PHYSICAL REVIEW B **69**, 155103 (2004)

Electronic structure of the complex hydride $NaAlH_4$

A. Aguayo* and D. J. Singh

Center for Computational Materials Science, Naval Research Laboratory, Washington, DC 20375, USA

(Received 1 January 2004; revised manuscript received 6 February 2004; published 9 April 2004)

Density-functional calculations of the electronic structure of the complex hydride $NaAlH_4$ and the reference systems NaH and AlH_3 are reported. We find a substantially ionic electronic structure for $NaAlH_4$, which emphasizes the importance of solid-state effects in this material. The relaxed hydrogen positions in $NaAlH_4$ are in good agreement with the recent experiment. The electronic structure of AlH_3 is also ionic. Implications for the binding of complex hydrides are discussed.

DOI: 10.1103/PhysRevB.69.155103 PACS number(s): 71.20.Ps, 61.50.Lt

The complex hydrides, $A_x(M\mathrm{H}_4)_y$, with $A=$Li, Na, K, Mg, Ca, Sr or a mixture of these and $M=$B or Al seem promising for of H storage since they contain very high weight percent of H, and much of the H content can be evolved at moderate temperatures.[1–5] However, hydrogen desorption from these materials is associated with their melts, and they were long viewed as intrinsically noncyclable. However, in 1997 Bogdanovic and Schwickardi reported that with certain metal additions, particularly Ti, $NaAlH_4$ can be cycled.[1] This discovery opened the door for consideration of these complex hydrides as cyclable hydrogen storage materials. However, this result has not been reproduced for other related complex hydrides and understanding of the basic material properties that govern the uptake of H is still not complete. What is known is that hydrogen desorption from $NaAlH_4$ takes place via a two-step process, forming first Na_3AlH_6, Al, and hydrogen and then NaH and Al metal. Desorption is associated with the temperature at which melting occurs. While the Ti addition is often referred to as a catalyst or dopant, the actual role of Ti in enabling the cyclability of $NaAlH_4$ has yet to be established.[6] Possibilities include catalysis as mentioned; modification of the thermodynamics of the decomposition, i.e., the balance between solid-state Ti containing $NaAlH_4$ and the decomposed NaH+Al+Ti mixture; modification of the microstructure of postdecomposition of NaH+Al mixture, e.g., by keeping the precipitated Al and the NaH from segregating over large distances, by enhancing the solubility of Al in NaH, or by the formation of Ti-Al alloys, such as $TiAl_3$, instead of precipitated Al, and others.[2,3,7–12]

Developing understanding of the various phases involved will likely be important for sorting out the physics of cyclable hydrogen storage in this material. Here we start with the simplest of these phases, $NaAlH_4$, by using density-functional calculations of the electronic structure, in comparison with results for NaH and AlH_3. Conventionally, the bonding in $NaAlH_4$ is viewed as that of a salt made of Na^+ cations and AlH_4^- anions, with the internal bonding of the AlH_4^- units being primarily covalent, consistent with the tetrahedral coordination of Al and what is expected in the liquid. We show that the electronic structure of solid $NaAlH_4$ is better described as mixed ionic, i.e., $Na^+Al^{3+}H_4^-$. Solid NaH is found to be ionic as expected. AlH_3 is also ionic but with a smaller band gap. The ionic nature of solid $NaAlH_4$ is understood as a result of long-range Coulomb interactions, implying a greater sensitivity of the electronic structure and therefore bonding of H in $NaAlH_4$ to substitutions and defects, than would otherwise be the case. Further, this provides an explanation for the association between the hydrogen desorption and melting.

The present calculations were done within the local-density approximation (LDA) to density-functional theory, using the general potential linearized augmented plane-wave (LAPW) method with local orbital extensions, as implemented in the WIEN2K code.[13–15] For consistency, the same LAPW sphere radii of $1.7a_0$ and $1.1a_0$ were used for the metal and hydrogen atoms, respectively, in all three compounds. Well-converged basis sets consisting of a LAPW cutoff, $k_{max}=5.91a_0^{-1}$, plus local orbitals were used (the effective dimensionless values of the basis cutoff were $Rk_{max}=6.50$ for H and $Rk_{max}=10.05$ for the metal atoms). The Brillouin-zone samplings were done using the special **k**-point method, with 21, 38, and 84 points in the irreducible wedge for $NaAlH_4$, AlH_3, and NaH, respectively. This was found to be well converged for these insulating materials. Additional calculations were done for $NaAlH_4$ using an independent LAPW code and for different H sphere radii between $1.0a_0$ and $1.3a_0$. The resulting electronic structures were indistinguishable.

$NaAlH_4$ occurs in a tetragonal structure (space group $I4_1/a$) with lattice parameters $a=5.021$ Å, $c=11.346$ Å, and its own structure type, which has two formula units per primitive cell.[16] Recent neutron measurements for $NaAlD_4$ (Ref. 17) confirm this structure, with slightly lower lattice parameters but rather different H positions. NaH occurs in the NaCl structure, with lattice parameter $a=4.88$ Å.[20] AlH_3 occurs in a rhombohedral structure (space group $R\overline{3}c$ or possibly $R\overline{3}$) with hexagonal lattice parameters $a=4.451$ Å, $c=11.766$ Å and two formula units per primitive rhombohedral cell (from neutron and x-ray diffraction).[21–23] In general, the structures of hydrides, particularly the H positions, are difficult to determine because the H has a very small x-ray-scattering factor and samples can differ in H stoichiometry and ordering. On the other hand, the metal atom positions, and especially the lattice parameters, are given to a high precision by diffraction experiments. Accordingly, here we fully relaxed the internal structures using LDA total energies and forces, keeping the presumably reliable experimental lat-

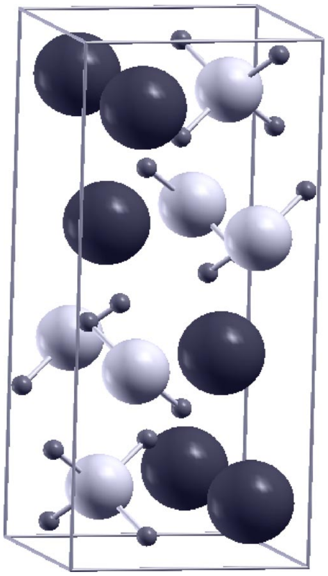

FIG. 1. Crystal structure of tetragonal $NaAlH_4$ with the relaxed atomic positions. The small spheres are H, the large dark spheres are Na, and the large light spheres are Al.

tice parameters fixed at the reported experimental values. For NaH there was no relaxation to do because both atoms are on high symmetry sites. For $NaAlH_4$ we obtain positions differing from the x-ray positions reported in Ref. 16, but in close agreement with very recent neutron results[17] and calculations.[18,19] The relaxed H positions (Wycoff notation, site $16f$) are $x=0.2364$, $y=0.3906$, and $z=0.5451$ as compared to $x=0.2371$, $y=0.3867$, and $z=0.5454$ from neutron scattering. This structure is illustrated in Fig. 1, which clearly shows the AlH_4 building blocks. The Al-H bond length in our structure is 1.652 Å. This is only a little bigger than the sum of the covalent radii of Al and H ($0.37\ \text{Å}+1.18\ \text{Å}=1.55\ \text{Å}$) and would seem to be a reasonable number for covalently bonded AlH_4^- units. For AlH_3 we relaxed in the lower symmetry $R\overline{3}$ space group considered by Zogal *et al.* Our positions differ somewhat from the x-ray structure of Ref. 23, but are consistent with the assignment of $R\overline{3}$ in the absence of H disorder. The Al-H nearest-neighbor distance in our structure is 1.731 Å, which is longer than in $NaAlH_4$ and is also longer than the sum of the Al and H covalent radii. It should be mentioned that this Al-H bond length is close to the value of 1.715 Å, from the structure of Turley and Rinn.[21,24] We also considered $R3$, but obtained no further relaxation (see below).

The calculated LDA band structure and corresponding electronic density of states (DOS) for $NaAlH_4$ are shown in Figs. 2 and 3, respectively. The total DOS is similar to that recently reported by Vajeeston and co-workers,[19] and is also similar to that reported for the related compound $LiAlH_4$.[25] We note that Vajeeston and co-workers used the generalized gradient approximation (GGA) as opposed to the present LDA calculations, indicating that the H positions and electronic structures of these compounds are not sensitive to the choice of LDA or GGA.

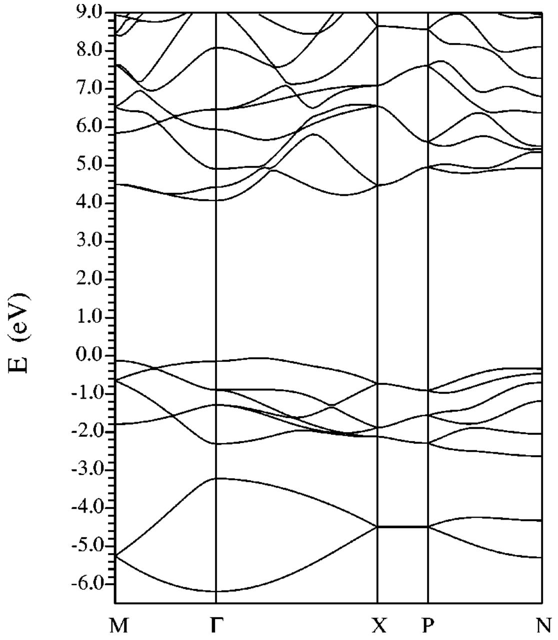

FIG. 2. LDA band structure of $NaAlH_4$ with the relaxed crystal structure. The band gap is between a H derived valence band and metal derived conduction bands.

The band structure has a large ~ 4 eV band gap, separating H derived valence bands from metal derived conduction bands. We emphasize that despite the seeming AlH_4 units in the structure, and the expected covalency of such chemical units, the calculated electronic structure is very ionic. In particular, it can be seen from Fig. 3 that the valence bands are strongly dominated by H, while the conduction bands have very much less H character. The valence bands consist of two crystal-field split manifolds, each ~ 3 eV in width. The calculated DOS of NaH and AlH_3 are shown in Figs. 4 and 5, respectively, along with the projections onto the H LAPW spheres.

Since the $1.1a_0$ spheres are not large enough to fully contain the $1s$ states of H^- ions, the H projection underestimates

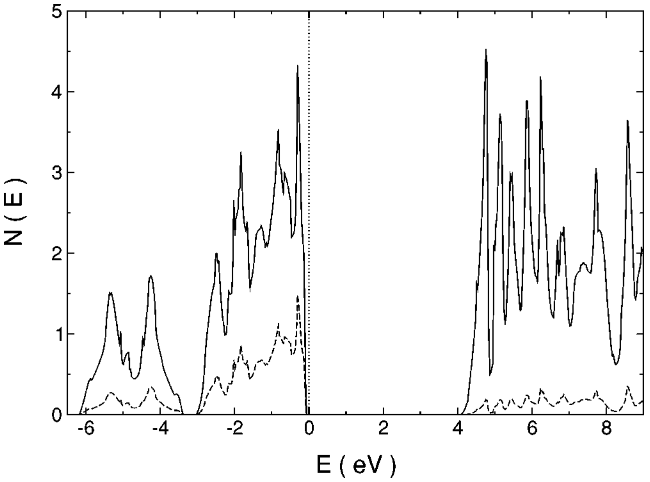

FIG. 3. Electronic density of states and projection onto the H LAPW spheres for $NaAlH_4$, in eV^{-1} on a per formula unit basis. Note the ionic nature shown by the very different hydrogen contributions to the valence and conduction bands.

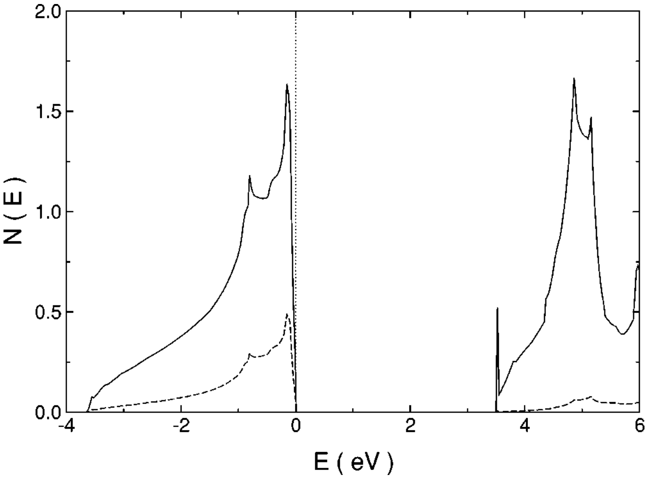

FIG. 4. Electronic density of states (eV^{-1}) and projection onto the H LAPW sphere for NaH.

the H contribution to the electronic structure. However, the ratio between the projections on H from different energy regions gives a good indication of the ratio of the H contributions to the electronic structure in those energy regions. The band structure of NaH is also strongly ionic, with a band gap slightly smaller than that of $NaAlH_4$. Smithson and co-workers[26] reported calculations for the related materials LiH and KH obtaining results which are qualitatively similar to our results for NaH.

AlH_3 is also ionic, but has a smaller ~ 2 eV band gap. The valence band width of AlH_3 is ~ 9 eV. It should be noted that Goncharenko and co-workers[22] had already conjectured that AlH_3 is ionically bonded based on its crystal structure.

Within a covalent picture, the electronic structure of the tetrahedral AlH_4^- complex would be described in terms of four H $1s$ orbitals (one per H) forming σ bonds with the $4sp^3$ hybrids of Al^-. The gap would be formed between the bonding and antibonding combinations. The large 4 eV gap would indicate strong bonding, and so one would expect the H contribution to the conduction bands and valence bands to be roughly the same. Additional Na s character could complicate this picture, but we find no significant Na character in the DOS in the energy window plotted. Clearly, our density of states is not consistent with this covalent model, since the amount of H character in the valence bands is much larger than in the conduction bands.

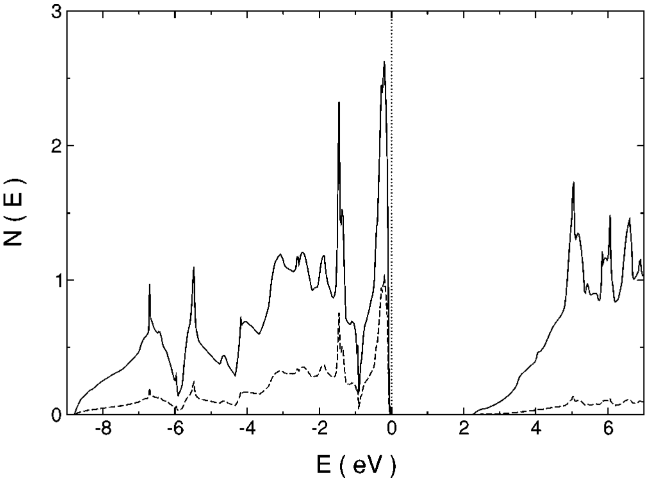

FIG. 5. Electronic density of states and projection onto the H LAPW spheres for AlH_3, in eV^{-1} on a per formula unit basis, using the relaxed crystal structure. Note the smaller band gap but still ionic nature.

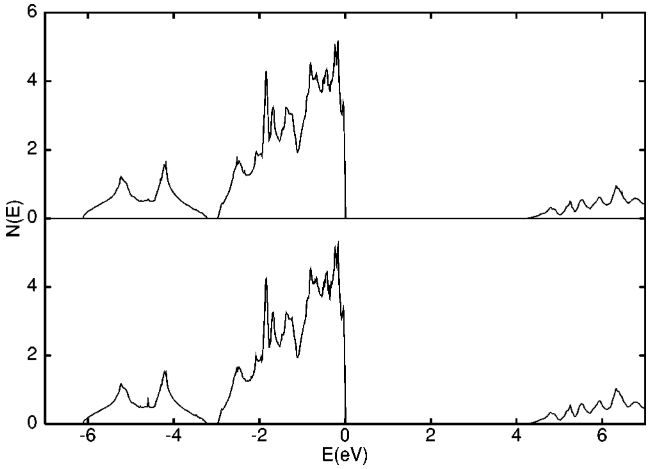

FIG. 6. Normalized projection of the density of states of $NaAlH_4$ onto the H LAPW spheres, in eV^{-1} on a per formula unit basis. The top panel shows the projection onto $1.3a_0$ LAPW spheres divided by the fraction of the H $1s$ charge that is contained in a sphere of this radius for an isolated H^- ion stabilized by a Watson sphere at $3.1a_0$ (the H-Al distance in $NaAlH_4$). This fraction is $0.60e/2e = 0.3$. The lower panel shows the same normalized projection with $1.0a_0$ spheres. The H $1s$ charge in the isolated ion sphere is then $0.38e$ (see text).

The simplest ionic picture would have full H^- ions stabilized by the Coulomb field. To approximate this we did atomic calculations in the LDA for H^- stabilized by a Watson sphere, charge $+e$ and radius equal to the H-Al distance in $NaAlH_4$. We found that $1.1a_0$ sphere would contain only $0.45e$ for this large ion; $0.38e$ and $0.60e$ would be contained in $1.0a_0$ and $1.3a_0$ spheres, respectively. In order to compare our electronic structure with such a simple ionic model, we did additional LAPW calculations with $1.0a_0$ and $1.3a_0$ H sphere radii. The resulting electronic structures were identical, as expected in a full potential method. The total charge inside each H sphere ranges from $0.45e$ for the calculation with $1.0a_0$ H spheres to $0.71e$ for that with $1.3a_0$ spheres. It is not possible to construct LAPW spheres that contain charge close to the total charge, since in the LAPW method the spheres must be nonoverlapping and cannot be too small. The short Al-H bonds in $NaAlH_4$ then constrain the available choices. The two panels of Fig. 6 show the H s projections of the density of states from the calculations with $1.0a_0$ and $1.3a_0$ H spheres, normalized by the fraction of charge inside the corresponding radius from the isolated H^- ion. As may be seen, the two curves are practically identical both in shape and magnitude supporting the view that the electronic structure is better described as ionic than covalent.

Although LDA and GGA calculations for $NaAlH_4$ give very similar electronic structures, the possible effect of beyond LDA (and GGA) corrections should be mentioned. The rare-earth trihydrides such as YH_3 are known to be insulators that could, at least nominally, be described as $Y^{3+}H_3^-$. In these materials, the LDA (and GGA) give metallic band structures, placing the lower lying, nominally H derived bands too high in energy.[27–30] More sophisticated many-body treatments give gaps.[31–34] The error in the LDA and GGA is due to electronic correlations on the H site.[31–36] In particular, the LDA and GGA make relatively large errors in the description of hydrogen atoms because of the noncancellation of the Hartree and exchange-correlation self-interactions in these approximations. The effect of correcting these errors deepens the effective potential on the H sites, thereby lowering the H derived bands and increasing the ionicity. If a similar effect is present in $NaAlH_4$, it would further strengthen the ionic character, relative to what is found in the present calculations.

The reason for the ionic electronic structure of $NaAlH_4$ can be understood as due to the long-range Coulomb interaction in solids. This Ewald contribution to the energy favors ionic electronic structures, and is well known to stabilize O^{2-} in metal oxides, for example, even though dimers and small molecules with the same metal-O neighbors may be covalent. Here H^- is stabilized in this way. In metal oxides, especially when there is some covalency between the O and nominally unoccupied metal orbitals, the O^{2-} ions are highly polarizable, as may be expected from the fact that O^{2-} outside the Coulomb field of the solid is not a stable ion. Following the arguments of Cohen,[37] which related ferroelectricity in oxide perovskites to ionic electronic structures with weak covalency of this type, and considering the electronic structure of AlH_3, it seemed worthwhile to check if ferroelectricity is present. Accordingly, we made small displacements of the atoms away from the relaxed positions within the reduced symmetry noncentrosymmetric space group $R3$ and calculated the restoring forces. However, no ferroelectric instability was found within this symmetry.

Returning to the bonding of $NaAlH_4$, we speculate about some expected consequences of the ionic electronic structure. First of all, since the bonding is stabilized by long-range interactions, rather than primarily short-range Al-H covalent bonds, it should be more sensitive to stoichiometry, defects, lattice parameter changes, and off-site substitutions, than in a salt made of strongly covalent AlH_4^- units. This implies tunability of the hydrogen binding, e.g., by alloying, which in turn would offer tunability of the thermodynamic balance between the solid and the dehydrided NaH + Al mixture. Arroyo y de Dompablo and Ceder have recently arrived at a similar conclusion about tunability of these complex hydrides based on total-energy calculations.[38] Second, it provides a natural explanation of why the hydrogen desorption is strongly connected with melting. Presumably, melting involves disruption of the H lattice and with it a loss of the long-range Coulomb stabilization of the H^- ions. The resulting loss of binding at melting then would result in H release from the material. Finally, we note that while our calculations are specific to $NaAlH_4$, the DOS of $LiAlH_4$ is qualitatively similar,[25] suggesting that similar physics may be operative there and in other related complex hydrides.

We are grateful for helpful conversations with M. Gupta, R. Gupta, G.-A. Nazri, P. Vajda, Z. Wu, B. Yebka, and K. Yvon. Work at the Naval Research Laboratory was supported by the Office of the Naval Research. The DoD-AE code was used for some calculations. The XCrysDen program was used to plot Fig. 1.

---

*Also at School of Computational Sciences, George Mason University, Fairfax, VA 22030.

[1] B. Bogdanovic and M. Schwickardi, J. Alloys Compd. **253-254**, 1 (1997).

[2] K.J. Gross, E.H. Majzoub, and S.W. Spangler, J. Alloys Compd. **356-357**, 423 (2003).

[3] B. Bogdanovic, M. Felderhoff, S. Kaskel, A. Pommerin, K. Schlichte, and F. Schuth, Adv. Math. **15**, 1012 (2003).

[4] M. Fichtner, O. Fuhr, and O. Kircher, J. Alloys Compd. **356-357**, 418 (2003).

[5] A. Zuttel, S. Rentsch, P. Wenger, P. Sudan, P. Mauron, and C. Emmenegger, J. Alloys Compd. **356-357**, 515 (2003).

[6] H.W. Brinks and B.C. Hauback, J. Alloys Compd. **354**, 143 (2003).

[7] E.H. Majzoub and K.J. Gross, J. Alloys Compd. **356-357**, 363 (2003).

[8] B. Bogdanovic, R.A. Brand, A. Marjanovic, M. Schwickardi, and J. Tolle, J. Alloys Compd. **302**, 36 (2000).

[9] B. Bogdanovic, M. Felderhoff, M. Germann, M. Hartel, A. Pommerin, F. Schuth, C. Weidenthaler, and B. Zibrowius, J. Alloys Compd. **350**, 246 (2003).

[10] D. Sun, T. Kiyobayashi, H.T. Takeshita, N. Kuriyama, and G. Jensen, J. Alloys Compd. **337**, L8 (2002).

[11] C. Weidenthaler, A. Pommerin, M. Felderhoff, B. Bogdanovic, and F. Schuth, Phys. Chem. Chem. Phys. **5**, 5149 (2003).

[12] M.P. Balogh, G.G. Tibbetts, F.E. Pinkerton, G.P. Meisner, and C.H. Olk, J. Alloys Compd. **350**, 136 (2003).

[13] D.J. Singh, *Planewaves, Pseudopotentials and the LAPW Method* (Kluwer Academic, Boston, 1994).

[14] D. Singh, Phys. Rev. B **43**, 6388 (1991).

[15] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, and J. Luitz, Computer code WIEN2K (Techn. Universitt Wien, Austria, 2001).

[16] V.K. Belskii, B.M. Bulychev, and A.V. Golubeva, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **B38**, 1254 (1982).

[17] B.C. Hauback, H.W. Brinks, C.M. Jensen, K. Murphy, and A.J. Maeland, J. Alloys Compd. **358**, 142 (2003).

[18] S.M. Opalka and D.L. Anton, J. Alloys Compd. **356-357**, 486 (2003).

[19] P. Vajeeston, P. Ravindran, R. Vidya, H. Fjellvag, and A. Kjekshus, Appl. Phys. Lett. **82**, 2257 (2003).

[20] E. Zintl and A. Harder, Z. Phys. Chem. Abt. B **14**, 265 (1931).

[21] J.W. Turley and H.W. Rinn, Inorg. Chem. **8**, 18 (1969).

[22] I.N. Goncharenko, V.P. Glazkov, A.V. Irodova, and V.A. Somenkov, Physica B **174**, 117 (1991).

[23] O.J. Zogal, P. Vajda, F. Beuneu, and A. Pietraszko, Eur. Phys. J. B **2**, 451 (1998).
[24] In terms of rhombohedral lattice vectors, our relaxed structure for AlH_3 has Al at (0,0,0) and (1/2, 1/2, 1/2) and H at (0.751, 0.389, 0.111). The lattice vectors are (α,β,β), (β,α,β), (β,β,α), with $\alpha = 4.3626$ Å and $\beta = 1.2153$ Å.
[25] P. Vajeeston, P. Ravindran, R. Vidya, H. Fjellvag, and A. Kjekshus, Phys. Rev. B **68**, 212101 (2003).
[26] H. Smithson, C.A. Marianetti, D. Morgan, A. Van der Ven, A. Predith, and G. Ceder, Phys. Rev. B **66**, 144107 (2002).
[27] O.J. Zogal, W. Wolf, P. Herzig, A.H. Vuorimaki, E.E. Ylinen, and P. Vajda, Phys. Rev. B **64**, 214110 (2001).
[28] J.P. Dekker, J. van Ek, A. Lodder, and J.N. Huiberts, J. Phys.: Condens. Matter **5**, 4805 (1993).
[29] Y. Wang and M.Y. Chou, Phys. Rev. Lett. **71**, 1226 (1993).
[30] Y. Wang and M.Y. Chou, Phys. Rev. B **51**, 7500 (1995).
[31] P. van Gelderen, P.A. Bobbert, P.J. Kelly, and G. Brocks, Phys. Rev. Lett. **85**, 2989 (2000).
[32] P. van Gelderen, P.J. Kelly, and G. Brocks, Phys. Rev. B **63**, 100301 (2001).
[33] T. Miyake, F. Aryasetiawan, H. Kino, and K. Terakura, Phys. Rev. B **61**, 16 491 (2000).
[34] Z.W. Wu, R.E. Cohen, and D.J. Singh, Phys. Rev. B **69**, 085104 (2004).
[35] K.K. Ng, F.C. Zhang, V.I. Anisimov, and T.M. Rice, Phys. Rev. Lett. **78**, 1311 (1997).
[36] R. Eder, H.F. Pen, and G.A. Sawatzky, Phys. Rev. B **56**, 10 115 (1997).
[37] R.E. Cohen, Nature (London) **358**, 136 (1992).
[38] M.E. Arroyo y de Dompablo and G. Ceder, J. Alloys Compd. **364**, 6 (2004).