LATTICE DYNAMICS OF THE MIXED CONDUCTING INTERMETALLIC COMPOUND, \( \beta \)-LiAl

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The intermetallic compound, B-LiAl, that crystallizes in the uncommon Zintl structure is a mixed-conducting electrode and has many unusual properties pointing to the existence of unusual bonding in the semi-metallic compound. In order to elucidate the nature of the bonding in LiAl, we have studied the lattice dynamics of B-LiAl by inelastic neutron scattering. Results for the phonon dispersion curves have been obtained for the principal symmetry directions. A force constant fit to the results indicates that the Al-Al force constants are unusually large. Pair potentials were constructed by conventional pseudopotential calculations. The pair interactions favoring the Zintl structure were used to compute phonon dispersion curves. Good agreement between theory and experiment can be obtained for the acoustic branches.

INTRODUCTION

Lithium-aluminum alloys are used as negative electrodes in the Argonne National Laboratory’s LiAl/LiCl/KCl/FeSb molten salt battery [1]. The α-phase of these Li-Al alloys is the most commonly used starting material. The present work on α-LiAl was motivated by the technological interest in the material and is part of an ongoing program at ANL studying the basic properties of mixed conductors.

Lithium and aluminum form an intermetallic compound [2] $\text{Li}_x\text{Al}_{1-x}$, for $-0.04 < x < 0.07$. This α-phase crystallizes in the uncommon (B32) Zintl structure [3]; the α-phase is stable up to the melting temperature 1000K [4]. The only known elements forming this structure are Li with Zn, Cd, Al, Ga and In and Na with In and Tl. The Zintl structure of α-LiAl consists of two interpenetrating diamond lattices, an Al diamond lattice with Li forming its own diamond lattice in the interstitial positions of the Al lattice. Both the Al and the Li atoms have 8 nearest neighbors, 4 Li and 4 Al. The lattice constant of α-LiAl for $x=0$ is 6.370Å [2] at room temperature giving rise to a nearest neighbor distance of 2.75Å -- a distance shorter than in pure Li or Al. The Al and Li atoms in α-LiAl are densely packed with no obvious channels for Li conduction. The compound, α-LiAl, contains two types of constitutional point defects [2,5], Li vacancies (V Li ) and Li-antisite defects (Al Li ). The total concentration is approximately 3% per atom and is not strongly dependent on composition. The diffusivity of Li is fairly high for all composition [6]. It is highest for Li-deficient compositions, $D_{\text{Li}}(\text{Li}) = 8 \times 10^{-6} \text{cm}^2/\text{sec}$ at 800K for $x=-0.035$ [7,8]. For $x>0$, a very rapid diffusion of Li [7,8] dominates the Li transport. The Li diffusion mechanism is presently not established for Li-rich compositions.

We describe here our experimental results for the phonon dispersion curves of α-LiAl obtained by inelastic neutron scattering [9]. The results have been fitted to a Born-von Karman model using force constants up to and including the first three neighbors. This study of the phonon dispersion curves has been done in order to obtain information on the Al-Al, Al-Li and Li-Li bondings in the material. In a pair potential model, the force constants are directly related to the first and second derivatives of the three pair potentials at the interatomic distances.

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Pair interactions constructed by conventional pseudopotential theory have, of course, been successfully applied to calculation of the phonon spectra of many crystals, including Li and Al. Moreover, they have also been successful in molecular dynamics simulations of liquid Al and liquid alkalis (Rb, Na), in which ion motions are not limited to small excursions from lattice points and the powerful constraints of crystallographic symmetry play no role. Accordingly, a significant aim of the work reported here has been to provide experimental information which, in conjunction with present theoretical capability, can be exploited in developing a quantitative understanding of the forces and ion motions in LiAl. The absence of structural "easy-conduction" paths adds weight to the effort.

The detailed electronic structure of B-LiAl has not been experimentally determined. The large concentration of defects makes it nearly impossible to use techniques like de Haas-van Alphen or cyclotron resonance. However, the electronic structure of B-LiAl has been investigated theoretically by several authors. Ellis and co-workers [10] have carried out molecular cluster calculations, and band structure calculations have been performed by Zunger [11] and by Asada et al. [12]. The band structure calculations predict that B-LiAl is semimetallic. Zunger [11] concludes from his calculations that the bonding in B-LiAl appears to be a composite of nonbonding Li-Li contacts, a weak covalent-ionic character in the Li-Al bond, and a metallic character in the Al-Al bond. However, the theoretical investigations referenced above do not agree on the detailed nature of the bonding in LiAl.

From the force constants for B-LiAl, the nearest-neighbor atomic relaxations [13] have been observed in the vicinity of vacancies can be calculated. Furthermore, the force constants are also important for the modelling of the experimentally observed vacancy ordering [13].

EXPERIMENTAL RESULTS

The phonon dispersion curves for B-LiAl have been studied for two single crystals. For both crystals, we used isotopically pure 7Li because of the high neutron absorption cross section for 6Li. One crystal was nominally stoichiometric (x=0) and had a volume of 2.1cc; the other crystal was Li-rich (x=.05) and had a volume of 3.3cc. The first crystal (x=0) was investigated at room temperature using a triple axis spectrometer installed at the Missouri University Research Reactor, Columbia, Missouri. The second crystal (x=.05) was studied at 80K using a triple axis spectrometer installed at the R2 reactor, Studsvik, Sweden. We used the conventional constant-Q technique [9] in both experiments. A preliminary report on the data from the first crystal has been published [14].

The results presented here are a composite of the data from the two experiments. We have not observed, within the experimental uncertainty, any dependence of the phonon dispersion curves on composition.

Figure 1 shows the results for the least squares fit of a Born-von Karman model to the experimental results obtained for phonon wavevectors $q$ propagating in a cube direction ($\Gamma$ to $X$). The least squares fit also includes experimental results for the [111] direction ($\Gamma$ to L). A total of about 50 phonon frequencies have been measured. Since the least squares fitted curves in Fig. 1 are close fits to the data, we have, for clarity, omitted the experimental points. We have no experimental results for the two highest branches (one longitudinal, the other transverse) shown in Fig. 1 as calculated from the model. This model also predicts that the intensities of the phonons belonging to these branches are very weak.

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**Fig. 1. Phonon Dispersion Curves for B-LiAl.**
In general, the experiment is a difficult one: a) both Li and Al are weak scatters, and b) the strong hybridization of the phonon branches (see Fig. 1) gives phonon intensities that vary strongly with momentum transfer.

The Born-von Karman model used in the least squares fit contained 12 force constants: 4 Al-Al constants (2 first neighbor and 2 third neighbor), 4 Li-Li constants (2 first neighbor and 2 third neighbor), and 4 Al-Li constants (2 first neighbor and 2 second neighbor). The force constants from the best fit show that the first neighbors dominate. For Al-Al the two first neighbor constants are ~ 30 kdyne/cm, for Li-Li 1-2 kdyne/cm, and for Al-Li 7-8 kdyne/cm.

DISCUSSION

The first neighbor force constants for Al-Al are very large when compared to the nearest neighbor constants of ~ 10 kdyne/cm in pure Al [15]. We have calculated dispersion curves for the Al on the diamond sublattice of LiAl and find that the phonon frequencies are high and comparable to those measured for Si [16]. (A note of caution: A Born-von Karman model does not fit the dispersion curves for Si [16] and Ge [17] due to covalent bonding. However, a Born-von Karman model gives an excellent fit to Al-LiAl).

The Li-Li force constants are small, but comparable to those for pure Li [18], and the Al-Li constants are intermediate between the strong Al-Al and the weak Li-Li constants.

A comparison between the first and second neighbor force constants for Al-Li indicates that a central force potential may not be a good description of the Al-Li bonding.

Theoretical pair potentials were constructed by conventional pseudopotential methods from model electron-ion potentials of Heine-Abarenkov type [19] and using Vashishta-Singwi [20] dielectric screening. The pair interactions, for LiAl, favor the Zintl structure as compared to the CsCl or a "clustered bcc" structure. The phonon dispersion curves that are calculated from these pair interactions reproduce the lowest branches of Fig 1. However, the nearly degenerate longitudinal modes at 8-9 THz cannot be reproduced by the present theoretical model.

Several variations, both of the electron-ion pseudopotential and of the dielectric screening, were explored within the general framework of the model. Their consequences, in conjunction with Al-Al and Al-Li force constants, suggest that a fully self-consistent theoretical treatment may be required for an adequate quantitative account.

REFERENCES