Electronic Structure, Bonding, and Lithium Migration Effects of the Mixed Conductor β-LiAl

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(Received March 5, 1996)

혼합 전도체 β-LiAl의 전자구조, 결합과 Li 이온 이동에 따른 영향

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(1996년 3월 5일 접수)

Abstract – Detailed experimental studies of the electronic structure of the valence and conduction bands of the mixed conductor β-LiAl indicate that a quasi-gap opens at the Fermi level, and the conduction states are highly localized, as opposed to the theoretical band structure calculations that predict predominant metallic behavior. Evidence for complex lithium migration effects involving the surface of LiAl, induced by particle (electron or ion) bombardment and mechanical treatment, has been obtained as a byproduct of these experiments.

요 약 – 전자구조(valence와 conduction band) 해석을 통하여 이론상으로 현저한 금속 특성을 갖는다고 알려진 혼합 전도체 β-LiAl은 실제 이론과는 달리 Fermi level에서 하나의 quasi-gap이 존재하고 conduction상태가 상당히 localized 되어 있음이 본 연구의 세부적 실험을 통하여 밝혀졌다. 또한 기계적 표면처리나 입자 bombardment(전자나 이온)을 통하여 야기되는, Li 이온의 복잡한 이동 거동에 관하여도 고찰하였다.

I. Introduction

The β-LiAl intermetallic compound is successfully used as a negative electrode in lithium-based high energy density batteries at both ambient and elevated temperatures[1-3]. The material has the advantage to possess mixed (electronic and ionic) conductivity, a stable electrode potential in repeated cycles of charging and deep discharging, and a lower reactivity with the molten electrolyte than lithium metal. On charging and discharging of a LiAl electrode, lithium is transported through the electrolyte due to concentration gradients, and should be able to exit and re-enter easily the electrode matrix with a desired efficiency as close as possible to 100%. Accurate determination of diffusion coefficients, the mechanism of ionic and electronic conductivity, and the surface interface properties of this material are therefore problems of interest from both practical and basic viewpoints.

Beta-LiAl is a rather intriguing material. Its physical properties resemble both those of metals and non-metals. The phase is stable over a stoichiometry range of 48-54 at% Li[4] and forms a highly ordered intermetallic compound with B32 (Zintl) structure[5]. It consists of two interpenetrating diamond-like sublattices, one for lithium and one for

aluminum. The aluminum lattice is rigid, while lithium is highly mobile, with a diffusion coefficient of about $10^{-5} cm^2/sec$ and an activation energy of 1.5 eV[6]. The crystal has a complex defect structure consisting of lithium vacancies (that dominate at low lithium content) and lithium anti-site defects (that dominate at high lithium content) [7, 8]. The electronic conductivity is very low, and the positive Hall coefficient indicate that the majority charge carriers are holes[9, 10]. The room temperature resistivity varies between 20 and 50 $\mu\Omega cm$ over the composition range of the beta phase[9, 10].

Band structure and cluster model calculations performed in various approximations[11] have indicated close similarities with the band structure of silicon. The valence band with a total width of about 9.5 eV is composed of three subbands almost completely separated from each other. The lowest subband is mainly of s-type, the next one is an s-p hybride, and the highest valence subband is dominated by p-states originating from both lithium and alminum. This suggested significant s-to-p charge promotion at both components, as opposed to earlier models that assumed Li-to-Al charge transfer[12]. There is a charge accumulation between the Al atoms in the aluminum sublattice, and a remarkable charge depletion along Li-Li directions. Thus, the Li-ionic cores are in a "non-bonding" state, this explaining the easy lithium migration through the solid. The low electronic conductivity is due to the very low density of states at the Fermi level. Bonding in LiAl has been described as polarized covalent (in the lower part of the valence band) and metallic (in the higher electronic states).

The experimental and theoretical treatments mentioned above refer to an infinitely large bulk material. In real, finite systems, surfaces are an integral component of the objects to be studied, and in particular in batteries surface/interface electrode processes may determine the conduc-tivity properties of the cell. We have recently initiated a systematic study of β-LiAl by using a number of complementary X-ray and electron excited techniques. This synergistic approach provided a wealth of information on the electronic structure and related properties of this material and permitted important correlations to be made between its structure at the atomic scale and its macroscopic behavior.

II. Experimental Condition

The measurements were performed on polycrystalline samples of composition $Li_{0.513}Al_{0.487}$ synthesized by solidification from the melt. The stringent requirements on surface sample preparation was necessary due to the high chemical reactivity of LiAl. For the clean surface, sample surface was revealed by two different techniques: one by fracturing or scraping with a diamond file, or the other by cutting with a bolt-cutter. After that, argon ion bombardment was applied on the freshed surface of sample. Electron bombardment was either a component part of the spectroscopic processes used (e.g. EELS, AES, APS, and also soft X-ray emission spectroscopy), or was purposely associated with an Auger measurement as discussed below.

Photoemission experiments were carried out at the synchrotron radiation facilities NSLS-Brookhaven, BESSY-Berlin, and DESY-HASYLA-Hamburg. The energy resolution in all these set-ups was estimated to be 0.3 eV. Calibration of the energy scale was done by reference to gold. Electron energy loss and Auger spectra were measured with a conventional PHI-595 Auger microprobe at the Materials Research Laboratory, Urbana-Champain. Appearance potential experiments used a home-made instrument constructed at the University of Utah[14]. The instrument was operated with electron excitation (100 - 1000 eV), and soft X-ray total yield detection.

III. Lithium Migration Effects Involving The Surface of LiAl, Induced by Mechanical Treatment and Particle (Ion or Electron Bombardment)

We have observed that all the methods used for preparation of clean surfaces resulted in a surface enrichment in lithium, in some experiments up to a complete coverage. The best case appeared to be fracturing, when the signal from both lithium and aluminum components could be measured, and the worst cases were cutting by a bolt-cutter and scraping, when aluminum was completely masked by lithium. This segregation effect caused by mechanical damage was presumably due to heating, or lowering of the crystal surface energy by the induced lattice strain. Ion bombardment resulted in mass removal from the surface of LiAl with preferential sputtering of the light component. In different experiments electron bombardment had opposite effects. In X-ray emission spectroscopy, an extended exposure to high energy electrons (10^3 eV) evaporated lithium from the surface[13]. Attempts to measure the appearance potential spectra of LiAl failed, might be due to massive surface accumulation of lithium.

Figure 1 shows the Auger spectra of a fresh LiAl sample fractured in ultrahigh vacuum (a) and of the same sample after argon ion bombardment (800 eV, 30 mA, 5 minutes) (b) and subsequent exposure to high energy electrons (10 keV, 15 A, 20 minutes) (c) Also shown are the Auger spectra of lithium and aluminum taken from literature[15].

A clear effect of ion bombardment (spectrum b) was the removal of most of the low energy fine structure which in spectrum (a) corresponded to Auger transitions involving lithium atoms. The total band width of the Auger spectrum was also significantly reduced. Based on the known sputtering yield data for various elements, it is understood that lithium was preferentially sputtered away from the LiAl surface. Spectrum (c) measured aft-
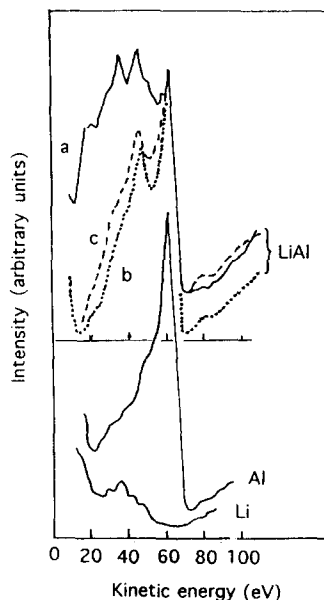

Fig. 1. Auger electron spectra of β-LiAl in the "as fractured" state (a); after ion bombardment (b); and after subsequent electron bombardment (c). Also shown are the Auger spectra of Li and Al.

er electron bombardment indicates a tendency toward recovery of the low energy part, which demonstrates an increased contribution from lithium atoms. Here again, electron bombardment apparently caused migration of lithium atoms from the bulk towards the surface. Neither the exposure to electrons during measurement of the Auger spectra, nor the final prolonged bombardment with high energy electrons resulted in any shifts or fluctuations of the Auger structures. This indicates that the electron bombardment had no significant effects on the chemical state and phase stability of the LiAl intermetallic compound. Also, the electronic conductivity of the sample was sufficiently high to prevent any charging effects even under impact of a massive electron dose.

All these experimental observations have at this stage only a documentary value. The dynamics of lithium migration through the lattice of LiAl is complex. More studies are needed to elucidate the
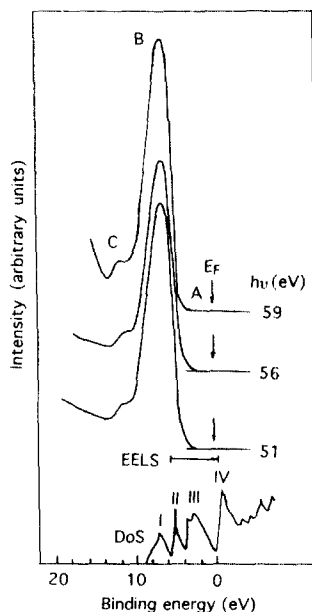
Fig. 2. A set of photoemission spectra of β-LiAl at various incident photon energies compared with the theoretical DoS curve (after [11]). An interband transition in EELS is marked by a horizontal arrow.

mechanisms of this process and its effects on the macroscopic behavior of the Zintl intermetallic compounds.

IV. Structure of Valence and Conduction Bands

Figure 2 shows a set of valence band photoelectron spectra of LiAl measured at three different photon energies, compared with the total density of states (DoS) distribution calculated by Hafner and Weber[11]. In general, the theory predicts correctly the position of the bands, but the intensity ratios are significantly different. The leading photoemission peak (B) corresponds to an envelope of bands I and II in the DoS curve. Structure C has no counterpart in the theoretical DoS distribution, and its origin is not yet understood. The photoemission intensity from the uppermost valence band (band III) is remarkably low. In fact this band
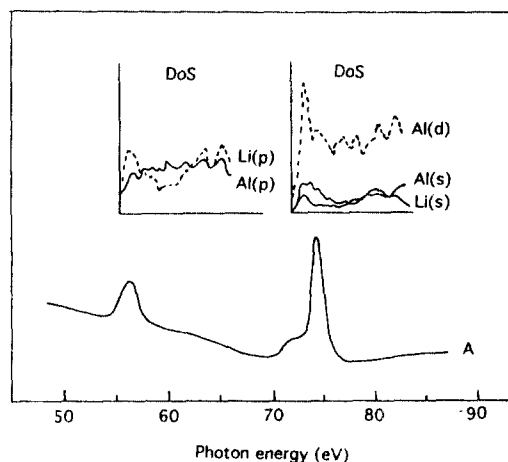

Fig. 3. Resonant photoemission from bands A at the Li-1s and Al-2p excitation edges.
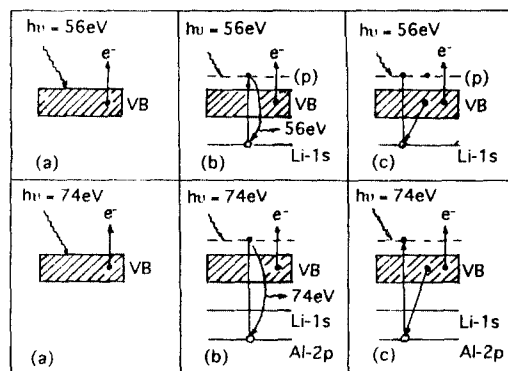

Fig. 4. Schematic diagram of processes that contribute to resonant photoemission; (a) direct photoemission; (b) exciton formation and decay by direct recombination; (c) exciton formation and decay by Auger electron emission.

is only measurable at incident photon energies close to 56 eV (Figure 1) and 74 eV (not shown), which correspond to the excitation edges of Li-1s and Al-2p core electrons, respectively. Since band III is dominated by p-type states originating from both lithium and aluminum, we conclude that the population of these states below the Fermi level is very low, and the s-to-p charge promotion, if at all present, is apparently much less significant than that predicted by theory. The resonant enhancement of the photoemission intensity from band A at the

Li-1s and Al-2p edges is clearly illustrated in Figure 3. We explain these resonances as the added contribution of three possible processes shown schematically in Figure 4. Process (a) represents direct photoemission from band lll. Processes (b) and (c) involve formation of an excitonic state (an excited state consisting of an electron lifted from a core level to and empty conduction band state, coupled to the core hole left behind) and its subsequent decay via either direct recombination (b) or Auger electron emission (c). Formation of excitons (quasi-bound electron-hole pairs) implies a high degree of localization of the conduction band states. In the case of LiAl, the very low population of the electronic states in band lll closest to the Fermi level resembles the existence of a band gap. Our electron energy loss experiment[16] identified a loss structure of 5.8 eV, which we interpret as an interband transition between the valence band ll and the first conduction band of high density IV. This transition, which is shown in Figure 2 by a horizontal arrow labeled EELS, confirms the position of the lowest conduction band at about 0.8 - 1.0 eV above the Fermi level, in agreement with the theory[11]. The distance between the low binding energy edge of the leading photoemission peak and the lowest conduction band (band IV) is about 5 eV. It is therefore understandable that, with such a wide "quasi-band-gap", formation of excitons is highly favored.

Acknowledgement

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