Electronic Structure of Lanthanum Hydrides with Switchable Optical Properties

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Recent dramatic changes in the optical properties of LaH_{2+x} and YH_{2+x} films discovered by Huiberts *et al.* [Nature (London) **380**, 231 (1996)] suggest their electronic structure is described best by a local model. Electron correlation is important in H^- centers and in explaining the transparent insulating behavior of LaH_3. The metal-insulator transition at $x \sim 0.8$ takes place in a band of highly localized states centered on the H vacancies in the LaH_3 structure. [S0031-9007(97)02330-2]

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Recently Huiberts *et al.* [1] reported dramatic changes in the optical properties of lanthanum and yttrium hydride films with changing hydrogen content, e.g., films that switch from a shiny mirror to a yellow transparent window in a time of order seconds. Although many metal-insulator transitions are known [2], it is very unusual and potentially of technological importance that the transition leads to spectacular effects in the visible. Huiberts *et al.* [1] point out that the electronic structure that underlies this behavior is poorly understood—indeed standard local density approximation (LDA) calculations do not predict a metal-insulator transition at all [3,4]. In this Letter we examine the role of electron correlation in these hydrides and argue it justifies a local description that derives from an ionic starting point.

The structural changes are especially small in the LaH_{2+x} films. The La atoms always form a fcc lattice with two H atoms always occupying tetrahedrally coordinated sites. As x changes from 0 to 1, the octahedrally coordinated site goes from empty to fully occupied and a good metal (LaH_2) evolves to a transparent insulator (LaH_3). The metal-insulator transition in the dc conductivity [1] occurs at an intermediate concentration, $x \sim 0.8$, far removed from a lightly doped semiconductor. This in turn suggests highly localized states associated with H vacancies in LaH_3. The key challenge is, first, to understand why the structural changes with changing hydrogen content are remarkably small, but the changes in spectral properties are dramatic at energy scales up to the visible, and, second, to understand the origin of the highly localized states at intermediate concentrations. We shall address these issues in turn.

We have performed self-consistent LDA calculations on LaH_2 and LaH_3. In agreement with previous results [3] there are two sets of states—low energy primarily $1s$-H states and higher energy states of mainly $5d$-La character. These results suggest assigning a formal valence H^-. In LaH_2 the H^- bands are filled leaving one electron per unit cell in the $5d$-La conduction bands leading to metallic behavior [3]. In LaH_3 the H^- bands can hold all six electrons per unit cell, but in the LDA calculations there is overlap between the H^- and $5d$-La bands leading to a semimetal rather than the observed transparent insulator.

The LDA calculations give an interesting insight why atomic H is easily incorporated in this structure. The net charge change between LaH_2 and LaH_3 is found to be remarkably small. The charge at the octahedral site [within a sphere of 2.533 atomic units (a.u.) radius] in LaH_3 is $1.588e$, while the charge in an empty sphere of the same radius in LaH_2 is $0.568e$. From the viewpoint of the charge distribution, LaH_{2+x} can be interpreted as neutral H atoms moving into or out of the octahedral interstitial sites, with negligible changes in the lattice structure [5].

The neutral H and H^- ions are difficult cases for LDA. To study the H^- ion, a careful treatment of the correlation between the two electrons is required [6–8] to obtain the binding energy ($\simeq$0.7 eV). This led us to examine the effect of correlations on the width of the H^- bands. The form of the H^- bands in a many body theory is determined by the spectrum of the states obtained by removing an electron from a lattice of H^- ions. For a single pair of ions a ${H_2}^-$ ion results. The ground state manifold of ${H_2}^-$ splits into odd and even parity states and this splitting determines the hopping matrix element of a single hole, $t(d)$. Note ${H_2}^-$ is a bound negative ion [9] for proton separations $d > 3$ a.u.—the range of interest here. Knowing $t(d)$ we can extend the calculation to a lattice of H^- ions (ignoring for the moment the La ions) using standard tight binding methods and obtain the band structure of a hole quasiparticle in a lattice of H^- ions.

Let $\psi_i(1,2)$ be the ground state wave function of two electrons in H^-, and $\phi_i(1)$ be the ground state of hydrogen atom. The three electron states of the ${H_2}^-$ with odd ($-$) and even ($+$) parities may be constructed using the single site (i and j) states: $\Psi_\pm = \Phi_{i,j} \pm \Phi_{j,i}$, where $\Phi_{i,j} = A[\psi_i(1,2)\phi_j(3)]$, and A is an antisymmetrizer. The corresponding energies are given by $E_\pm = \langle\Psi_\pm|h|\Psi_\pm\rangle/\langle\Psi_\pm|\Psi_\pm\rangle$, where h is the Hamiltonian for the ${H_2}^-$ system, including the kinetic and Coulomb energies [10]. We choose a variational state of Chandrasekhar

[7] for H^-:

$$\psi(1,2) = (e^{-ar_1-br_2} + e^{-ar_2-br_1})(1 + c|\vec{r}_1 - \vec{r}_2|)\chi\,, \tag{1}$$

where r are the electron radial coordinates, χ is the spinor for a singlet, and $a = 1.075$, $b = 0.478$, $c = 0.312$ in a.u. This simple wave function describes two intra-atomic correlated electrons well, and its energy is very close to the best estimate of Hylleraas [8] involving 24 variational parameters. The states for ${H_2}^-$ thus constructed become exact in the limit $d \gg 1$. The effective hopping integral for an electron between two H sites can be obtained, $t(d) = (E_- - E_+)/2$. At $d = 4$, the ground state energy estimated in this method is $E_- = -1.032$ a.u., very close to the best available result of -1.034 a.u. for ${H_2}^-$ using the more complicated variational method [9]. This suggests that the ground state of ${H_2}^-$ at these separations is very well described by a linear combination of H^- and H states, and justifies our approach.

The two shortest interhydrogen distances in LaH_3 are those between nearest neighbor (nn) tetrasites and octasites (denoted as $H_{\rm tet}$ and $H_{\rm oct}$) and nn tetrasites which are denoted as t_2 and t_1, respectively. These distances are $\sqrt{3}\,a_0/4$ and $a_0/2$ (a_0: the lattice constant), respectively (4.58 and 5.29 a.u.), giving values $t_2 = -0.748$ eV and $t_1 = -0.523$ eV. The H^- bands in tight binding representation are the eigenstates of the Hamiltonian

$$\mathcal{H}_{\rm tb} = \sum_{\vec{k}} c^\dagger(\vec{k})M(\vec{k})c(\vec{k})\,, \tag{2}$$

where $c^\dagger(\vec{k})$ is a three-component vector, representing the three H states in a unit cell, and

$$M(\vec{k}) = \begin{pmatrix} \varepsilon_t & t_1\alpha(\vec{k}) & t_2\beta(\vec{k}) \\ t_1\alpha(\vec{k}) & \varepsilon_t & t_2\beta^*(\vec{k}) \\ t_2\beta^*(\vec{k}) & t_2\beta(\vec{k}) & \varepsilon_o \end{pmatrix}, \tag{3}$$

with

$$\alpha(\vec{k}) = \sum_{\tau=x,y,z} 2\cos(k_\tau/2)\,, \tag{4}$$

$$\beta(\vec{k}) = \sum_{\sigma_1,\sigma_2=\pm 1} e^{i(\sigma_1 k_x + \sigma_2 k_y + \sigma_1\sigma_2 k_z)/4}. \tag{5}$$

Note we now use the lattice parameter a_0 (5.60 Å) as the length unit. The atomic energy levels at $H_{\rm tet}$ and $H_{\rm oct}$ (ε_t and ε_0) we estimate using the LDA calculations as follows. At the high symmetry Γ point, one can identify in the LDA a four by four matrix corresponding to the three H and one La-6s states in a unit cell of the fcc lattice. We can map this matrix onto a three by three submatrix describing the effective three H bands with the same three lower eigenenergies. The highest energy band, representing the La-6s state, is pushed well above the bottom of the La-5d conduction band due to the strong hybridization, and can be projected out. We define the bottom of the La-5d conduction band in the LDA to be zero energy level, and thus obtain the LDA values of $\varepsilon_t^{\rm LDA} = -3.2$ eV, and $\varepsilon_0^{\rm LDA} = -2.6$ eV. In the LDA, the H^- ion eigenvalue lies above the energy zero, so that the actual atomic energy levels in our appraoch should be lower than the LDA values by 0.7 eV. We thus obtain $\varepsilon_t = -3.9$ eV, and $\varepsilon_0 = -3.3$ eV.

In Fig. 1(a) the resulting energy bands are plotted. We find a small gap, which is not sufficient for a transparent insulator. However, we have neglected the La^{3+} ions in estimating (t_1, t_2). In an ionic picture the La^{3+} ions generate a crystal field at the H sites whose effect can be estimated as follows. Let the interaction between an electron in ${H_2}^-$ and the other ions be $h' = -\sum_{\vec{R}} Z(\vec{R})e^2/|\vec{r} - \vec{R}|$, with $Z = 3$ for La^{3+}, and $Z = -1$ for H^- ions, and $\vec{R}$ the ion position. The energies for ${H_2}^-$ of two $H_{\rm tet}$ are modified, due to the crystal field, to $E'_\pm$, which is obtained by adding h' to h. The reduction of t_1 due to the crystal field is found to be $\delta t_1 = 0.230$ eV, where the contribution from within a cubic unit cell is 0.085 eV. The estimate for t_2 is more complicated because of the Madelung constants. Assuming the same percentage reduction, we

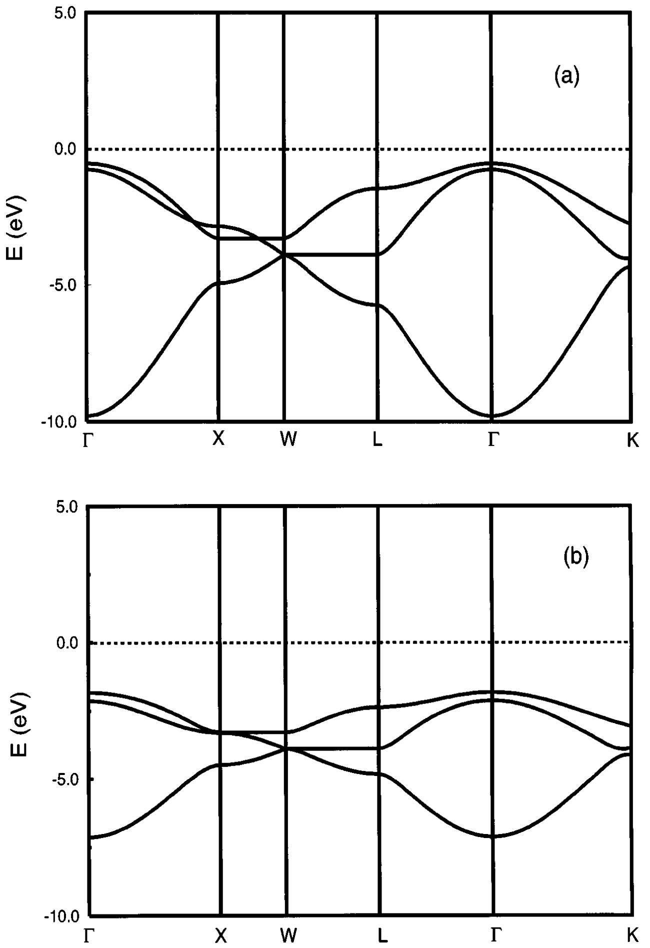

FIG. 1. The valence bands of LaH_3 calculated from the single hole hopping in H^-. The dashed lines indicate the bottom of the conduction bands in LDA. (a) Without crystal fields. (b) With crystal fields.

estimate the hoppings in the presence of the crystal field, $\tilde{t}_1 = -0.293$ eV, $\tilde{t}_2 = -0.419$ eV. The estimate is based on an ideal ionic approach, and neglects the screening effect, so that the actual reduction of t's are surely smaller. With the new values $(\tilde{t}_1, \tilde{t}_2)$, we obtain strongly narrowed H^- bands (see Fig. 1) and a transparent insulating ground state. This idealized ionic approach overestimates the narrowing and neglects the effects of hybridization on the hopping integrals. These, however, are weak at the top of the H^- bands and are mainly important only at energies well below the Fermi energy.

Turning to the metal-insulator transition in LaH_{2+x} as x increases, we can view it starting either at the metallic $(x = 0)$ or insulating $(x = 1)$ end points. In the former case, the introduction of a neutral H atom into a H_{oct} site creates a $s = 1/2$ magnetic impurity, which couples to the conduction $5d$-La electron spins. The effective Hamiltonian is a Kondo model,

$$\mathcal{H}_{\rm eff} = \sum_{\vec{k},\sigma} \varepsilon(\vec{k}) d^{\dagger}_{\vec{k},\sigma} d_{\vec{k},\sigma} + J \sum_{i} \vec{S}_i \cdot \vec{s}_i \,, \tag{6}$$

where i runs over all the occupied H_{oct}, $\vec{S}$ and $\vec{s}$ are the electron spins of the neutral H and of the conduction electron [annihilation operator d_k with energy $\varepsilon(\vec{k})$] states. The latter represent linear superposition of the La-$5d$-e_g states around three degenerate X_1 points, which is of s-wave symmetry and can couple to the $1s$-H state. The antiferromagnetic coupling $J \sim 0.7$ eV in free space [11], and may be renormalized by a numerical factor in hydrides. In this Kondo description conduction electrons are captured by the neutral H atoms at H_{oct} sites to form tightly bound singlets and LaH_3 is viewed as a Kondo insulator with a large band gap.

Starting from insulating LaH_3, removing neutral H atoms causes vacancies at octasites (H^V_{oct}) which donate an electron to the conduction band. In a conventional semiconductor such as in the doped Si, the impurity state is described by an effective mass theory, and the result is a hydrogenlike bound state with a large effective Bohr radius a^*_B of the order of 100 Å due to the light mass and the large dielectric constant. The critical impurity concentration x_c at which the system becomes metallic is given by Mott criterion $x_c \sim (l/a^*_B)^3$, where l is the interatomic distance. Because of $a^*_B \gg l$, x_c is very small (0.1% for Si). The vacancy state in LaH_{2+x} is very different, however. Experimentally, it is found that the semiconducting states extend to $x = 0.25$ for lanthanum hydrides, and to an even larger value for yttrium hydrides [1,12]. Below we shall show that the vacancy state in lanthanum hydrides is an octahedral s-like La-e_g state with an extremely small size.

The La-$5d$-e_g and H_{oct} electrons hybridize strongly to form bonding (mainly H) and antibonding (mainly e_g) states. A vacancy of H_{oct} breaks the bonds locally and the e_g electron becomes locally nonbonding, which has a much lower energy than the antibonding e_g states away from the vacancy. Therefore, in addition to serving as a positive charge center as in conventional n-type semiconductors, H^V_{oct} creates a potential well for the e_g state electron. The latter is nonperturbative, and is responsible to the unusual concentration dependence of the semiconductor.

Consider an s-symmetric octahedral e_g state (S-state hereafter) around a H^V_{oct} as shown in Fig. 2. The H^V_{oct} vacancy breaks the bonds on the octahedron and reduces the anitbonding energy of the S-state. This S-state is very localized because the neighboring octahedral s-state is antibonding and has a much higher energy. We can estimate the depth of the potential well, V_0, within a perturbation theory up to the second order in $V_{sd\sigma}$, the hopping integral between an atomic $d_{3z^2-r^2}$ and its neighboring H_{oct} with the orbits towards each other. Let Δ be the atomic energy difference between La-$5d$ and H_{oct}, then $V_0 = -6V^2_{sd\sigma}/\Delta$. This is 2/3 of the antibonding energy $9V^2_{sd\sigma}/\Delta$ at the X_1 point in LaH_3. The latter is estimated to be ~6 eV from LDA [13], so that $V_0 \sim -4$ eV. We may also compare this S state to the nonbonding t_{2g} state. The latter is the lowest energy conduction state of LaH_3, and would be a starting point for an effective mass theory in conventional semiconductors. The S state has much better kinetic energy as evidenced from LDA for LaH_2 [3,13,14]. A more detailed calculation based on a tight binding model of nn hopping between La sites estimates the kinetic energy gain of the S state over the t_{2g} state is ~0.9 eV. This is about enough to compensate for the loss of the antibonding energy of the S state with the neighboring occupied H_{oct} atoms, which is $1.5V^2_{sd\sigma}/\Delta \sim 1$ eV. The S state has better Coulomb attraction to the vacancy, because its orbit is oriented towards the central effective charge. Therefore

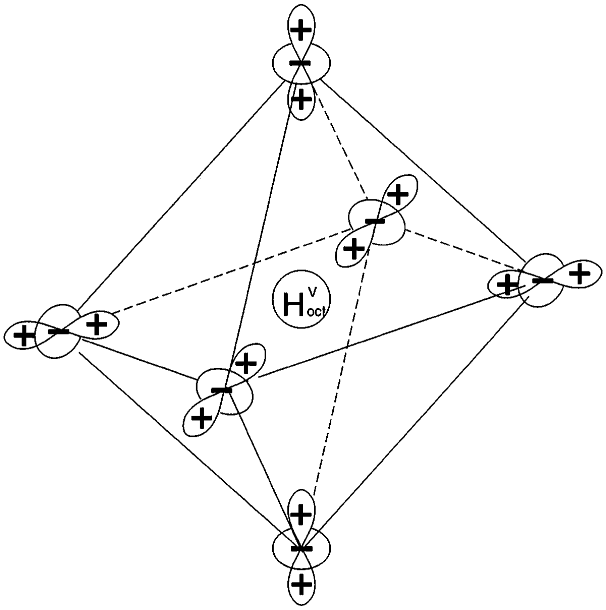

FIG. 2. Diagrammatic illustration of the proposed H_{oct} vacancy state in LaH_3. The center circle represents a H vacancy, forming an n-type impurity center. The surrounding orbits represent phases for the local s-like octahedral La-$5d$-e_g state.

the S state should have lower energy than the t_{2g} state, and be the lowest energy state for H_{oct} vacancy. The localized vacancy state here is similar to the carbon vacancy state in TiC, where the C vacancy leads to the well localized impurity states [15]. We emphasize that the potential well generated by the H_{oct} vacancy is primarily short ranged, different from the ideal long-range Coulomb force. The effective radius of the impurity state is only half of the lattice constant.

The localized nature of the vacancy state in LaH_{2+x} is consistent with the temperature dependence of the resistivity data. Shinar *et al.* [12] reported a phase transition at temperature around 250 K for x between 0.8 and 0.9. Above that temperature the resistivity shows variable range hopping; below that temperature, it is caused by coherent state of the defect band. Localized states are a prerequisite for variable range hopping. The coherent state accompanies the onset of superlattice order in the H_{oct}^V vacancies.

The precise nature of the transition in optical properties is not well understood yet. Since the dc conductivity is insulating only in the disordered state of H_{oct}^V, and is metallic in the ordered one, we argue that the transition should be a disorder driven Anderson transition, instead of a Mott type correlation driven transition.

In conclusion, we have studied the electronic structure of LaH_{2+x} starting from the H^- ionic picture emphasizing the electron correlation. Our calculations give an insulator for LaH_3, in agrement with the recent experiments. We propose that a H vacancy in LaH_3 introduces an s-wave state centered at the vacant octasite, with a highly localized form. This state of the vacancy explains why the semiconducting behavior LaH_{2+x} is so stable over a wide range of concentration x ($0.8 < x < 1$), and is consistent with the experimental observed variable range hopping mechanism for the resisitivity in these materials. The recent experiments of Huiberts *et al.* [1] have raised many interesting questions in the study of metal hydrides. The precise nature and criterion of the optical transition from transparent to reflecting needs be examined. The role of quantum diffusion of the hydrogen at low temperatures, the order-disorder transitions, and the interactions between octahedral H vacancies are all interesting open questions.

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