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Nature of the insulating state in LaH_3

X. W. Wang
Department of Physics, Florida International University, University Park, Miami, Florida 33199

Changfeng Chen
Department of Physics, University of Nevada, Las Vegas, Nevada 89154

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This paper reports a combined first-principles and many-body study of the nature of the insulating state in LaH_3, focusing on the role of the electron correlation, which has been suggested as the mechanism responsible for the observed insulating behavior. The first-principles local-density-approximation (LDA) calculation produces a correct lattice constant but results in a semimetallic ground state, contrary to a recent optical experiment that showed that LaH_3 is an insulator with a gap of 1.8 eV. An extended Hubbard model is constructed for LaH_3 with its parameters extracted from the results of LDA total energy calculations. An exact-diagonalization study is then carried out to study the effect of the many-body correlation. The results show that the model produces an insignificant reduction of band overlap, thus demonstrating that the insulating ground state of LaH_3 is not a Hubbard-type correlation-driven insulator. [S0163-1829(97)51732-2]

The hydrogen-metal system has been the focus of a considerable amount of research activities.[1] Besides important applications such as hydrogen storage, the changes of physical properties as functions of hydrogen concentration and temperature are often the issues of interest. In particular, the metal-insulator transition that occurs in several rare-earth hydrides has been intensely studied.[2,3] Recently, Huiberts *et al.* reported[4] drastic changes of the optical property of LaH_{2+x} with a small amount of hydrogen concentration change. A film of La hydride could switch from a mirror to a transparent window in a few seconds. The technological application of such a reversible fast switching mirror can be far-reaching.

The crystal structure of LaH_3 is cubic, with La atoms forming an fcc lattice, and hydrogen atoms occupying both the tetrahedral and octahedral sites (see Fig. 1). The addition of a hydrogen atom to the La crystal produces three s-character bands below the La d band. There is strong hybridization between the La s band and the hydrogen s band that causes a large gap in the s band complex. The conduction bands are the La d bands. A band gap would appear if the bottom of the La d band is above the top of the three occupied s bands. In such a case the La can be viewed as fully ionized.

An early non-self-consistent band-structure calculation on LaH_3 showed[5] that the d band was indeed above the top of the s bands, resulting in a direct gap of 1.6 eV. However, later self-consistent calculation showed[2] convincingly that the early success was fortuitous. In fact, to date no self-consistent calculation based on local-density approximation has produced an insulating ground state for the rare-earth trihydrides.

The possibility of lattice distortion or hydrogen displacement causing a gap has been studied.[6] It was found that even with large hydrogen displacement, there is still no gap in the LDA ground state. It was proposed[6] that the ground state of trihydrides is semimetallic with low density of states, and that Peierls instability of the lattice causes an excitonic ground state, in which the electrons and holes are localized, leading to the insulating state. However, the nature of this excitonic state is not well understood, and it is generally expected that the excitonic gap would be small. However, the optical and other experiments as discussed by Huiberts *et al.*[4] have clearly demonstrated that the ground state is an insulator with a gap of 1.8 eV.

In light of the failures of LDA calculations in producing a band gap, in particular the lack of a gap after extensive LDA calculations on lattice distortion and hydrogen displacement, it is generally believed that the insulating state is caused by the electron correlation effects. However, to quantitatively approach the problem from first principles is prohibitively complicated. Recently, Ng *et al.* calculated[7] the electron hopping parameters in the hydrogen sublattice using a correlated molecular wave function of H_2. They then estimated the effect of the crystal field on the hopping parameters,

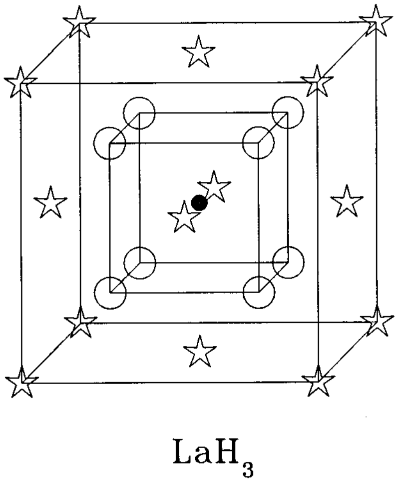

FIG. 1. Crystal structure of LaH_3. The stars show the fcc La lattice, while open circles are the tetrahedral hydrogen atoms. Only one octahedral hydrogen is shown as the filled circle.

assuming that the La and H are point charges. It was shown[7] that the crystal field reduces the hopping parameters by 46%, and the reduction is large enough to narrow the valence bands and open a gap, making LaH_3 insulating.

In this paper, we report a study of LaH_3 using a combination of LDA and many-body calculation schemes. A similar approach was employed in the study of the insulating behavior of alkali atoms adsorbed on a GaAs(110) surface with satisfactory results.[8] Our approach is to construct a realistic model Hamiltonian in the Hubbard formalism with its parameters extracted directly from LDA calculations. The goal is to investigate whether such a realistic model can capture the electron correlation that is responsible for the insulating behavior. The results show that the electron correlation in the model has little effect on opening up the insulating gap, thus indicating that LaH_3 is not a Hubbard-type correlation-driven insulator.

We model the system with an extended Hubbard model with on-site and nearest-neighbor intersite interaction terms. The single-particle spectrum is described by an orthogonal tight-binding (TB) model. Although charge-density analysis showed[2] that there is a considerable amount of charge on the La site, the top of the valence band is dominated by hydrogen character. Accordingly, our TB model has three sites per unit cell centered on the hydrogen atoms. The Hamiltonian is

$$\begin{aligned} H=&\sum_{i\in tet,oct;\sigma}\epsilon_i c^\dagger_{i\sigma}c_{i\sigma}+\sum_{ij;\sigma}t_{ij}c^\dagger_{i\sigma}c_{j\sigma}\\ &+\frac{1}{2}\sum_{i\sigma}U_i c^\dagger_{i\sigma}c_{i\sigma}c^\dagger_{i-\sigma}c_{i-\sigma}+\sum_{\langle ij\rangle;\sigma\sigma'}K_{ij}c^\dagger_{i\sigma}c_{i\sigma}c^\dagger_{j\sigma'}c_{j\sigma'}. \end{aligned} \tag{1}$$

Here the ϵ's are the on-site energies for tetrahedral and octahedral sites, and U and K are the on-site and the nearest-neighbor intersite interaction terms.

With six electrons per unit cell the H bands are fully occupied. The excitation energy can be obtained by calculating the energy cost of removing one electron from the system. In the mean-field limit, our model gives a negative excitation energy, reflecting the fact that the LDA ground state is metallic. The goal of this work is to examine if many-body interaction, as described in the Hubbard formalism, can open a gap in the excitation spectrum.

The standard local-density functional approach is used to calculate the electronic structure and total energy. A norm-conserving pseudopotential method[9] is used to generate La pseudopotential. A smoother hydrogen pseudopotential is formed to reduce the high Fourier component. Plane waves up to a kinetic energy of 20 Ry are used to expand the electronic wave functions. A grid of 19 k points in the irreducible Brillouin zone (BZ) is used throughout.

To test the LDA setup, the equilibrium lattice constant of LaH_3 was determined by minimizing the total energy. The lattice constant was found to be 10.6 a.u., in good agreement with other LDA calculations.[3] After obtaining the equilibrium lattice constant, the band structure is calculated (Fig. 2). The calculated band structure is also in good agreement with earlier LDA studies.[2,3] The main feature is the three hydrogen-induced bands formed below the La d band. The overlap between these bands and the La d band is about 1.2 eV, making the ground state metallic. The overlap we found is larger than earlier calculations,[2] which could be due to the different LDA exchange-correlation schemes used.

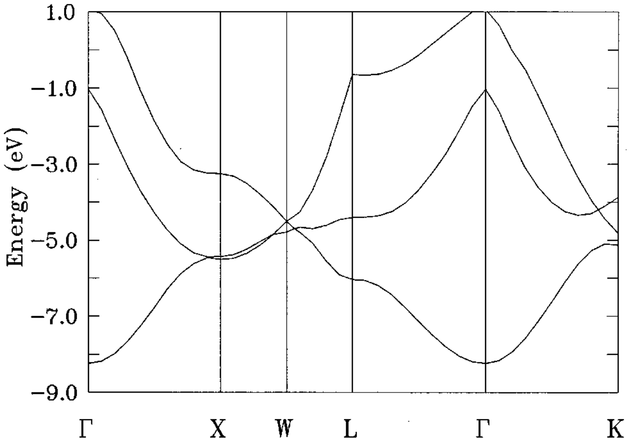

FIG. 2. Band structure of LaH_3, obtained from the LDA calculation.

A typical procedure to determine the specific TB model that is sufficient to describe the system is to include parameters up to a certain neighboring distance, and then determine their value by least-squares fitting to the first-principles band structure. To make sure that the parameters determined through such a fitting scheme are physical, we have analyzed the symmetry of the LDA bands and performed TB fitting in each symmetry subbands.

We first performed TB fitting to the band structure of LaH_2, where there is no octahedral hydrogen. There are only two hydrogen-induced bands and we started with a TB model with hopping parameters up to third neighbor. Notice from the structure (Fig. 1) that there are two inequivalent hopping parameters along the [111] direction, one across the La and the other across the (empty) octahedral site. So the TB model with up to third neighbor has four hopping parameters. Our fitting results show that a good fit can be achieved with only two hopping terms. They are the nearest neighbor hopping along the [100] direction and the third neighbor hopping along the [111] direction across the La. We label them t_1 and t_2, respectively. It is easy to see that t_2 is important because of the positive La ionic potential. The TB band structure is given by the following 2×2 matrix:

$$\begin{pmatrix} \epsilon_t & t_1\alpha(\mathbf{k})+t_2\beta(\mathbf{k}) \\ t_1\alpha(\mathbf{k})+t_2\beta^*(\mathbf{k}) & \epsilon_t \end{pmatrix}. \tag{2}$$

Here $\mathbf{k}$ is the k vector $(2\pi/a)(k_x,k_y,k_z)$, and

$$\alpha(\mathbf{k})=\sum_{i=x,y,z}2\cos(\pi k_i), \tag{3}$$

$$\beta(\mathbf{k})=4\left\{\prod_{i=x,y,z}\cos(\pi k_i)-i\prod_{i=x,y,z}\sin(\pi k_i)\right\}. \tag{4}$$

The LaH_3 band structure is fitted with four hopping parameters. The additional parameters are the octahedral to tetrahedral hopping along the [111] direction, t, and the octahedral to octahedral hopping along the [110] direction, t_o. The TB Hamiltonian is

$$\begin{pmatrix} \epsilon_t & t_1\alpha(\mathbf{k})+t_2\beta(\mathbf{k}) & t\gamma(\mathbf{k}) \\ t_1\alpha(\mathbf{k})+t_2\beta^*(\mathbf{k}) & \epsilon_t & t\gamma^*(\mathbf{k}) \\ t\gamma^*(\mathbf{k}) & t\gamma(\mathbf{k}) & \epsilon_o+t_o\chi(\mathbf{k}) \end{pmatrix}, \tag{5}$$

where $\gamma(\mathbf{k})$ and $\chi(\mathbf{k})$ are defined as

$$\gamma(\mathbf{k})=4\left\{\prod_{i=x,y,z}\cos\left(\frac{\pi}{2}k_i\right)+i\prod_{i=x,y,z}\sin\left(\frac{\pi}{2}k_i\right)\right\} \tag{6}$$

and

$$\chi(\mathbf{k})=4\{\cos(\pi k_x)\cos(\pi k_y)+\cos(\pi k_y)\cos(\pi k_z)+\cos(\pi k_z)\cos(\pi k_x)\}. \tag{7}$$

With four hopping parameters (t_1, t_2, t, and t_o) and on-site energies for the octahedral and tetrahedral sites, a very good TB band structure is obtained (see Fig. 3). The values of the hopping parameters, together with the on-site energies and interaction parameters, are listed in Table I. We have noticed that the values of t_1 and t_2 for LaH$_3$ are the same as for LaH$_2$, so the presence of octahedral hydrogen does not alter significantly the hopping parameters between tetrahedral hydrogen atoms. This is consistent with LDA charge analysis[2,3] which shows that octahedral hydrogen behaves very much like a neutral hydrogen atom added to the octahedral site without affecting the crystal field. This also demonstrates the importance of self-consistency in estimating the crystal-field effect on the hopping parameters.

The interaction parameters U and K are determined through fitting the mean-field energy of the model Hamiltonian (1) to the LDA total energy as described previously.[8] Various occupation schemes are employed and self-consistent LDA total energies are calculated. The total energies are then fitted to a polynomial, and the coefficients of the second order are equated to the energy terms in the model Hamiltonian that are second order in occupation numbers. To ensure the occupation of either the octahedral or the tetrahedral sites the k-point W in the BZ is used. At this k point, the tetrahedral and octahedral orbitals belong to different representations of the symmetry group so there is no mixing. Only symmetric charge-transfer schemes are used to avoid creating an artificial electric dipole field affecting the total energy. And for schemes that add or remove electrons from the system, a compensating uniform charge background is added to ensure charge neutrality.

The first scheme adds charge to either the tetrahedral or octahedral sites, the second scheme adds charge to both sites, and the last scheme transfers charge between tetrahedral and octahedral sites. For each scheme the amount of charge added is kept at less than 0.6 electrons per unit cell, while the remaining 5.4 electrons are distributed on a grid of 19 k points used for lattice-constant calculations. It is found, as expected, that the U term for the octahedral and tetrahedral site are of the same size at 0.9 eV. Interestingly, the intersite interaction parameter, K, is negative at -0.08 eV. Table I lists all the hopping and interaction parameters. The reliability of the parameters is estimated based on the variations due to different occupation schemes. The accuracy for on-site U value is within 0.1 eV, and for K it is within 0.04 eV.

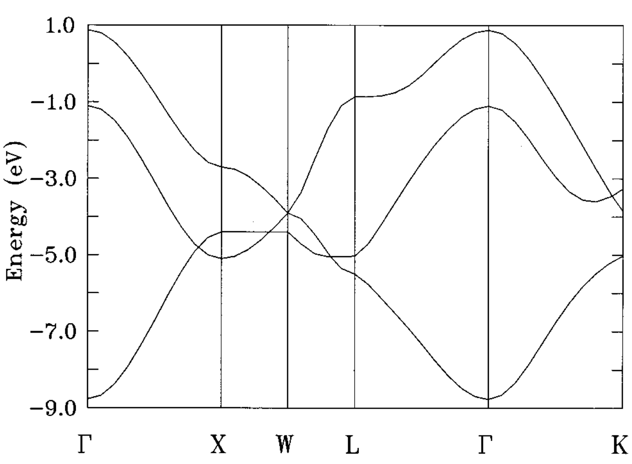

FIG. 3. Band structure of LaH$_3$, obtained from the tight-binding model.

With all the Hamiltonian parameters extracted from LDA calculations, we proceed to study the many-body correlation effects using a symmetry projected exact diagonalization approach.[10] Since only the H sites are explicitly considered in the present model, we choose a H-only cluster with symmetry compatible with the fcc crystal structure. A 24-hydrogen (8 octahedral and 16 tetrahedral) cluster with periodic boundary conditions is used in the calculation. It samples the Γ, three X, and four L points of the fcc BZ. The symmetry projection procedure maps out states belonging to different irreducible representations of the space group of the cluster, which is the direct product of the point group T_d and the translational group of the periodic cluster structure. Hamiltonian matrices of definite symmetry indices are constructed and numerically diagonalized. In this work, we focus on the effects of the many-body interaction on the bandwidth and the band edge at Γ. A significant band narrowing or downward shift of the top of the H band at Γ, or both, will open a gap and produce an insulating state.

We have calculated the many-body electronic structure using the parameters in Table I. The results show that interaction indeed reduces the bandwidth and lowers the top of the band (at Γ point), as expected from the many-body correlation in general. The top of the band is lowered by 0.23 eV and the overall bandwidth (as measured at the Γ point) is reduced by 0.38 eV. However, the magnitude for both is too small to produce an insulating state, since the overlap between the La $5d$ band and the top of the H band is 1.2 eV in the LDA calculation. A careful analysis of the calculated results revealed that the on-site interaction U has limited influence on the many-body electronic structure, while K affects significantly both the bandwidth and the band edge. Nevertheless, there is no gap produced when the parameters

TABLE I. The single-particle and interaction parameters for Hamiltonian (1), all in units of eV. The symbols are explained in the text.

ϵ_t	-3.9	ϵ_o	-3.6
t_1	-0.2	t_2	-0.4
t	-0.7	t_o	0.2
U	0.9	K	-0.08

were varied within a reasonable range of uncertainty.[11] The sensitive dependence of the shift of the band edge on the K term can be understood by the fact that the negative K increases the energy of a hole on the octahedral site as compared to a hole on the tetrahedral site, and since the top of the Γ point is mainly of the octahedral component, the state lowers when interaction parameters are turned on.

We have performed the exact diagonalization calculations using a 12-hydrogen cluster to check the finite-size effect and have found little difference in the calculated band narrowing and shift of the top of the H band at Γ. This indicates that the finite-size effect is not an issue of concern here. We have also performed the calculation with various TB models for both the 12-hydrogen and the 24-hydrogen cluster. The results are consistent with those presented above, although some slight quantitative differences do exist, as expected.

In summary, we have constructed a realistic model Hamiltonian for LaH_3 with all the parameters extracted from first-principles LDA calculations, and have performed an exact diagonalization calculation to study the role of electron correlation in determining the nature of the ground state. It has been found that the correlation effects, as modeled in the Hubbard formalism, are unable to produce the experimentally observed insulating state. However, it should be made clear that there are two correlation effects in this problem. This work has accounted for the Hubbard-like effect. Another effect is on the effective electron hopping between the hydrogen atoms as pointed out by Ng *et al.* in Ref. 7, which is not included in the present work.

The La d orbit is not explicitly included in the present model. A strong correlation between the valence bands and the d orbit may result in a high quasielectron energy in the La d band and produce a gap. However, we do not think this is a likely scenario. On the other hand, our model only has a single orbit per site, hence the intrasite correlation is not fully included. Although the LDA calculations for interaction parameters have included, to a certain degree, the correlation effect within a site, the dynamical effect may not have been adequately accounted for. Ng *et al.* calculated[7] the hopping parameters from a correlated molecular wave function, but as mentioned before, it is difficult to include the crystal-field effect in a realistic and self-consistent way. Calculations with fully correlated crystal wave functions using, for example, the variational quantum Monte Carlo method[12] that can treat both the intrasite correlation and crystal-field effects may be able to better address this issue but is beyond the scope of this work.

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