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Self-consistent electronic structure of lanthanum dihydride and lanthanum trihydride

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The electronic structures of lanthanum dihydride and trihydride have been evaluated self-consistently using a semirelativistic Korringa-Kohn-Rostoker method. The results indicate a charge transfer to the tetrahedral hydrogen for the dihydride, but no charge transfer to the additional octahedral hydrogen for the trihydride. The energy gap in the trihydride is found to be greatly reduced from the value obtained from non-self-consistent calculations, but otherwise the effects of self-consistency are minor. The results are discussed together with recent experimental and theoretical studies which have focused on the observed metal-semiconductor phase transition.

I. INTRODUCTION

The rare-earth hydrides, LaH_x, exhibit numerous changes in physical properties as functions of hydrogen concentration and temperature. Of particular interest is an apparent metal-semiconductor transition, which occurs as the concentration of hydrogen is increased above 2.8 protons/metal atom.[1-3] A number of mechanisms for the transition have been proposed including localization of states in the defect band, small distortions of the hydrogen lattice, and the onset of an excitonic insulator phase. The appropriateness of each mechanism depends on the details of the underlying electronic structure. Although several studies have helped in providing realistic electronic structures of the rare-earth hydrides, all of the calculations performed thus far have ignored self-consistency and relativistic effects. The results from two of these calculations on LaH_3 differ in predicting a semiconductor or semimetal ground state. To try to resolve this issue and to gain a more complete picture of the rare-earth hydrides, we present self-consistent calculations of the electronic structures of LaH_2 and LaH_3 including relativistic effects which are important for heavier elements. In the remainder of this introduction we place these calculations in context by briefly reviewing previous theoretical and experimental results. In Sec. II we describe the methods and give details of the calculations, in Sec. III the results are presented, and in Sec. IV the relevant experimental data are reviewed and compared with the results of our calculations.

Early conductivity measurements indicated that the density of electronic states falls continuously to zero as hydrogen is added to lanthanum dihydride.[1-3] Measurements of the La Knight shift,[4] as well as low-temperature specific-heat measurements,[5] also show decreasing densities of states at E_F as the hydrogen concentration increases. Recent photoemission experiments[6] are consistent with a semiconducting electronic structure for hydrogen concentration greater than about 2.9. A variety of more recent experimental data make the situation even more intriguing. Nuclear magnetic resonance (NMR) measurements of the spin-lattice relaxation time T_1 for LaH_3 and LaD_3 as a function of temperature show $(T_1T)^{1/2}$ to be constant, which is indicative of a metal, while the Knight-shift measurements on the same sample indicate a metal at high temperatures but a transition to semiconductor behavior below ~ 210 K.[7] Measurements of resisitivity with decreasing temperature on a sample of $LaH_{\sim 2.85}$ show a factor-of-2 upward jump in the resistivity at 196 K and semiconducting behavior extending down to about 80 K, where the resistivity stops increasing so rapidly and eventually saturates at $\sim 2\times 10^{-2}\ \Omega$ cm.[8] Precise heat-capacity measurements at low temperatures for LaH_3 and LaD_3 show no evidence for an electronic contribution (i.e., they are consistent with no electronic states at E_F); however, at higher temperatures narrow peaks (λ-type anomalies) appear in the data.[9] We return to some of the questions raised by these measurements in Sec. IV.

The first determination of realistic electronic structures for a hydride was made by Switendick for the model systems YH_0, YH_1, YH_2, and YH_3.[10,11] Subsequent photoemission and optical measurements by Weaver *et al.*,[12,13] as well as improved electronic structure calculations of ScH$_2$ and YH$_2$,[14,15] confirmed the band picture of the trivalent metal hydrides. From these studies the basic features of the electronic structure were established, and proved to be more complex than the simple protonic and anionic models. The general picture which results from this work is that the proton potential is very attractive and those metallic states with wave functions which overlap the hydrogen site are greatly affected. With these trivalent metals, for each hydrogen atom within the unit cell a band forms below the set of bands with predominant metal *d* character. The newly formed bands are not composed of states of entirely hydrogen *s* character, but also contain states with substantial metal *d* character—indicative of metal–hydrogen covalent bonding. For the purposes of identification it is convenient to refer to these new bands as hydrogen-induced or hydrogen-derived bands. Thus, for the dihydride two bands form below the *d* bands, and these bands accommodate four of the five valence electrons. The fifth valence electron partially fills the metal *d* bands, and the material is metallic. The trihydride is a semiconductor since the three bands which form below the metal *d* bands accommodate all of the six valence electrons.

The earlier calculations have been supplemented by more recent calculations of Switendick for Y$_4$H$_9$ and Y$_4$H$_{11}$.[16] These supercell calculations, as well as similar calculations by Fujimori and Tsuda[17] on cerium hydrides, yield results similar to the stoichiometric calculations; namely, for each hydrogen within the unit cell a band forms below the metal *d* bands. The bands which are formed by the addition of hydrogen cannot accommodate the three metal valence electrons until there are three protons/metal atom. The conclusion that LaH$_3$ is a semiconductor requires that these hydrogen-induced bands form below and do not overlap the metal *d* bands. Two recent calculations disagree on this point. Non-self-consistent calculations of the electronic structure of LaH$_3$ by Gupta and Burger[18] and of CeH$_3$ by Fujimori *et al.*[19] indicate that a gap exists between the hydrogen-induced bands and the metal *d* bands; however, calculations by Kulikov and Zvonkov[20] yield overlapping bands for LaH$_3$.

None of the calculations of one-electron band structures is sufficient to explain the metal-semiconductor transition away from stoichiometry. As a result of his calculation, Kulikov proposed that the small band overlap and the resulting nesting of hole and electron pockets of the Fermi surface lead to an excitonic insulator phase[21] at low temperatures. Fujimori and Tsuda *et al.*[17] attribute the semiconducting phase to an order-disorder transition in the octahedral hydrogen sublattice. Such a transition has been observed by neutron diffraction for CeH$_{2.75}$.[22] They argue that at high temperatures the disorder within the octahedral sublattice results in Anderson-type localization. It should be noted that the two mechanisms assume opposite interpretations of the experimental results. Kulikov and Zvonkov conclude that the low-temperature phase is semiconducting, while Fujimori *et al.* conclude that it is metallic. This conflict in theoretical models was part of the motivation for the self-consistent calculations presented in this paper.

II. CALCULATIONAL DETAILS

The structure of ideal LaH$_2$ is the calcium fluorite type in which the metal atoms occupy an fcc lattice and the protons occupy the tetrahedral interstices. For the trihydride an additional proton is added at the octahedral interstice of the fcc lattice. The crystal structure is shown in Fig. 1. The calculations use the actual lattice constants: 10.7051 a.u. for the dihydride and 10.5946 a.u. for the trihydride.[23]

The self-consistent band structures of LaH$_2$ and LaH$_3$ were obtained employing the usual muffin-tin-shape approximation for the crystal potential. Following previous workers we chose the muffin-tin radii such that the spheres centered on metal sites extend 65% of the distance to the tetrahedral hydrogen positions.[10,14,15] The tetrahedral hydrogen sphere radii were chosen to be 35% of the nearest-neighbor lanthanum-hydrogen distance. The radius of the muffin-tin sphere surrounding an octahedral interstice was chosen as large as possible consistent with nonoverlapping spheres in order to minimize the interstitial volume. As a result the radii of the spheres about the tetrahedral and octahedral sites

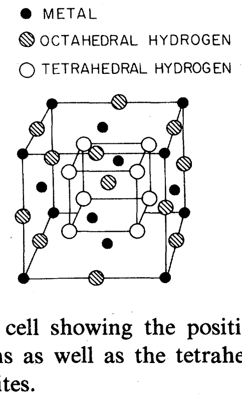

FIG. 1. Cubic cell showing the positions of the fcc lattice of La atoms as well as the tetrahedral and octahedral hydrogen sites.

are quite different, and the ratio of the volumes, Ω(tetrahedral)/Ω(octahedral), is 0.3247. In the calculaton of LaH_2 the sphere at the octahedral site was included although no proton was placed at the center. Calculations of the electronic structure of ScH_2 have indicated the importance of this interstitial sphere in making small but significant shifts of the band structure which improved agreement with optical and photoemission measurements.[15] Inclusion of the empty sphere facilitates the comparison of the results for LaH_2 and LaH_3 as well. The total volume of the unit cell occupied by muffin-tin spheres constitutes 67% of the volume of the unit cell, a number which compares well with the 74% obtained for the close packing of hard spheres or the 68% for a bcc lattice of hard spheres.

The eigenvalues and eigenvectors were found using the Korringa-Kohn-Rostoker (KKR) method with the wave function expanded through $l=3$ in the La sphere and $l=1$ in the other spheres. This means the unoccupied $4f$-electronic states of lanthanum are included. Although the f states are unoccupied in both fcc lanthanum and lanthanum hydride, the wave functions in the second band of the hydrides have appreciable $l=3$ or f character, which arises from the tails of atomic functions on neighboring sites rather than atomic f orbitals; therefore, expansion of the wave functions through $l=3$ is important. Relativistic corrections corresponding to the mass enhancement and Darwin term were included exactly by the method of Koelling and Harmon.[24] The energy shifts from the spin-orbit interaction, which splits degenerate states of similar l character along lines or at points of high symmetry, were calculated perturbatively.

During the initial iterations the eigenvalues and wave functions were determined on a grid of 10 points evenly distributed within the irreducible $\frac{1}{48}$ of the Brillouin zone. For the final iterations the number of points was increased to 60. In both cases the points were chosen according to the algorithm of Chadi and Cohen.[25]

The self-consistent crystal potential was calculated using the local-density approximation of Hedin and Lundqvist for the exchange-correlation contribution.[26] The core-charge density of the metal was recalculated for each iteration.

The convergence criteria for the dihydride and the trihydride were determined independently. The iterations of LaH_2 were continued until the charge within any muffin-tin sphere varied by less than 0.001 electron between iterations. The convergence of LaH_3 was determined from the gap energy between the third and fourth bands. Iterations were continued until changes in the direct and indirect gaps were less than 0.1 mRy. This convergence criterion was quite stringent and also guaranteed that the charge within any muffin-tin sphere varied by less than 0.001 electron between iterations. For the final iteration the eigenvalues and eigenfunctions for 13 bands were determined at the 60 special points and an additional 12 high-symmetry points. To determine the density of states (DOS), the resulting eigenvalues were fit by least squares to 38 symmetrized plane waves with a maximum rms error of 6 mRy. For bands below or near the Fermi level, the maximum rms error was 2.3 mRy. The DOS and angular-momentum-decomposed DOS were obtained using a linear interpolation scheme for 2048 tetrahedra within the irreducible $\frac{1}{48}$ of the Brillouin

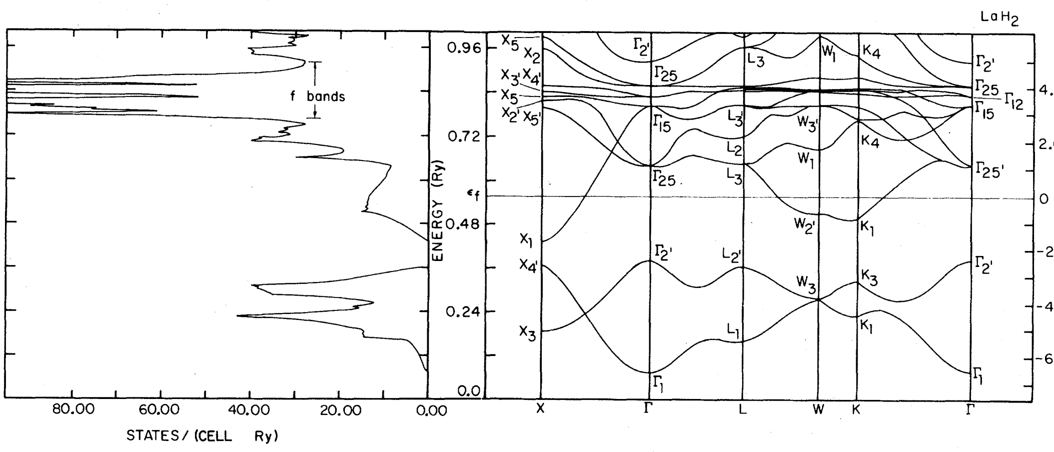

FIG. 2. Electronic band structure and density of states of LaH_2.

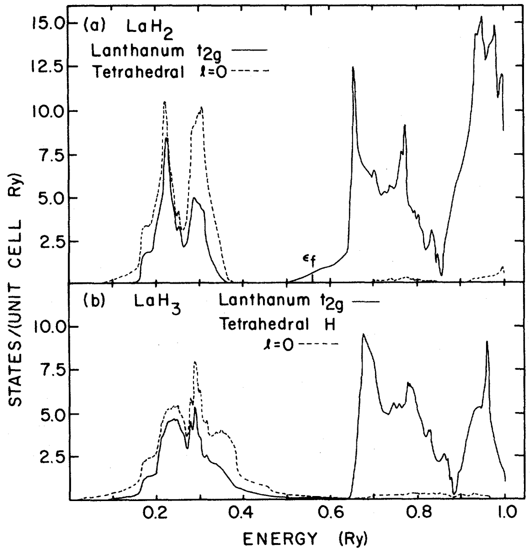

FIG. 3. Lanthanum t_{2g} and tetrahedral hydrogen ($l=0$) contributions to the electronic DOS for (a) LaH_2 and (b) LaH_3.

zone. The weights for the angular-momentum decompositions of the DOS were obtained by continuing the radial integrations beyond the muffin-tin sphere to a Wigner-Seitz or atomic sphere. The larger spheres account for the total volume of the crystal, and although they are not uniquely defined for compounds, they do provide a convenient method of assigning angular-momentum character to the electronic density in the interstitial region.

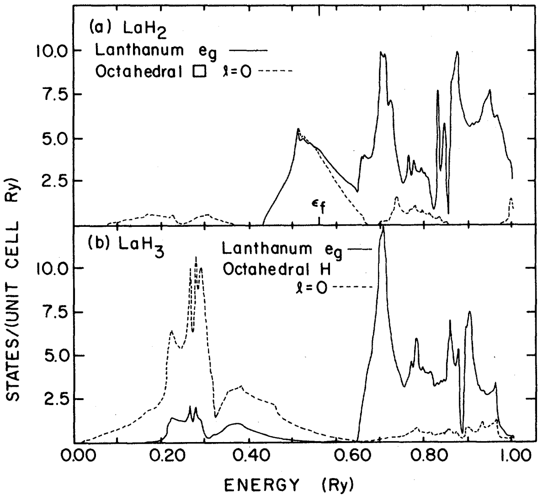

FIG. 4. Lanthanum e_g and octahedral hydrogen ($l=0$) contributions to the electronic DOS for (a) LaH_2 and (b) LaH_3.

III. RESULTS AND ANALYSIS

The calculated band structure and total DOS of LaH_2 are shown in Fig. 2 and closely resemble other published results for transition-metal dihydrides[10,14,15,18,19] where the nature of the bands and the implications for bonding have been discussed. Consequently, we give only a brief description of our results to facilitate comparison with previous work. The discussion is aided by considering the angular-momentum-decomposed DOS [parts (a) of Figs. 3 and 4]. The lower two bands of LaH_2 are composed almost entirely of states with *s*-like character about the tetrahedral sites and *d*-like (t_{2g}) character on the La site. The tight-binding or linear combination of atomic orbitals (LCAO) calculation of Fujimori *et al.* ascribes a greater percentage of character to tetrahedral 1*s* orbitals[19] than our value of $\sim 60\%$. Both approaches are correct in their description of the total charge density (or DOS) but differ, as they must, in their representation of the components. The tight-binding analysis yields 1.8 electrons per 1*s* orbital on a tetrahedral site,[19] but the *s*-like wave function on hydrogen is quite extended and much of the charge would be within La muffin-tin spheres. Quantitative statements about ionicity are therefore dubious.

The preferential coupling of the tetrahedral site orbitals to La *d* orbitals with t_{2g} symmetry is simply due to geometry. Each La site sits in the middle of a cube with eight tetrahedral sites at the corners. An equal occupation of the three t_{2g} orbitals (which is dictated by cubic symmetry) results in charge density maxima along the [111] and equivalent directions, which point toward the tetrahedral sites. The octahedral sites, on the other hand, are located in the equivalent [100] directions along which orbitals of e_g symmetry point; therefore, there is a correlation of La e_g and octahedral-site charge density. This is especially true for the occupied portion of the complex of *d* bands which cut the Fermi level (Figs. 3 and 4) in LaH_2. Since no proton is present at the octahedral site, the octahedral contribution for LaH_2 arises from the tails of the La *d* orbitals which extend into the rather large octahedral sphere.

The calculated band structure and total DOS of LaH_3 are shown in Fig. 5. With the addition of a proton on the octrahedral site a third band forms below the metal *d* bands. The angular-momentum decomposition of the DOS [parts (b) of both Figs. 3 and 4] shows the first two bands have not only maintained a large tetrahedral $l=0$ and La t_{2g} character but have also acquired additional octahedral

$l=0$ and some La e_g character. The third band is predominantly of octahedral $l=0$ and La e_g character, which is consistent with the results given for CeH_3 by Fujimori *et al.*,[19] who described the third band as consisting of "bonding states between the metal and octahedral hydrogen orbitals." The bonding character of these additional states is probably responsible for the lattice contraction as hydrogen is added to the dihydride.

The LaH_3 band structure of Fig. 5 has a direct gap at Γ of 12.8 mRy and an indirect gap between Γ and L of only 0.2 mRy. The indirect gap is very small and will be sensitive to potential approximations. For example, a calculation with all muffin-tin spheres of equal volume (a less than optimal geometry) resulted in an increased gap of ~ 10 mRy but little change in the overall band structure. The local approximation for exchange and correlation is also known to underestimate gaps in semiconductors (e.g., for Si the theoretical gap using the Hedin-Lundqvist exchange-correlation potential is about half the experimental value). The energy shifts due to spin-orbit coupling are also comparable to the band gap and are important for determining the nature of the bands at the gap edges. Using degenerate-state perturbation theory we estimate the splitting of the Γ_{25} level to be 6.9 mRy and the L_3 level to be 8.2 mRy, which is enough to cause a band overlap of 3.9 mRy between Γ and L. It is doubtful that this small band overlap would be maintained in a completely self-consistent calculation (in which spin-orbit coupling and a miniscule occupation of the fourth band were included throughout). At the initial iteration a small band overlap did exist; however, with further iterations the gap developed and stabilized and we expect this would also occur in a fully relativistic calculation. We are thus unable to confirm the existence of a gap, except to say if it exists it must be on the order of a few mRy.

In their non-self-consistent calculations using the augmented-plane-wave (APW) method for LaH_3, Gupta and Burger[18] found an indirect gap of 0.041 Ry, while Kulikov and Zvonkov,[20] with the use of a modified KKR method, found a band overlap of 0.029 Ry. Both of these nonrelativistic calculations employed the Slater approximation for exchange with $\alpha=1$, and as a consequence one should expect smaller bandwidths than ours. This is indeed the case for the Gupta and Burger calculations. For example, the width of their lower two bands $(E_{\Gamma_2'}-E_{\Gamma_1})$ for LaH_2 is 0.271 Ry compared with our 0.307 Ry. Their larger gap in the trihydride is also consistent with the known trend from calculations for semiconductors that show a larger gap is obtained with a stronger exchange-correlation potential. We have no explanation, however, for the larger bandwidths found by Kulikov and Zvonkov $(E_{\Gamma_2'}-E_{\Gamma_1}=0.435$ Ry for $LaH_2)$ and their band overlap for LaH_3. They do warn, however, that they are using a simplified calculational method and that their results should be considered only qualitatively; in this respect there is agreement among all three calculations.

Finally we turn to the subject of charge transfer. For transition-metal and rare-earth dihydrides it has been well established both experimentally and

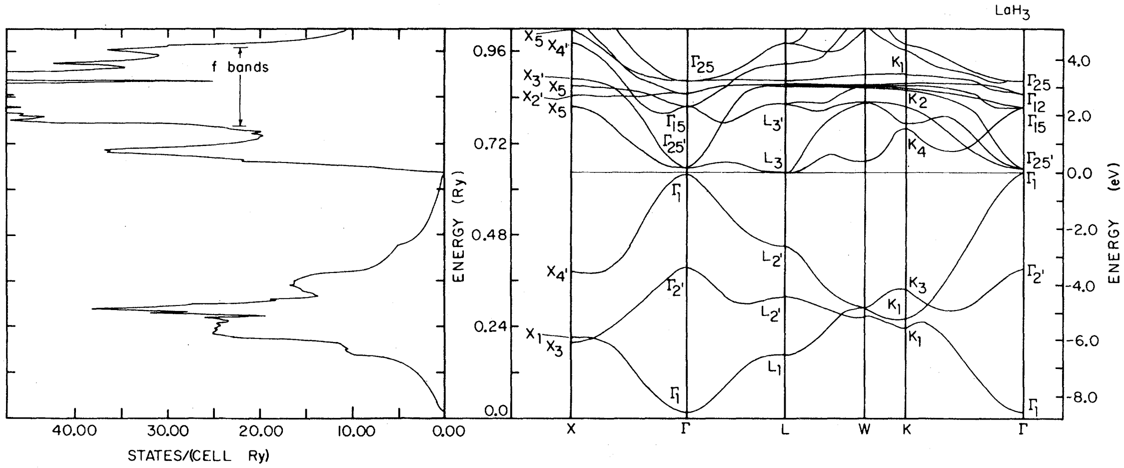

FIG. 5. Electronic band structure and DOS of LaH_3.

theoretically that there is a transfer of charge from the metal to the hydrogen on the tetrahedral sites (see, for example, the discussion in Ref. 15). This is demonstrated for LaH_2 in Table I which compares the charge within each muffin-tin sphere for the case of overlapping neutral atoms and the final self-consistent results. The results are similar to self-consistent calculations for YH_2 and ScH_2 (Refs. 14 and 15): there is an increase of ~ 0.2 electron in the tetrahedral sphere, a decrease of ~ 0.2 in the octahedral sphere, and a decrease of ~ 0.01 inside the La sphere. A radial distribution of this shift in charge would look very similar to that of ScH_2 as shown in Figs. 4 and 5 of Ref. 15. A similar analysis of charge transfer for LaH_3 is also contained in Table I. The self-consistent charge inside the La and tetrahedral spheres is nearly identical to that for LaH_2. The additional hydrogen adds just a bit over one electron to the octahedral sphere relative to LaH_2, and the total charge within this sphere is just slightly less than for the overlapping neutral atoms. Thus the octahedral site can be considered neutral, as has been suggested previously.[18,19]

IV. DISCUSSION OF EXPERIMENT AND THEORY

In this section we review the relevant experimental results and discuss their significance in view of previous work and the calculations presented in this paper. Although the discussion will focus on the stoichiometric compounds for which our calculations apply, we also consider illuminating experiments over the entire lanthanum hydride system. To approach the interesting question of the ground state of LaH_3 it is useful as well to understand the dihydride and the changes induced by the addition of hydrogen.

A. Optical properties

Photoemission and optical experiments together with band theory have been very successful in establishing the electronic structure of YH_2 and ScH_2.[12–15] Similar experiments have recently been reported for the lanthanum hydride system by Peterman *et al.*[6] From their determination of the optical conductivity $\sigma(\omega)$ for $LaH_{2.04}$, these authors conclude there is a substantial occupation of octahedral sites giving rise to low-energy interband transitions at ~ 0.4 eV; this is consistent with previous studies which showed premature octahedral-site occupation in those dihydrides with nominally CaF_2 structures having large lattice constants.[12,14,27–29] Peterman *et al.* suggest that the rise in their $\sigma(\omega)$ starting near ~ 1.1 eV is associated with the expected onset of interband transitions from the third band at the Fermi level along L-Q-W to the fourth band. Their data also contain two features at energies of 1.9 and 2.3 eV, although the origin of the these features is not discussed. From our calculation (see Fig. 2) the onset transition energy is expected to be 1.75 eV while Gupta and Burger[18] obtain 1.3 eV. The smaller value by Gupta and Burger is due to their use of a strong exchange potential ($\alpha = 1$ in the $X\alpha$ scheme), appropriate for non-self-consistent calculations, which narrows their bands. Both their valence-band width and conduction-band width are 13% smaller than ours. The corresponding onset in ScH_2 was found using thermomodulation experiments[12] at 1.3 ± 0.1 eV compared with a theoretical value of 1.4 eV from self-consistent calculations[15] using the same methods we have used for LaH_2. Thus the rather poor agreement which we obtain with experiment for the onset (1.75 eV vs 1.1 eV) demands a closer look. One might be tempted to believe our bands are too broad, but most any mechanism which

TABLE I. Charge inside muffin-tin spheres for the beginning iteration involving overlapping neutral atoms and the final self-consistent iteration.

	La	H_t	$H_0/\square$
Atom only	54.4419	0.5738	0.7998
LaH_3 overlapping atomic densities	55.0003	0.7972	1.4586
LaH_3 self-consistent	54.9536	0.9946	1.4454
LaH_2 overlapping atomic densities	54.9052	0.7776	0.6199
LaH_2 self-consistent	54.9424	0.9948	0.4236

would narrow the d-like band complex would also narrow the lower two hydrogen-derived valence bands. This would be in direct conflict with the photoemission experiments on $LaH_{1.98}$ also reported by Peterman *et al.*,[6] which indicate a valence-band width of ~6 eV while Fig. 2 indicates a theoretical bandwidth of ~4.2 eV, and Gupta and Burger obtain ~3.7 eV.[18] This incompatible desire to simultaneously widen the theoretical hydrogen-derived bands and narrow the metal d bands may indicate problems caused by the premature filling of octahedral sites which is expected to be substantial because of the large lattice constant of LaH_2. Peterman *et al.* observe a red shift or lowering in energy of interband features in their optical spectra as more octahedral sites are filled. It is possible that the filling of octahedral sites at the $x = 2.04$ concentration has already red shifted the onset of interband transitions and good agreement with the band structure for LaH_2 in the ideal CaF_2 structure should not be expected. Another possible effect resulting from random octahedral-site occupation is the breakdown of k conservation for optical transitions. The theoretical absorption would then show a steep rise beginning at 1.1 eV (as in the experiment) corresponding to transitions from states near E_F to states within the peak in the DOS 1.1 eV above E_F (Fig. 2). Finally, the presence of octahedral hydrogen broadens the hydrogen-derived features in the DOS and accounts at least partially for additional broadening of the hydrogen-induced bands beyond the bandwidth predicted by theory. Indeed it seems remarkable that the total width of the hydrogen-derived bands measured for $LaH_{1.98}$ is as wide as for $LaH_{2.89}$ while the corresponding theoretical bandwidth for stoichiometric $LaH_{2.0}$ is roughly 1.5 times narrower than for $LaH_{3.0}$. Thermomodulation experiments, which have been so useful for understanding the electronic structure of YH_2 and ScH_2,[18,14] would help determine the energy of the critical-point transition $W_2' \rightarrow W_1$.

NMR[27] electron spin resonance (ESR),[28] and neutron scattering[29] experiments may be of value in determining octahedral-site occupation as the hydrogen concentration is varied.

B. Specific heat

Specific-heat measurements for LaH_2 and the pure metal also raise questions concerning possible complications caused by premature octahedral-site occupation. Low-temperature measurements on fcc La metal[30] yield an electronic contribution γ of 11.5 ± 0.3 mJ/mole K^2 corresponding to a DOS at the Fermi level, $N(E_F)$, of 66.4 states/Ry atom. The most recently calculated $N(E_F)$ for fcc La metal is 27.5 states/Ry atom, which implies an electron-phonon enhancement factor λ of 1.42,[31] a value which may be a bit high but is consistent with the high superconducting transition temperature. The reported value of γ, for $LaH_{2.03}$, is 8.5 mJ/mole K^2 corresponding to $N(E_F) = 49.3$ states/Ry cell,[32] while our calculated value is only 11.6 states/Ry cell, implying a ridiculously high value of $\lambda = 3.25$ for a metal which was not found to be superconducting above 0.33 K.[33] As expected with narrower bands than ours, Gupta and Burger find a higher $N(E_F)$, 15.05 states/Ry cell,[15] which still requires an enormous λ of 2.28 and is far from their determination of $\lambda = 0.13$ for LaH_2 using the approach of Gaspari and Gyorffy.[34] Using the value of λ, 0.13, and our $N(E_F)$ we would expect an experimental γ value of only 2.27 mJ/mole K^2. This would be much more in line with the trend found experimentally for the dihydrides of Sc, Y, and Lu, where γ values for the pure metals of 10.33, 8.2, and 8.19 mJ/mole K^2 are reduced to 1.95, 1.92, and 2.17 mJ/mole K^2 for the corresponding dihydrides.[35] These give a ratio of (γ of metal/γ of dihydride) of 5.3, 4.3, and 3.8 for Sc, Y, and Lu, respectively, which compares with our "theoretical" ratio for La of $11.5/2.27 = 5.1$ as opposed to the experimental ratio of $11.5/8.54 = 1.35$. We believe this represents a serious discrepancy between the reported γ value and both our calculations and the experimental trends found for other dihydrides. Either the experimental value (based on data[32] only between 5.5 and 10.5 K) is in error, or the premature filling of octahedral sites has introduced another mechanism (tunneling) which also yields a linear term in the low-temperature specific heat. We do not believe the electronic structure of the ideal LaH_2 could be modified sufficiently by octahedral-site occupation to account for the discrepancy.

Very precise low-temperature specific-heat experiments on LaH_3 and LaD_3 have just recently been completed and further complicate the situation.[9] The LaD_3 sample exhibited four sharp λ-type anomalies at 211, 230.5, 233.5, and 274.3 K, while the LaH_3 sample showed slightly broader anomalies at 230 and 270 K which are believed to correspond respectively to the 211-K transition and the two transitions of 230.5 and 233.5 K of LaD_3.[9] The shift in transition temperature is due to the smaller vibrational amplitude of the deuterium. The transitions near 290 K in LaD_3 probably correspond to additional ordering of the deuterium nuclei.[9,36] while the transition at 211 K is associated with the metal-to-semiconductor phase change.

C. Electrical resisitivity

Experiments measuring the electrical resistivity provide valuable information related to the electronic states at the Fermi level, and such measurements have been made for a number of rare-earth hydrides. Libowitz has given a review of this work through 1972.[3] Although increased disorder and a lower DOS at E_F are characteristic of the dihydride when compared to the metal, neither difference is influential in determining the electrical resistivity of the material. In fact, the room-temperature resistivities of the dihydrides are much smaller than those of the pure metal.[1,37,38] This behavior is not surprising; the decrease results from the electronic states at the Fermi energy being insensitive to the tetrahedral-site disorder and from the increase in acoustic-phonon frequencies or hardening of the elastic force constants which accompanies the bonding of the hydride. For a simple model[39] the resisitivity is proportional to average atomic displacement, $\sim T/(M\Theta_D^2)$. The Debye temperature Θ_D, as measured by specific-heat experiments,[35] essentially doubles in going from the metal to the dihydride, and the phonon frequencies associated with the rare-earth metal increase by 50%.[40,41] Thus a decrease in the room-temperature resistivity is expected.

Upon the addition of hydrogen to the dyhyride the behavior changes, and the resistivity rises steadily as octahedral sites are occupied. At concentration near $x=2.8$ the resistivity rises sharply, and the increase is identified with transition into a semiconducting region. The increase in resistivity beginning near $x=2$ and coinciding with the rapid occupation of octahedral sites is consistent with the predominantly octahedral character of states near the Fermi level [Fig. 4(a)]. Electrons in these states scatter from protons in octahedral sites, but are much less affected by vacancies on tetrahedral sites [Fig. 3(a)].

To investigate the nature of the semiconducting transition, resistivity measurements on CeH_x single crystals with concentrations near $x=2.80$ were made as a function of temperature by Libowitz *et al.*[1] For samples with $x=2.71$, 2.74, and 2.77 there is about a factor-of-3 jump in the resistivity accompanied by a small tetragonal lattice distortion as the temperature is lowered through $T\approx245$ K. At lower temperatures the resistivity decreases as for a metal, but there is considerable scatter in the data (possibly from poor contacts[1]), while increasing the temperature above the transition results in a decrease in resistivity. For the $x=2.81$ sample there is also a jump of about a factor of 5 in the resistivity at $T\approx234$ K, but the resistivity on both sides of the transition behaves as expected for a semiconductor with an activation energy of 0.10 eV for $153\leq T<234$ K and ~0.05 eV for $234<T\leq295$ K. The measurement by Libowitz and Pack on a $CeH_{2.85}$ sample gave similar behavior with activation energies of 0.31 and 0.15 eV, although there was no apparent jump in the resistivity near $T\simeq210$ K when the change of slope takes place. It would thus appear that the activation energy or gap grows larger as the hydrogen concentration increases above 2.80. Therefore the gap near the stoichiometric limit would be expected to be on the order of a few tenths of an eV or greater for $CeH_{3.0}$. For $LaH_{3.0}$, however, our calculations indicate a much smaller gap.

Recently, resistivity measurements on lanthanum hydride crystals have been undertaken in this laboratory by Finnemore and Manzini.[8] Their preliminary results for $LaH_{\sim2.49}$ are shown in Fig. 6 and for $LaH_{\sim2.85}$ in Fig. 7. The data for the lower concentration resemble the behavior expected for an order-disorder transition occurring near $T\simeq270$ K which may be related to an ordering of the hydrogen as observed by NMR on a sample of $LaH_{2.65}$,[42] by neutron diffraction on CeH_x samples,[22] and deduced by Bashkin *et al.* using differential thermal analysis (DTA) on neodymium hydride samples.[43] The data shown in Fig. 6 for the high-concentration sample is at first glance similar to the data for the $CeH_{2.81}$ sample of Libowitz *et al.*[1]; however, the factor-of-2 jump in the resistivity occurs at 196 K and can be characterized in the high-temperature

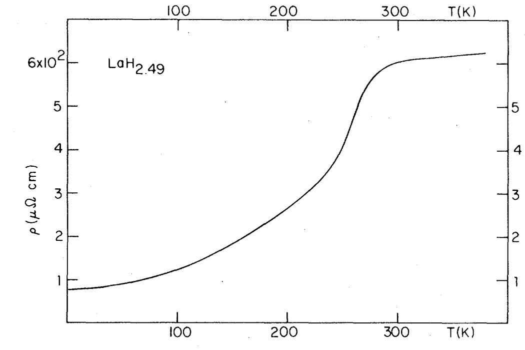

FIG. 6. Electrical resistivity of $LaH_{\sim2.49}$ from Ref. 8.

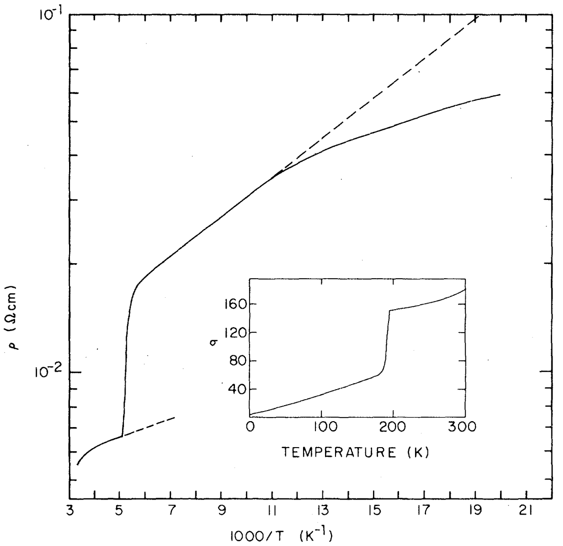

FIG. 7. Electrical resistivity of $LaH_{\sim 2.85}$ from Ref. 8.

region below 300 K by an activation energy of only 5×10^{-3} eV (0.4 mRy), and in the low-temperature region ($100 < T < 196$ K) by an activation energy of 1.1×10^{-2} eV. Also interesting is the behavior as the temperature is lowered below 100 K where the resistivity is seen to saturate near 0.25 Ω cm. This saturation value depends sensitively on hydrogen concentration and could be just the effect of the octahedral holes acting like impurities in a doped semiconductor; however, this is also the predicted behavior for an excitonic insulator with impurities.[44] Resistivity measurements have focused on the hydrogen concentration region near the switch over from metallic to semiconducting behavior. Measurements over a wide temperature range on a single crystal with $x=3.0$ would be very valuable, but are tremendously hindered by the extreme brittleness of such samples.

D. NMR results

NMR measurements have been made on LaH_x powder samples spanning the entire concentration range. Schreiber and Cotts performed an extensive investigation on samples ranging from $x=0.78$ to 2.85,[4] and Barnes *et al.* have extended such measurements through $x=3.0$.[7] The results near the dihydride concentration were the first to indicate the premature filling of octahedral sites starting near $x=1.92$. The lanthanum Knight shift at 400 °C shows a steady decrease as hydrogen is added to the dihydride[45] consistent with the decrease of electronic states at E_F. However, rather than going to zero for x approaching 3.0 as anticipated by Schreiber and Cotts, Barnes *et al.* found a significant and constant Knight shift indicative of a metal for temperatures above 210 K and then a transition to semiconducting behavior with the Knight shift becoming vanishingly small at low T.[7] They deduced an activation energy for LaD_3 of 0.10 eV in the semiconducting region. This is larger than the activation energy obtained from the resistivity measurements on the $LaH_{2.85}$ sample (Fig. 7) which means the energy gap increases with hydrogen concentration as already noted for CeH_x.

Although the lanthanum Knight shift for LaD_3 indicates a transition to semiconducting behavior at 210 K, measurements of the spin-lattice relaxation for the proton smoothly followed a Korringa relation down to 77 K, indicative of a metal[7]; however, Barnes and his group have very recently discovered the strong effect of paramagnetic impurities (even at the (1−5)-ppm level) in many hydride samples and now believe the apparent Korringa relation may be due to such impurities.[4,5] From their La line-shape analysis Barnes *et al.* suggest the metal-semiconductor transition at 210 K is accompanied by the random displacement of octahedral D atoms to off-center positions[7]; however, neutron scattering results indicate D-atom displacement occurs near 230 K.[36] There are transitions at both temperatures according to specific-heat measurements.[9] No distortion of the La lattice in this temperature range has been detected by NMR,[46] x-ray,[47] or neutron scattering experiments.[48]

E. Theoretical discussion

In trying to sort out a clear explanation for the experimental data consistent with our calculations we appreciated the observation by Mott which Libowitz used to precede his discussion of the electronic structure of the rare-earth hydrides: "There are almost as many theories of temperature-dependent metal-semiconductor transitions as there are authors."[3] It is not our intention, in this paper at least, to advocate a theoretical model to explain all the phase transitions observed. However, mention should be made of a bold attempt by Kulikov and co-workers at explaining the data via excitonic insulator and Jahn-Teller-type transitions.[20]

The excitonic state or condensation of electron-hole pairs in very-narrow-gap semiconductors or semimetals has been extensively studied theoretically,[21] but has never been confirmed experimentally. In the nearly stoichiometric trihydrides Kulikov suggests that the tetragonal distortion is essentially a Jahn-Teller transition which splits the Λ_3 band along the symmetry line from Γ to L (Fig. 5). The so-called metal-semiconductor (MS) transition is independent of the tetragonal distortion and represents the semimetal to excitonic transformation. The condensation of electrons near l with holes near Γ results in a charge-density wave characterized by a wave vector along the [111] direction. This could explain the [111] off-center displacement of the octahedral hydrogen.[48] These ideas do seem compatible with the data; however, in their theoretical study Brinkman and Rice argue that for semimetals in which there is no direct band overlap the transition to the excitonic state is not favorable.[49] We therefore feel it is more likely that transitions involving small hydrogen displacements are probably not driving the MS transition nor is the transition due to an excitonic phase. The transition for the stochiometric trihydride is probably the first-order transition expected for thermal population of the conduction band in a narrow-gap semiconductor with the carrier concentration as the order parameter.[49]

V. CONCLUSIONS

In spite of the great difficulty in preparing and characterizing samples with respect to hydrogen concentration and octahedral-site occupation, numerous experiments have been made on the lanthanum hydride system. These experiments have provided basic information about the electronic structure and have revealed several phase transitions as a function of temperature and concentration. The work presented in this paper was aimed at establishing a clearer picture of the electronic structure for the stoichiometric compounds. In comparing with optical properties the calculation suggested the premature filling of octahedral sites had a larger effect on properties of LaH_2 than for ScH_2 or YH_2. Also the calculation for the electronic specific heat for the dihydride disagrees with the only reported experimental value, but is consistent with other heat-capacity measurements on dihydrides of Sc, Y, and Lu. The self-consistent calculation for the trihydride yielded a semiconductor with a 0.2-mRy band gap. This is smaller than the only reported experimental value ($\sim$7 mRy) obtained from Knight-shift measurements on LaD_3, but the discrepancy is not unreasonable considering the smallness of the gap. We have also tried in this paper to give an impression of the current experimental situation concerning transitions involving tetragonal distortion of the La lattice, hydrogen displacements, and MS phases. This fascinating wealth of phenomena is just starting to be unraveled both experimentally and theoretically and should certainly serve as motivation for future studies.

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