScH_x and YH_x have been well-described, there are many interesting questions which remain to be addressed in the cubic La-H system, a system with a wider composition range. The optical data presented here were all taken at 4.2K but temperature-dependent changes in the electronic structure are also of interest. Studies of lattice constant versus temperature or composition remain to be undertaken. The optical results presented here, and especially the photoemission results in Fig. 35 (85,86), disagree

Figure 35. Photoelectron energy distribution curves for LaH_x normalized to the emission of the $\text{La } 5p_{3/2}$ core. Energies are referenced to E_F for $x = 1.98$ and $x = 2.48$; for $x = 2.89$ the $5p$ cores are aligned with those of $\text{LaH}_{2.48}$ because the Fermi level cannot be identified

sharply with the only available band structure calculations of LaH_2 and LaH_3 . In these calculations (74), as in the calculation of YH_3 presented in Chapter III, the trihydride bonding bands were significantly lower in energy relative to the Fermi level than were the dihydride bands. The results shown in Fig. 35 show little change in the position of these bands, indicating that a better band calculation is needed.

VII. REFERENCES

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