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Electronic structure of the $LiMgH_3$ class of compounds: Cluster calculations

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The lattice spacing and the electronic structure of $LiMgH_3$, $NaMgH_3$, and $LiCaH_3$ have been calculated by modeling these hydrides as clusters with modified perovskite structure and using the self-consistent-field linear-combination-of-atomic-orbitals molecular-orbitals theory. This yields lattice constants of 3.47, 3.53, and 4.07 Å for $LiMgH_3$, $NaMgH_3$, and $LiCaH_3$, respectively. The electronic structure of $LiMgH_3$ is characteristic of an insulating material. The gap at the Fermi energy in the density of states of $LiMgH_3$ is, however, significantly less than that of $LiBeH_3$ and is insensitive to moderate changes in the interatomic spacing. On the other hand, $LiCaH_3$ and $NaMgH_3$ are both found to exhibit metallic character with the Fermi energy lying in regions of high electron density of states.

I. INTRODUCTION

Recently, Overhauser[1] suggested that $LiBeH_3$, if metallic, could have an electron density as high as that in metallic hydrogen and thus could be a high-temperature superconductor. Following that suggestion, a number of electronic-structure calculations[2–6] have been performed on this system. These have included clusters modeled as fragments of the bulk[2,3] as well as band-structure calculations[4–6] using a variety of approximations. The electronic densities of states calculated using all these methods exhibit a large gap at the Fermi energy signifying an insulating material. No recent experimental investigations are known to the authors that could verify the predictions of these electronic-structure studies. A part of the reason for the lack of experimental evidence is that $LiBeH_3$ is hard to prepare since beryllium is highly poisonous.

In a later paper Overhauser[7] suggested that $LiMgH_3$ might be a better candidate for study. The idea that a $LiBeH_3$ class of light nontransition-metal hydrides could have a high electron density approaching even that of metallic hydrogen is certainly a fascinating one. Although the theoretical studies[2–6] in $LiBeH_3$ have proved the contrary, we have calculated the electronic structures of $LiMgH_3$, $NaMgH_3$, and $LiCaH_3$ to see if any of these could exhibit metallic behavior. We have assumed these compounds to have modified pervoskite structure as proposed by Overhauser.[1] We have calculated the equilibrium lattice constants for these systems self-consistently by minimizing the total energy.

The expectation that $LiMgH_3$, $NaMgH_3$, and $LiCaH_3$ could become metallic stems from the fact that the Na atom is bigger than the Li atom, as are Mg and Ca compared to Be. Consequently, the electronic orbitals of Na, Mg, and Ca are more extended than those in Li and Be. This is illustrated in Fig. 1. The more extended the electron orbitals, the greater the possibility that they can overlap with orbitals at the adjoining sites. It is this overlap that is necessary for metallic bonding and/or delocalization of electrons.

In Sec. II we describe the details of our calculations. The results are discussed in Sec. III and a summary of conclusions is presented in Sec. IV.

II. CALCULATIONS

The total energy, equilibrium lattice constant, electronic density of states, and the electron-charge density distribution in $LiMgH_3$, $NaMgH_3$, and $LiCaH_3$ were calculated using the molecular-cluster approach based upon the self-consistent-field linear-combination-of-atomic-orbitals molecular-orbitals (SCF-LCAO-MO) theory. In this approach the bulk crystal is modeled by a cluster of finite number of atoms fixed at their crystallographic positions. No approximation is made concerning the shape of the potential well around the atom.

The procedure of using clusters as models of solids[8] has

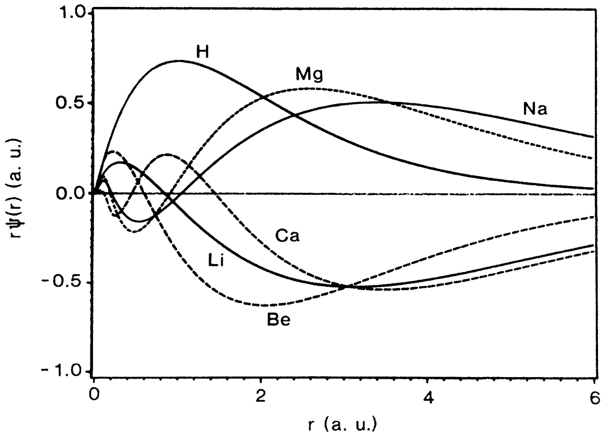

FIG. 1. Plot of the valence-state wave functions $r\psi(r)$ of H, Li, Be, Na, Mg, and Ca.

been successfully used for many years. The only difficulty with this approach is that the limitations in computing resources restrict the size of the cluster that can be treated within an *ab initio* self-consistent scheme. Thus the question of how well a cluster electronic structure mimicks its bulk characteristics always remains a nagging problem. Our experience has shown that the electronic structure of the central atom of a cluster surrounded by two to three nearest-neighbor shells of atoms represents a bulk atom very well. On the other hand, the equilibrium lattice constant is not sensitive to the cluster size and can be determined with the use of a minimal size cluster.

In the molecular-orbitals theory the wave function of the system is represented by a Slater determinant formed out of molecular orbitals, Ψ_i, which are expressed as linear combinations of atomic orbitals, ϕ_j, namely

$$\Psi_i(\mathbf{r}) = \sum_j C_{ij}\phi_j(\mathbf{r}) \ . \tag{1}$$

These $\phi_j(\mathbf{r})$'s are atomic orbitals centered on different atoms corresponding to the cluster-point-group geometry. The coefficients C_{ij} are obtained variationally by solving the Schrödinger equation

$$H\Psi_i = \varepsilon_i \Psi_i \tag{2}$$

self-consistently. The Hamiltonian, H, is given in the conventional atomic units as

$$H = -\tfrac{1}{2}\sum_i \nabla^2 + V_{\text{Coul}} + V_{\text{ex}} + V_{\text{corr}} \ . \tag{3}$$

The kinetic and Coulomb energy terms are treated exactly while the exchange and correlation terms can be obtained from density-functional[9] or quantum-chemical[10] methods.

The equilibrium lattice constant was obtained from the minimum in the total-energy curve plotted as a function of the lattice constant. For this purpose the total energy of five-atom clusters of $LiMgH_3$, $NaMgH_3$, and $LiCaH_3$ were obtained self-consistently in the unrestricted Hartree-Fock (UHF) technique.[10] It has been well established[11] that correlation has little influence on the equilibrium-interatomic distance. The GAUSSIAN-86 software[12] was used for the computations of the total energies. The Gaussian basis sets used for this purpose included 1*s*, 2*s*, and 2*p* functions for the H atoms. For the Li atoms, 3*s* and 3*p* functions were added, and for the Na and Mg atoms 4*s*, 4*p*, and 3*d* functions were also included. For Ca atoms, the corresponding additions were for 5*s*, 6*s*, 7*s*, 8*s*, and 5*p* functions.

The electron density of states and charge densities on much larger clusters were calculated using the density-functional theory and the discrete variational method (DVM).[13] In this technique, numerical basis functions were used. The bases for H and Li were 1*s*, 2*s*, and 2*p*. For Mg atoms, the 1*s* orbital was kept frozen and variation was performed with 2*s*, 2*p*, 3*s*, and 3*p* functions. Tests with 3*d* functions showed that there was virtually no effect on the properties due to these functions. Therefore, for the sake of economy, *d* functions were not used for the final calculations. For Na and Ca atoms, 1*s*, 2*s*, and 1*s*, 2*s*, and 2*p* were kept frozen, respectively. The valence electrons were represented by 2*p*, 3*s*, and 3*p* for Na and 3*s*, 3*p*, 3*d*, and 4*s* for Ca. The molecular energy levels, ε_i, were obtained by solving Eq. (2) self-consistently using the DVM.

In a LCAO-MO calculation, the energy levels are discrete. It is only when the clusters become extremely large that the discrete levels broaden and form bands resembling the bulk band structure. Since in most cluster models the sizes are small due to computational limitations, the electron density of states, $D(\varepsilon)$, is constructed from the molecular-orbital energies ε by representing[13] each discrete level by a Lorentzian of width γ, namely

$$D(\varepsilon) = \sum_{\nu,n,l} d_{nl}^{\nu} = \sum_{p} \frac{g_p\gamma/\pi}{(\varepsilon-\varepsilon_p)^2+\gamma^2} \ , \tag{4}$$

where g_p is the degeneracy of the level ε_p. The broadening parameter γ is conventionally taken to be equal to 0.2 eV while ν defines an atom and (n,l) define the quantum states of the *p*th molecular orbital.

III. RESULTS

A. $LiMgH_3$

The equilibrium lattice constant of $LiMgH_3$ was obtained by minimizing the total energy on a five-atom cluster having the formula unit $LiMgH_3$. The Li and Mg atoms occupied the corner and body center of a cubic lattice respectively, while hydrogen atoms were placed at the nearest face-centered sites. The total energies for this system are plotted as a function of lattice constant a (defined as the distance between two corner atoms) in Fig. 2. A minimum occurs at $a = 3.47$ Å, which is significantly larger than our calculated[2] value of 2.98 Å in $LiBeH_3$. This is understandable since Mg is a bigger atom than Be. The calculation was repeated for the same cluster using the DVM (Ref. 13) and the local-density approximation to exchange and correlation. The energy minimum obtained with this method corresponded to a lattice constant of 3.48 Å.

To ensure that the electronic structure of $LiMgH_3$ can

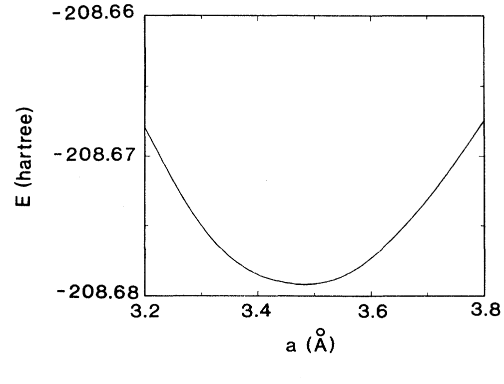

FIG. 2. Variation of total energy as a function of lattice constant a in $LiMgH_3$.

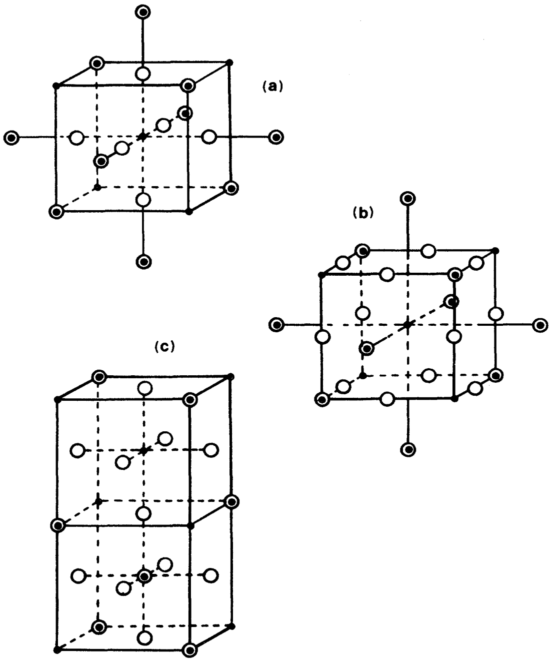

FIG. 3. Geometries of (a) 21-, (b) 27-, and (c) 25-atom clusters used in the DVM calculations. The open circles represent hydrogen atoms. The solid circles and the double circles represent the two different types of metal atoms used in each case.

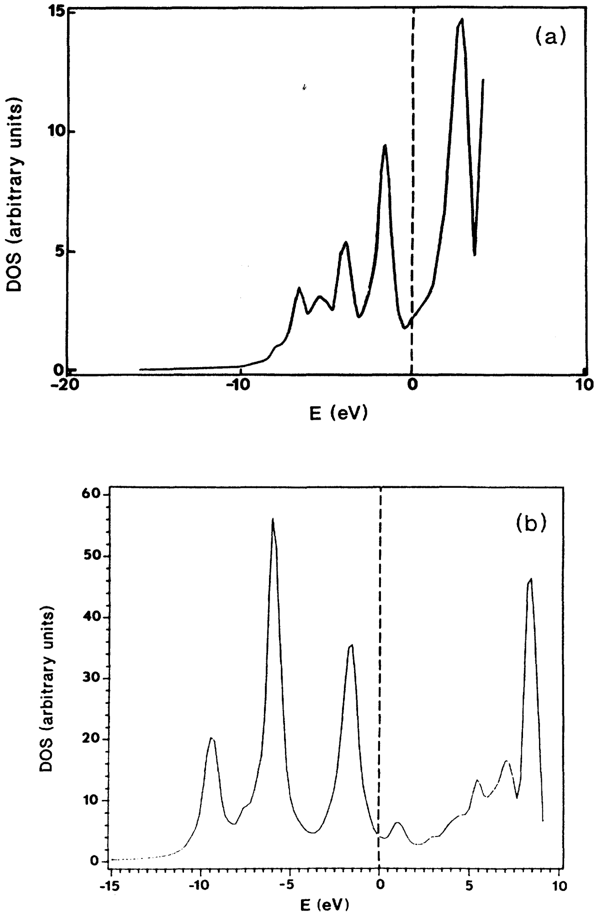

FIG. 4. Total density of states (TDOS) in (a) $LiMgH_3$ and (b) $LiBeH_3$. The Fermi level is shown by a dashed line.

be reliably obtained from cluster models, we have considered larger clusters consisting of more than 20 atoms. Since the HF calculations are computationally demanding and correlation plays an important role on the electronic structure, we have adopted the density-functional theory within the local-density approximation to calculate the electronic energy levels, density of states, and charge densities. The calculations have been performed using the DVM. We have used three different model clusters (as in our earlier work[2] on $LiBeH_3$). These are shown in Fig. 3. The geometry of 21-atom clusters $LiLi_4Mg_4H_6Mg_6$ and $MgMg_4Li_4H_6Li_6$, having T_d symmetries and being composed of a central Li(1) or Mg(1) atom with all the neighbors up to a distance a (a being the lattice constant), is shown in Fig. 3(a). Figure 3(b) represents 27-atom clusters $LiLi_4Mg_4H_{12}Mg_6$ and $MgMg_4Li_4H_{12}Li_6$, having T_d symmetry and composed of a central Li(2) or Mg(2) atom and its nearest neighbors up to a distance of a. Figure 3(c) shows the 25-atom cluster $LiMgHH_2H_8Li_4Li_2Mg_4Mg_2$, with C_{2v} symmetry composed of all atoms encasing two perovskite cubes of side a placed atop each other. This nomenclature of the clusters is to emphasize the fact that the various subsets of like atoms are treated as distinct from each other for electron charge and potential analysis. We have chosen the size and geometrical arrangements of these clusters to ensure that the central atoms in all the clusters [i.e., Li(1), Li(2), Mg(1), Mg(2), or H] have at least all their nearest neighbors. This is necessary to minimize the effect of surface atoms on the site-decomposed density of states of the central atom.

The local density of states around Li(1), Li(2), Mg(1), Mg(2), and H sites were calculated in a manner similar to that in Eq. (4). Since these atoms represent the central sites in the clusters presented in Figs. 3(a), 3(b), and 3(c), we believe that these local densities of states (LDOS) are mostly bulklike. The total density of states (TDOS) was calculated by adding the LDOS for Li(1)+Li(2)+Mg(1)+Mg(2)+6H such that it represented $LiMgH_3$ composition. This is plotted in Fig. 4(a) and compared with the corresponding result for $LiBeH_3$ in Fig. 4(b). We note from Fig. 4(a) that a gap of approximately 1 eV exists in the density of states at the Fermi energy in $LiMgH_3$ and is much reduced from the corresponding gap in Fig. 4(b) for $LiBeH_3$. The density of states at the Fermi energy, however, appears to be small but finite. This originates from the broadening of the MO levels just below the Fermi energy as described in Eq. (4). This, however, does not signify that $LiMgH_3$ is metallic. As a matter of fact, the gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital is about 1 eV as mentioned and $LiMgH_3$ is not metallic.

An analysis of the electronic charge-density profile also leads to the same conclusion. In Figs. 5(a) and 5(b) we plot the electron-density contours along the (110) plane containing Li and Mg at the center of the cluster, respectively. Note that there is a strong bond between H and the central Li and/or Mg atom and that other atoms do not take much part in bonding. These contours bear a strong resemblance to the electron-density profile in $LiBeH_3$.[2]

We have also calculated the TDOS in $LiMgH_3$ for two other lattice constants, one contracted and the other expanded by 5% from their equilibrium values noted earlier. The results are plotted in Figs. 6(a) and 6(b). There is very little change in these TDOS from that in Fig. 4(a). Therefore, it could be safely concluded that moderate pressure cannot alter the electronic properties of $LiMgH_3$.

The electronic structure of $LiMgH_3$ can also be studied by analyzing the net charge on the atoms. From an analysis of the Mulliken population we find that the charges on Li, Mg, and H are 2.36, 11.61, and 1.35, respectively. Both Li and Mg lose electrons while H gains electrons. However, the electronic structure of H in this hydride cannot be identified as an H^- ion as in the case of insulating lithium hydride. In $LiMgH_3$ the H-induced state lies about 8 eV below the Fermi edge while the energy of the 1*s* orbital in the H^- ion is approximately at -0.1 eV.

B. $LiCaH_3$ and $NaMgH_3$

While $LiMgH_3$ is found to be insulating like $LiBeH_3$, the fact that the "band" gap in the former is considerably reduced from that in the latter has prompted us to investigate heavier hydrides having the same modified perovskite structure and similar chemical composition. We have studied $NaMgH_3$ and $LiCaH_3$ as model systems. Na is bigger than Li as Ca is bigger than Mg. However, the chemistry of Na and Ca is similar to that of Li and Mg, respectively. Since bigger atoms have more extended electronic states (see Fig. 1), it is logical to assume that in the above "heavier" metal hydrides, the electronic overlap may be significantly larger than that in $LiMgH_3$, thus causing a narrowing of the gap. This could also be seen from the bond lengths and binding energies of the corresponding dimers. Using the UHF procedure for exchange and the Möller-Plesset scheme[10,12] for correlation we have calculated these quantities for LiH, BeH, NaH,

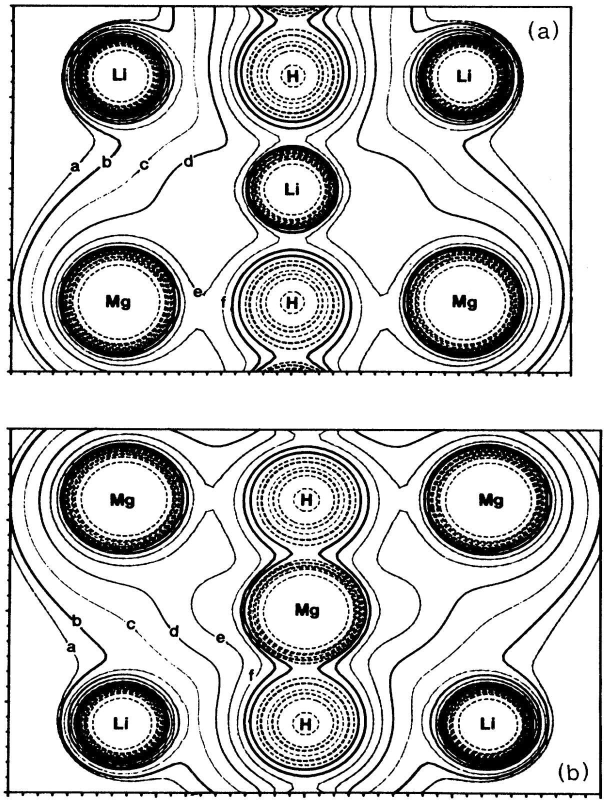

FIG. 5. Electron charge-density distribution along the (110) plane of $LiMgH_3$ (21-atom cluster) with (a) Li at the center and (b) Mg at the center. The values of the densities are denoted $a-f$ representing 0.005, 0.006, 0.008, 0.11, 0.015, and 0.02 atomic units, respectively.

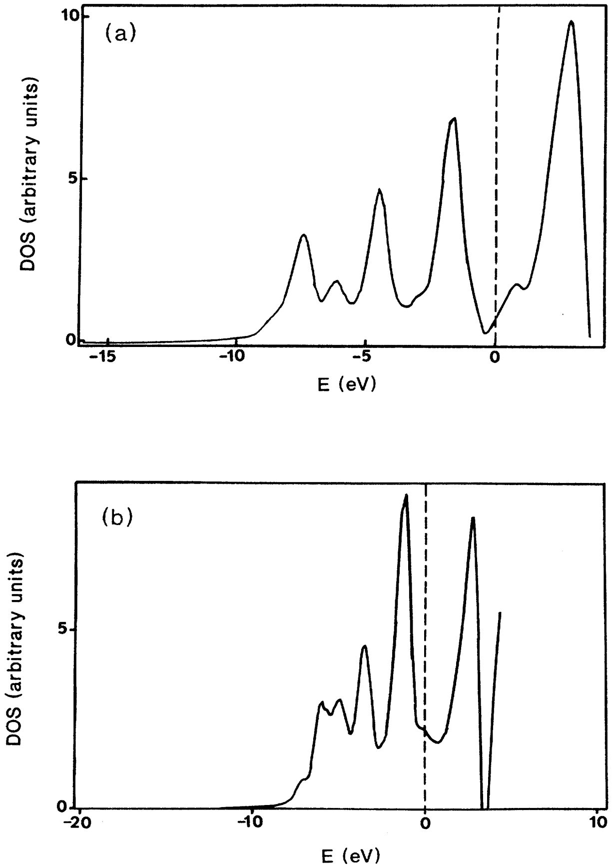

FIG. 6. TDOS in $LiMgH_3$ cluster (as given in Fig. 4) with the lattice constant (a) contracted and (b) expanded by 5% from the equilibrium value.

TABLE I. Binding energies, bond lengths, and Mulliken populations at various sites of the dimers LiH, BeH, NaH, and MgH.

System	Bond length (Å)	Binding energy (eV)	Population at metal site	Population at H site
LiH	1.59	2.33	2.64	1.36
BeH	1.34	2.00	3.81	1.19
NaH	1.91	1.55	10.68	1.32
MgH	1.74	1.14	11.78	1.22

and MgH dimers. The results are given in Table I. Note that the bond length in NaH is longer than that in LiH, as expected. However, the binding energy of NaH is significantly smaller than that of LiH. This reduced binding implies that the electrons in NaH are less likely to be concentrated along the bond than those in LiH. The comparison between BeH and MgH is similar. However, the comparison between the results of LiH and BeH (or similarly with NaH and MgH) illustrates the effect of electron localization on the binding energy and bond length more clearly. Be and Mg atoms have closed shells and their electrons are more localized than those of Li and Na, respectively (see Fig. 1). Thus, the binding energy and bond length of BeH (MgH) are smaller than those in LiH (NaH). These systematics are also reflected in the Mulliken charge on these atoms. The charge transfer from Be and Mg to H is less than those from Li and Na to H. These differences in the electronic structures of the dimers of these systems suggest that the electronic structure of bulk $NaMgH_3$ and $LiCaH_3$ can be significantly different from that in $LiMgH_3$ and $LiBeH_3$.

The equilibrium lattice constants of $NaMgH_3$ and $LiCaH_3$ were calculated, as mentioned before, using five-atom clusters and the UHF procedure. The total energies of these clusters as functions of lattice constants are plotted in Figs. 7(a) and 7(b), respectively. From the minima in these energies we determine the equilibrium lattice constants to be 3.53 and 4.07 Å for $NaMgH_3$ and $LiCaH_3$, respectively. Using these distances, the electronic structures of $LiCaH_3$ and $NaMgH_3$ were calculated by modeling these as clusters of 21, 27, and 25 atoms with Li(1), Li(2), Na(1), Na(2), Mg(1), Mg(2), Ca(1), Ca(2), and H atoms occupying central locations (see Fig. 3). The TDOS for these systems were calculated using the DVM similar to that described above for $LiMgH_3$ and are plotted in Figs. 8 and 9 for $NaMgH_3$ and $LiCaH_3$, respectively. Note that in both systems the nature of the density of states around the Fermi energy is characteristically different from that discussed in Fig. 4. In addition, the Fermi energy lies in a region of significantly high electron density of states. These features are characteristic of metallic behavior.

It is also interesting to compare the electron-density profiles among these three hydrides. In Figs. 10(a) and 10(b) we plot the electron-density contours on the (110) plane of $NaMgH_3$ with Na and Mg at the center of the cluster. Similar plots are given for $LiCaH_3$ with Li and Ca at the center in Figs. 11(a) and 11(b), respectively.

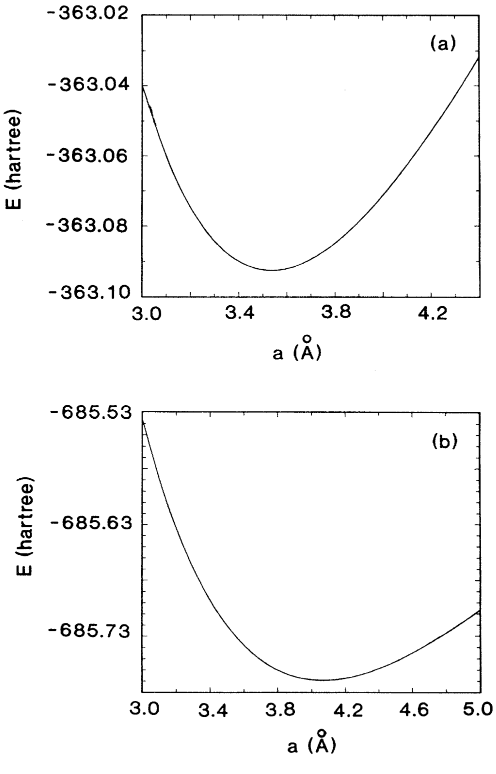

FIG. 7. Variation of total energy as a function of lattice constant in (a) $NaMgH_3$ and (b) $LiCaH_3$.

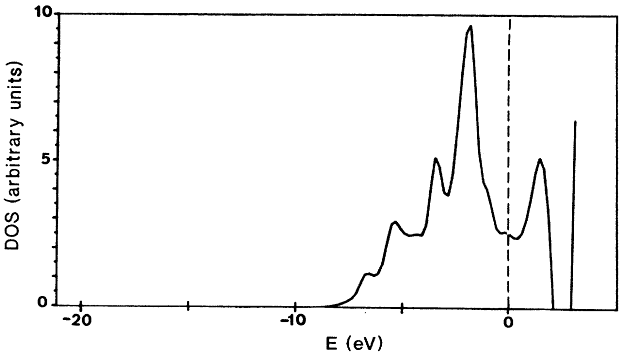

FIG. 8. The TDOS in $NaMgH_3$.

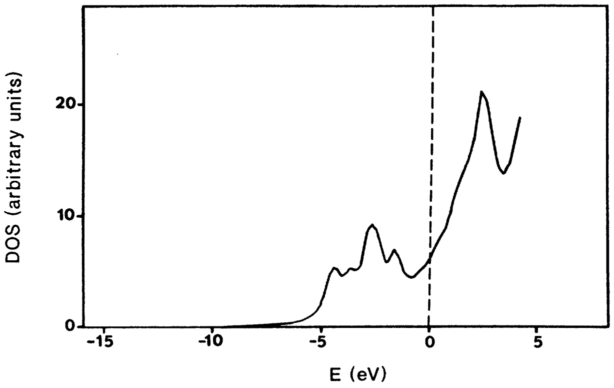

FIG. 9. The TDOS in $LiCaH_3$.

First we compare the electron-density contours in Figs. 5(a), 10(a), and 11(a). As one moves from $LiMgH_3$ to $NaMgH_3$ and $LiCaH_3$, more and more metal atoms take part in bonding. The electron density along the chainlike corridor increases simultaneously. Similar behavior is apparent from a comparison of Figs. 5(b), 10(b), and 11(b). Results of the density of states and electron-density contours of $NaMgH_3$ and $LiCaH_3$ indicate that the metallicity of these hydrides is due to the increased concentration of electrons along the chain and increased participation of metal atoms in the bonding process.

IV. CONCLUSIONS

In summary, we have carried out electronic-structure calculations of $LiMgH_3$, $NaMgH_3$, and $LiCaH_3$. The re-

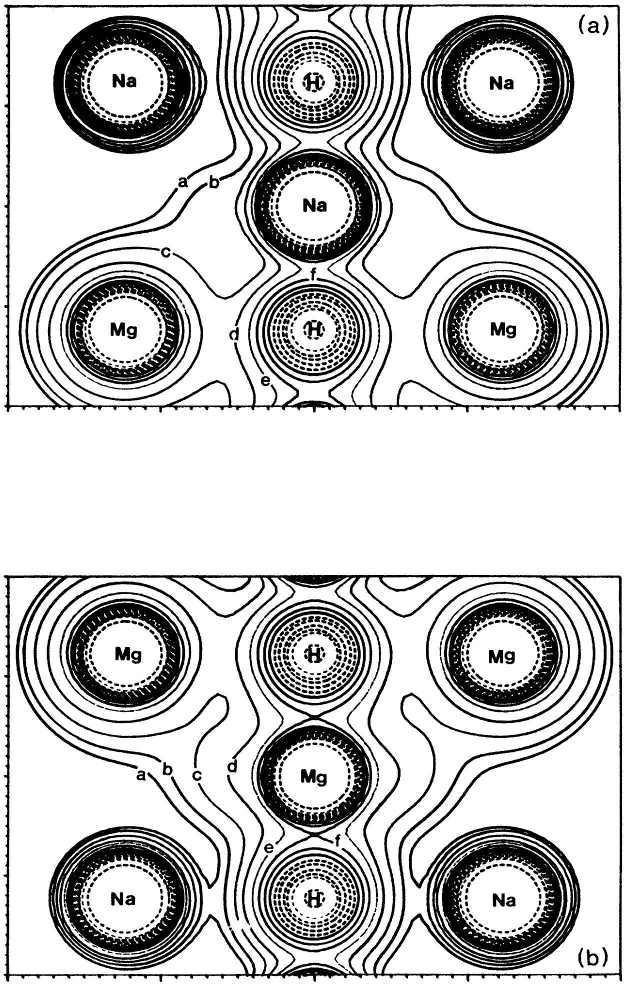

FIG. 10. Electron-density profile in 21-atom clusters of $NaMgH_3$ with (a) Na and (b) Mg at the center. The values of the densities are denoted by letters as described in Fig. 5.

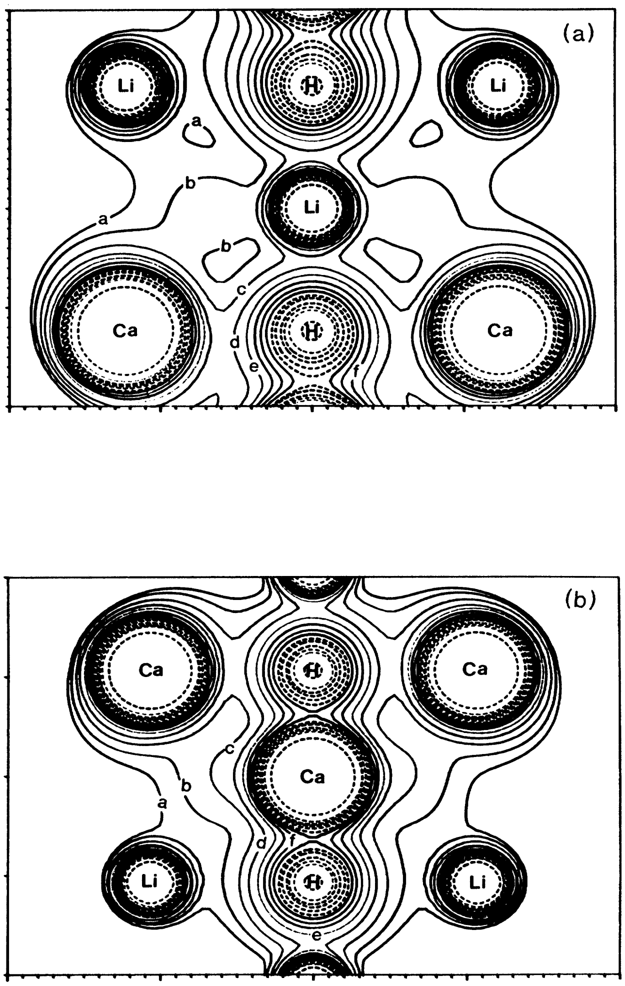

FIG. 11. Electron-density profile in 21-atom clusters of $LiCaH_3$ with (a) Li and (b) Ca at the center. The values of the density contours are as given in Fig. 5.

sults indicate that $LiMgH_3$ is an insulator, although its band gap is substantially reduced from that in $LiBeH_3$. The electron density of states and electron density profiles in $NaMgH_3$ and $LiCaH_3$, on the other hand, indicate that these compounds could be metallic. We are carrying out band structure calculations in these systems using the LMTO method.[14] The results are planned to be published in a forthcoming paper. To our knowledge, these compounds have not yet been synthesized. It will certainly be of interest to see if these compounds crystallize in the proposed modified perovskite structure and if they are metallic.

ACKNOWLEDGMENTS

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