Self-consistent electronic structure of the intermetallic compound LiAl

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The electronic structure of the intermetallic compound LiAl, which has a *B32* structure, has been studied by a self-consistent linear-muffin-tin-orbital method within the atomic-sphere approximation and in the local-density formalism. The overall band structure and density of states have a reasonable resemblance with those obtained previously by Zunger, except for several important differences near the Fermi energy. Whereas our results for ideal LiAl give poor agreement with experiments on real ("vacancy-defect") LiAl, we obtain much better agreement after accounting for the presence of vacancies by shifting the Fermi level in a crude rigid-band manner corresponding to the vacancy concentration of roughly two percent estimated experimentally: The shifted results give satisfactory agreement with magnetic-susceptibility and Knight-shift experiments and predict *p*-type conduction for the real "defect-phase" LiAl, in agreement with recent experimental findings.

I. INTRODUCTION

Recently, an intermetallic compound having B32 (Zintl¹) structure, LiAl, has attracted considerable interest since it is considered as a promising candidate for an electrode material in a high-energy-density Li-S battery. The B32-type compounds have an interesting crystal structure, described as two interpenetrating diamond lattices, one constituent forming each diamond sublattice (see Fig. 1). Each atom has four like and four unlike atoms on the nearest-neighbor sites and its local site symmetry is tetrahedral. This group if found in a relatively limited number of combinations of I-II (LiZn, LiCd) and I-III (LiAl, LiGa, LiIn, NaTl) elements.

The experimental data obtained so far on the I-III compounds of this group are summarized as follows: (a) small metallic conductivity^{2,3} and *p*-type conduction,⁴ (b) small Knight shifts at both I and III nuclei,^{5,6} (c) small paramagnetism and diamagnetism,^{7,8} and (d) a defect lattice,^{3,9} i.e., a subtraction phase which has a finite concentration of vacancies even at very low temperature.¹⁰

Theoretical investigations on LiAl have been carried out by Ellis *et al*.¹¹ using a molecular cluster method with nine atoms, and by Zunger¹² using the (LCAO) discrete variational (DVM) energy-band



FIG. 1. Crystal structure of the B32 (Zintl) phase.

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method. They found large intra-atomic promotion from s to p electrons, but small intersite charge transfer. In a rather complete and detailed study, Zunger presented¹² a band structure which has very small overlap between the mostly filled lowest four and higher bands. This result explains the semimetallic experimental situation of LiAl stated above, but since no partial density of states were presented, direct comparisons with experiment are difficult to make.

In view of the recent great interest in the electronic structure of this material, we have calculated the energy-band structure of LiAl using the linear muffin-tin-orbital (LMTO) method. Here we present detailed information on the electronic structure which allows us to make quantitative comparisons with experiments such as magnetic susceptibility and Knight shift. The resulting band structure and thus the total density of states (DOS) are found to be qualitatively similar to those presented by Zunger. However, there are striking differences in several details of the band structure near the Fermi energy (E_F) which yield higher DOS and more metalliclike behavior (i.e., higher conductivity) for (ideal) LiAl instead of the low conductivity semimetallic structure found in the DVM calculations.¹² A preliminary non-self-consistent augmented-planewave calculation by Switendick¹³ also shows a similar location of the Fermi level. Our (and Switendick's) band structure for (ideal) LiAl predicts a large magnetic susceptibility and very large Knight shifts at both Li and Al nuclei resulting from a large partial DOS at E_F of s symmetry at the respective atom sites-a result which is completely at variance with the semimetallic behavior observed experimentally. However, as stated above, real LiAl crystals contain a large number of vacancies, even those with stoichiometric composition.³ Hence one needs to take this vacancy effect into account if one is to make comparisons of the band theoretical results calculated for ideal LiAl with the real "defect-phase" LiAl. Thus, as a first step we take the effect of vacancies into consideration by shifting E_F in a rigid-band manner. When this is done, the Fermi level falls near the bottom of the DOS valley with considerably diminished partial DOS at E_F of s symmetry for both Li and Al sites and this new Fermi level predicts values of both the magnetic susceptibility and Knight shift in reasonable agreement with experiment. Furthermore, the new Fermi level predicts definite p-type conduction carried mostly by the hole pocket around the Γ point. We find that the intersite charge transfer is

very small, but that the intrasite promotion is considerably larger, the same behavior as found previously for LiA1.^{11,12} The bond character of the B32compounds will be discussed in connection with this intrasite rearrangement.

II. METHOD

The self-consistent (SC) band-structure method employed is essentially the same as that described previously¹⁴ and is based on the LMTO method developed by Andersen.¹⁵ The atomic-sphere approximation¹⁵ (ASA) is employed with R_{WS}^{Al} = 1.1274 R_{WS}^{Li} , where $R_{WS}^{Al(Li)}$ is the radius of Wigner-Seitz (WS) sphere of Al(Li). This ratio is chosen so as to get reasonably small discontinuities of the potential at each WS sphere boundary from the SC results. This choice gives almost neutral WS spheres for this material. The intersite charge transfer brought about in the course of SC iterations is estimated by the difference in the electron number inside the WS sphere between the first superposition of neutral ground-state atoms and the last converged SC ouput. Charge transfer results in ionic character and additional Coulomb contributions to the (Madelung) potential which are calculated by lattice-sum techniques,¹⁴ whereas the exchange and correlation contributions to the potential are handled by the local density-function formalism.¹⁶

The canonical band SC iteration technique¹⁴ is initially employed to make the LMTO-SC iterations employed later less expensive. In each iteration the resulting potential is calculated from the LMTO band structure determined at 16 k points in the irreducible $\frac{1}{48}$ Brillouin zone. The SC iterations are terminated when the potential difference for the outermost 9 radial mesh points (159 logarithmic mesh points from near the nucleus to the WS sphere) gets smaller than a few mRy. The partial and total DOS are calculated by the linear tetrahedron method¹⁷ using results calculated at 89 k points (8 divisions from Γ to X) in the $\frac{1}{48}$ irreducible Brillouin zone.

The LMTO basis contains s, p, d for Al and s, p for Li, resulting in an eigenvalue problem of size 26×26 . The convergence is improved by including additional basis functions (f and d, respectively) to the three-center terms. It should be noted that the B32 structure with its two penetrating diamond lattices is about as closed packed a structure as is the bcc lattice. This makes it especially suitable for study with the LMTO method.

III. RESULTS AND DISCUSSION

A. Band structure and density of states: Ideal LiAl

The SC band structure of LiAl is presented in Fig. 2. The partial and total DOS's calculated by the tetrahedron scheme using the band structure and associated partial weights are shown in Fig. 3(a), 3(b), and 3(c). Overall, the band structure and the total DOS resemble very well those of Ref. 12 (no partial DOS were given there). We list in Table I a comparison of energy separations obtained in the two calculations. The energy separation between Γ_1 and Γ_{25} agrees very well,¹⁸ although our $\Gamma'_{25} \rightarrow \Gamma_{15}$ separation is roughly half that of Ref. 12 and our dispersion along W to L is slightly different from that given there. The agreement for the valence-excited separation is less satisfactory than that for the valence-valence separation. The most significant and important difference between the two band structures is in the dispersion of the lowest conduction band (i.e., the fifth band) from Γ_{15} to X_1 . Our band structure (and that of Switendick's¹³) shows a monotonic decrease from Γ_{15} to X_1 , whereas that of Zunger has its minimum at roughly $\frac{2}{3}$ of the distance from Γ to X. The indirect gap $(\Gamma'_{25} \text{ to } X_1)$ is 62 mRy for our band structure and 13 mRy for that of Ref. 12 and is essential for determining the height of the valley in the DOS near E_F for LiAl. As seen in Fig. 3(c), the fairly large overlap in our band structure brings about a rather shallow valley of DOS near E_F and results in a fairly large DOS at the E_F . This is an apparently



FIG. 2. Self-consistent band structure of LiAl. Dashed lines indicate doubly degenerate levels. The two horizontal lines E_F and E'_F indicate Fermi levels for ideal and real "defect-phase" LiAl, respectively, as explained in the text.



FIG. 3. Density of states in LiAl: (a) partial density of states in the Li Wigner-Seitz sphere, (b) that in the Al Wigner-Seitz sphere, and (c) total density of states in a unit cell. The two Fermi levels, E_F and E'_F are designated by straight lines and correspond to ideal and real "defect-phase" LiAl, respectively, as explained in the text. The shaded area in (c) accommodates 0.16 electrons in a unit cell, corresponding to the electron deficiency resulting from vacancy concentration of 2%.

unfavorable result with which to explain the experimental findings so far, if we use this band structure with E_F directly to compare with experiment.

In the total DOS curve of Fig. 3(c), we recognize that the DOS in the interesting energy range is divided into four main parts: the first is from the bottom of the lowest band (Γ_1) to ~0.03 Ry [the energy at which the lowest band touches the X point (X_1)] and has its peak at ~ -0.075 Ry coming from the singularity near L'_2 ; the second starting from ~0.03 Ry with its very sharp peak at ~0.07 Ry coming from the very flat dispersion near L_1 is terminated at ~0.17 Ry by a steep peak belonging

for	various	levels	in	Al	with	those	of Zunge	r (Ref.	12)
					Pr	esent		Ref.	(12)
(val	lence-val	ence)							
X_1	$\rightarrow X_4$				0	.223		0.21	7
$L_{2'}$	$\rightarrow L_1$				0	.136		0.15	0
L_1	$\rightarrow L_{3'}$				0	.367		0.33	9
(val	ence-exc	ited)							
Γ_1	$\rightarrow \Gamma_{25'}$				0	.702		0.69	4
X_4	$\rightarrow X_1$				0	.193		0.25	6
$L_{z'}$	$\rightarrow L_3$				0	.051		0.11	0
X_1	$\rightarrow \Gamma_{25'}$	•			0	.062		0.01	3
							,		
Γ,,	$\to \Gamma_{15}$				0	.017		0.03	5
L_3	$\rightarrow L_1$				0	.050		0.04	6

TABLE I. Comparison of energy separation (in Ry)

to the third part (which comes from the flat band near W_2 ; the third part contains a second broad peak coming from the bands near X_4 which decreases almost monotonically up to ~ 0.43 Ry where very flat dispersion starts from X_1 , from which the highest fourth part begins. The partial DOS projected for the Li and Al sites are roughly similar to each other, but we see in the first part a very large A1s component, which shows that the lowest occupied band is of predominantly Als-like character. Another big difference between the Li and Al partial DOS's is in the third part, where we see a fairly large Lis build-up at the first peak of this range, but only a decreasing Als component. [In Ref. 12 it is stated that the lowest band is predominantly of Li2s character hybridized with Al 3s, which contradicts what we see from Fig. 3(a) and (b). This difference may be due to the different definitions of partial weights used: In our case partial *l* character is defined in a one-center expansion,

while in the LCAO convention the Li 2s, for example, only labels the basis function constructed from the atomic Li 2s function which may penetrate the Al sites and vice versa].

The most striking feature seen from Fig. 3(a) and 3(b) is the very large p component in the DOS both for the Li and Al sites. In view of the close resemblance of the DOS curves for the respective atom sites with that of the tetrahedrally bonded IV - IV semiconductors,¹⁹ we agree that the strikingly large s to p promotion both for the Li and Al sites, which were found in the previous studies of LiAl,^{11,12} is closely related to the formation of diamondlike bonding, i.e., sp^3 bonding, for both Li and Al. Of course, this sp^3 bonding cannot be complete since the ratio of the s component to that of the p component in the total number of electrons in Li and Al WS spheres deviates significantly from $\frac{1}{3}$ as seen in Table II.

Zintl and Brauer¹ and Hückel²⁰ proposed that in the I-III compounds having B32 structure, the alkali metal transfers its valence electrons to the III atom (which behaves like Ge or Si and forms a diamond lattice) and becomes an almost nonbonding atom. This would suggest a convenient way to explain why Li atoms are easily taken out of the material and thus why the defect phase is formed in the LiAl crystal. But if the bond character of the Li atom in LiAl is almost nonbonding, we should observe in the partial DOS analysis predominantly s character at the Li site. We see, however, almost no indication of such an occurrence in Fig. 3(a). Therefore the situation proposed by Zintl and Brauer¹ and Hückel²⁰ is not well realized in LiAl; the sp³ bonding proposal for the B32 I-II has been contradicted also by experiment.⁷

Table II presents the total number of electrons in their respective WS spheres of radii R_{WS} , n_{WS}^{total} , at the first stage of superposition of ground-state neutral atoms and at the last converged SC iteration.

TABLE II. Number of valence electrons inside Wigner-Seitz sphere of radius R_{WS} .

	Superposition of atomic charge ^a		R _{ws}		Intersite charge			
	config.	$n_{\rm WS}^{\rm total}$	(a.u.)	$n_{\rm WS}^s$	n ^p _{WS}	transfer ^b n_{WS}^d	$n_{\rm WS}^{\rm total}$	
Li	$2s^{1}$	1.01	2.763	0.346	0.643		0.99	-0.02
Al	$3s^2 3p^1$	2.99	3.115	1.147	1.653	0.206	3.01	0.02

^aAtomic charges are calculated self-consistently using $\frac{2}{3}$ Slater exchange.

^bIntersite charge transfer is defined as the difference of n_{WS}^{total} between the final converged band calculation and the first superposed crystal charge.

Symmetry-partitioned electron numbers of the SC output, $n_{WS}^{sp,d}$, are also listed, where the *s* and *p* components are taken for the Li site. We see that the intersite charge transfer, which has been tentatively defined as $(n_{WS}^{total})_{SC} - (n_{WS}^{total})_{superpose}$, is very small (-0.02 electrons from a Li atom to an Al atom, as in the earlier results^{11,12}), but the sign of charge transfer is opposite to that believed for Li compounds. However, since this quantity is strongly dependent on the definition of the starting state (especially for the very small transfer found here), one may safely conclude that the intersite charge transfer in the LiAl compound is very small.

B. Band structure and density of states: Vacancy LiAl

It has now been well established that the stoichiometric ideal LiAl structure is not obtained experimentally. Even "stoichiometric" LiAl (which is supposed to have the same concentration of Li and Al atoms) has been found to have vacancies on the Li sites.³ For this reason, the results obtained for ideal LiAl and given in subsection II A above, may not be applicable to measurements, such as magnetic susceptibility and Knight shifts, which are made on real LiAl. Hence in this section we consider a crude rigid-band approach in order to model the effect of Li vacancies on the band structure and DOS. These results are then used to discuss experiments on vacancy LiAl in the next subsections.

We show in Fig. 2 two horizontal dashed lines with E_F and E'_F where, as before, E_F is the Fermi energy for the ideal LiAl, and now E'_F is that for the real "defect-phase" LiA1. It is estimated³ that "stoichiometric" LiA1 has 4% vacancies on the Li sites and 2% Li atoms on the Al sites, and hence has on the whole, 2% vacancies in LiA1. Thus, per unit cell there are (0.98)(2)(4) = 7.84 electrons in a

TABLE III. Magnetic susceptibility of LiAl due to outer electrons in units of 10^{-6} emu/mole.

		experimental ^c		
	$ ho(E_F)^{ m a}$	Pauli and Landau		
Ideal	7.08	11		
Defect phase ^b	2.76	4.4		

^aTotal density of states at Fermi energy (states/Ry unitcell spin).

^bFermi level is shifted by 0.017 Ry corresponding to the vacancy concentration of 2%.

^cReference 7.

real "defect-phase" LiAl and the new Fermi energy E'_F is obtained by shifting E_F by 17 mRy in a rigid-band manner according to the vacancy concentration.

In Fig. 3(a) - 3(c), we illustrate the effect of these two Fermi levels. The shaded area in Fig. 3(c) corresponds to (8)0.02 = 0.16 electrons in a unit cell. The consequences of these shifts are quite interesting and important. The total DOS at E'_F diminishes to roughly $\frac{1}{3}$ of that at E_F from which—as we shall see later—satisfactory agreement with the experimental susceptibility is found (cf. Table III). The partial DOS of a symmetry at the Li(Al) site at E'_F is roughly $\frac{1}{20}(\frac{1}{6})$ of that at E_F , which enables us to have reasonable agreement with the experimental Knight shift for the Li(Al) nucleus (cf. Table IV).

C. Magnetic susceptibility and Knight shifts

 Yao^7 measured magnetic susceptibilities of several B32 compounds and derived a fairly small paramagnetic susceptibility attributed to the outer conduction electrons of LiA1. The Knight shifts measured by Schone and Knight⁶ on LiA1 gave a vanishingly small Knight shift at the Li nu-

		Table	e IV. Kn	ight shifts in	n LiAl.	
			$\rho_s(E_F)^a$		Knight shift (%) Experiment ^c	
		$ \Psi(0,E_F) ^2$ (a.u.)		Theory (contact)		
Ideal	Li Al	0.831 8.10	0.580 0.785	0.021 0.169	Li < 0.05	pure metal Li 0.025
Defect phase ^b	Li Al	0.821 8.03	0.030 0.117	0.0011	$A1 < 0.01 \pm .003$	Al 0.16

^as density of states in a Wigner-Seitz sphere, in unit of states/Ry spin atom.

^bFermi level is shifted by 0.017 Ry corresponding to a vacancy concentration of 2%. ^cReference 6.

cleus (which is at most $\frac{1}{5}$ that of pure Li) and a small shift at the Al site (of at most $\frac{1}{16}$ that of pure Al). These experiments indicate that in real LiAl the DOS at the Fermi energy is quite low, i.e., in a semimetallic situation. We present here estimates of these two quantities evaluated using the results of our LMTO calculations. In Table III, we list the calculated values of the magnetic susceptibility due to conduction electrons and compare with the experimental results. The Pauli paramagnetic susceptibility is evaluated by the usual formula and the Landau diamagnetic contribution is taken to be $-\frac{1}{3}$ of the Pauli paramagnetism. The total DOS at $E_{F'}$ for the real "defect-phase" LiAl is $\sim 40\%$ of that for the ideal LiAl case and gives a magnetic susceptibility of 4.4×10^{-6} emu/mole compared to 5×10^{-6} emu/mole derived from experiment, indicating quite satisfactory agreement.

The Knight shifts due to the Fermi contact term in the hyperfine interaction are evaluated by use of

$$K_{\text{contact}}^{\text{theory}} = (16\pi/3)\mu_B^2 |\Psi(0, E_F)|^2 \rho_s(E_F) , \quad (1)$$

where $|\Psi(0,E_F)|^2$ and $\rho_s(E_F)$ are a probability density at the nucleus and s symmetry DOS per spin, respectively, both at the Fermi level. We list in Table IV, $|\Psi(0,E_F)|^2$, $\rho_s(E_F)$ and $K_{\text{contact}}^{\text{theory}}$ for the two Fermi-level locations as well as the experimental value. Clearly, the use of $K_{\text{contact}}^{\text{theory}}$ alone for both the Li and Al nuclei in the ideal LiAl gives results which are very far from the experimental values. However, those corresponding to the real defect phase show reasonable agreement with experiment. Although greatly reduced from the ideal case, the value for the Al nucleus is still two or three times bigger than the experimental value. The reason for the discrepancy is not clear in the present stage; it might be improved by refinements of either experiment or theory, or both.

D. Electrical conductivity

The electrical resistivity of stoichiometric LiAl in the temperature range 77–300 K measured by Cristes *et al.*² indicates poor conductivity $(\sim 2 \times 10^{-5} \Omega \text{ cm} \text{ at } 273 \text{ K})$ with a linear increase of the resistivity with temperature over the temperature range which is roughly 2 times and 7 times larger than those of pure Li and Al, respectively. Hall-coefficient measurements⁴ have found *p*-type conduction for LiAl. The present band structure with shifted Fermi level as in Fig. 2 clearly predicts the *p*-type conduction in the real defect-phase LiAl. The large hole pocket surrounding Γ overwhelms the small electronic pockets at the X points. Since the resistivity of LiAl must be closely related to the existence of scatterers (vacancies on the Li sites and Li atoms on the Al sites), it is difficult to discuss the resistivity quantitatively at this stage. The abrupt increase of resistivity² with Li concentration over 48-52 at. % might be closely correlated with the increase of Li-atom defects on the Al sites,³ since the Li atom (valency 1) on the Al site (valency 3) must be much more effective (roughly 2 times) as a scatterer than a vacancy on the Li site.

So far, we have shown fairly successful comparisons of our calculations with the experiments of magnetic susceptibility, Knight shift, and (more qualitatively with) the electrical conductivity. We hope further experiments, such as soft x-ray K_{β} , $L_{\text{II}-\text{III}}$ emission, specific heat, and nuclear spin lattice relaxation rates at very low temperature will substantiate our calculation. Although a more advanced treatment of the random defects like the coherent potential approximation would be desirable, the rigid-band treatment employed in the present work is admissible, at least as a first step, especially for the vacancies on the Li sites.

In conclusion, we find that the assumption of vacancy concentration is crucial in explaining the observed properties of LiAl and, from the DOS diagram it is expected that the properties are fairly stable for Li-rich concentrations, whereas for Alrich compositions increasing DOS and different properties are expected. Experimentally,⁶ it is found that Al-rich compositions actually give higher NMR signals; this may be explained in the rigidband model but can also be due to vacancy or Al cluster formation.

Finally, the origin of the discrepancy between our results and those of Ref. 12 need to be understood. The two methods differ greatly in their approach and in the technical details of their execution. Our muffin-tin LMTO results are, in principle, not as accurate as the full potential results obtained with the LCAO-DVM approach. However, there are quite a few other differences between the two methods which may also affect the results, including questions about the LCAO-DVM procedure such as variational freedom in the basis set, the number of kpoints used in the SC procedure, how this affects the determination of $\rho(\vec{r})$, and, in the case of metals, E_F . Clearly, angle-resolved photoemission experiments are needed to determine the dispersion of the bands, particularly in the region around the Xpoint in the zone; this will yield a direct indication of the validity of any band structure.

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