

Electronic structure and bonding in NaLi, LiMg and LiAl alloys: a MS X_α SCF approach

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Abstract. A MS X_α SCF method has been initiated to calculate the charge distribution, bonding properties and the density of states in NaLi, LiMg and LiAl alloys. No ionicity is seen in NaLi but a high covalency of different degree is detected in all the three alloys. The ionizations potentials calculated are 5.05, 5.5 and 5.58 eV respectively. Comparison with other calculations and experiments is found to be in fair agreement.

Keywords. Multiple scattering X_α self consistent field; bonding; alloys; electronic structure.

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1. Introduction

The electronic structure calculations by different cluster methods are widely used to study the localized properties in solids. The main points of interest have been bonding properties, transition between different energy states, magnetic properties, gap levels in semiconductors (Adachi *et al* 1979; Khowash *et al* 1985; DeLeo *et al* 1984) etc. Of the many calculation procedure the multiple scattering X_α self-consistent field (MS X_α SCF) method (Johnson 1967, 1968, 1971; Slater 1972, 1974) stands out. In this paper, we report the electronic structure, bonding properties and the density of states for NaLi, LiMg and LiAl alloys. Alkali metal dimers (NaLi) can be efficiently used as high power lasers near the infrared region. LiAl being light in weight and at the same time not easily breakable has attracted attention due to its potential usefulness in high energy density batteries as an anodic material and relatively high electrochemical activity. The equilibrium geometries and the bond length of small clusters of different sizes of LiNa, LiMg and LiAl have recently been given considerable importance (Rao *et al* 1986, 1987).

2. Methods

The MS X_α SCF method (Johnson 1967, 1968, 1971; Slater 1974) considers a cluster scooped out of the solid. The rest of the solid manifests its presence by providing a static electrostatic field through the Watson sphere truncation technique. The cluster is divided into: (i) atomic region with a spherical potential; (ii) interatomic region with a volume averaged potential, and (iii) extramolecular region where the potential

is in muffin-tin-form. The local X_α approximation to the exchange energy (Slater 1951) is used to obtain the eigenvalues and eigenfunctions by a rigorous solution of Schrodinger equation in every region.

The α values (Schwartz 1976) chosen for Li, Na, Mg and Al are 0.78147, 0.73115, 0.72913 and 0.72853, respectively. The muffin-tin radius for Li extends to its atomic radius value. Since the cation-anion distance is not exactly equal to the sum of the respective atomic radii, adjustments are made for the central cation radius in order to match the experimental bond distance. The justification of this kind of adjustment is reported elsewhere (Khan and Khowash 1987). The cation-anion distance obtained from the experiments is 2.21, 2.22 and 2.23 a.u. respectively, for the NaLi, LiMg and LiAl alloys. The cluster consists of a metal atom at the centre and six Li atoms occupying the octahedral positions. This octahedral configuration has been obtained by Rao *et al* (1986) through total energy minimization of the cluster with respect to all possible configurations. In our calculations we use structurally symmetrized wavefunctions as initial inputs for the octahedral symmetry as given by Ballhausen (1962).

3. Results and discussion

We use a MS X_α fully self-consistent field method to calculate the charge distribution in the different regions of the cluster as shown in table 1. The charge transferred from the cations is approximately 0.9, 1.4, and 1.5 electrons respectively. In contrast, the ligand ion charge remains constant. The charge in the interatomic region is a contribution from both the cation and the anions and thus is a measure of covalency (Khowash 1986). We now define a charge transfer diagram (see figure 1). Each point on the diagram represents self-consistently calculated charge subtracted from the atomic number. The length $\sqrt{(\Delta\rho_c)^2 + (\Delta\rho_l)^2}$, is called the root mean squared charge transfer for the redistribution to take place. The coordinate of a point along the ionic line gives the r.m.s. charge transfer between cations and anions only—a measure of ionic bond strength while the length perpendicular to ionic line is the r.m.s. charge transfer from atoms to the interatomic and extramolecular region—a measure of covalent bond strength (Khowash 1986; Khan and Khowash 1987). The unphysical region suggests that the total number of electrons in the cluster is conserved. According to this analysis, NaLi shows no ionic character at all with large covalency. LiMg and LiAl, on the other hand, show different degrees of ionicity and covalency, each increasing with atomic number. The numerical values of these covalent bond

Table 1. Charge distribution in the different regions of the NaLi, LiMg, and LiAl clusters in units of electrons.

Region	Na	Mg	Al
Central ion	10.1	10.6	11.5
Ligand ion	2.1	2.1	2.1
Intersphere charge	4.1	4.9	5.1
Extramolecular charge	2.2	1.9	1.8
Constant potential	-0.96	-0.95	-0.96

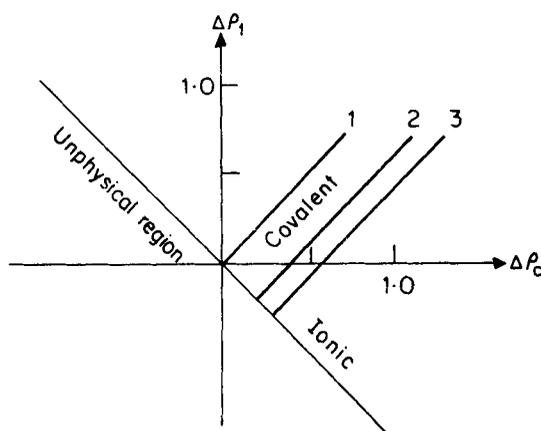


Figure 1. Covalent bond strengths for NaLi, LiMg, and LiAl in units of e .

strengths in units of electrons are 1.28, 1.66 and 1.80 respectively. This can be compared with the small covalent bond strength of 0.3 and 0.1 e reported earlier (Khan and Khowash 1987) for LiF and NaCl respectively. Zunger (1978) in his band study found the Al—Li bond to have an asymmetric build-up of charge along the bond. Strong hybridization of Al and Li states throughout the valence band is observed. A large accumulation of charge towards Al identifies the bond to be an ionically polarized covalent character. This is consistent with our calculated ionic and covalent bond strengths in LiAl alloy.

The bonding parameters are usually obtained by matching the parametrized orbital form factors with neutron scattering or nuclear magnetic resonance data. Our basis functions are the same as the molecular orbitals used in the ligand field theory. We calculated the bonding parameters, λ_σ , in these materials as 3.7%, 5.5% and 5.8% respectively. This increasing trend is in agreement with our calculated bond strengths from the charge transfer diagram.

The discrete self-consistent one-electron energy spectra obtained as a solution of Schrodinger equation are then broadened with a Lorentzian of constant width to get a continuous density of states. It has been pointed out recently that the densities obtained from small clusters resemble the bulk closely (Khowash and Khan 1986; Lee *et al* 1984). It should be noted, however, that the constant width of the Lorentzian does not affect the localization or delocalization of any state. The fully self-consistent wavefunction of a particular state contains contributions from atomic and interatomic regions. The magnitude of these contributions decides the state to be either atomic-like or of covalent character. The total density of states for NaLi is shown in figure 2a. The population analysis of the s -peak centred around -7.2 eV indicates a large contribution ($\sim 75\%$) from the interatomic and extramolecular region (from now onwards denoted as IE) and relatively small contributions from Na $3s$ (16%) and Li $2s$ (9%). The p -like peak at -5.6 eV has a larger IE contribution (84%) along with hybridized Na and Li functions. This indicates a large mixing between the cations and the anions. The partially filled p level accommodates five electrons and therefore may undergo a Jahn-Teller distortion. In general the splitting of this partially filled level may vary from a few meV to an eV depending upon the system of interest. It is well known that the Jahn-Teller splitting in metals is very small and therefore can

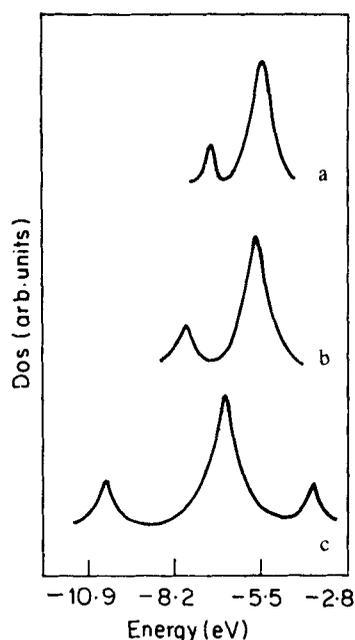


Figure 2. Total density of states in the valence region for (a) NaLi, (b) LiMg and (c) LiAl alloys obtained by broadening the discrete energy levels with a Lorentzian of constant width.

be neglected for most practical purposes. Thus, no distortion is included in our calculations and so the three-fold p levels are degenerate maintaining the octahedral symmetry. In the case of LiMg (figure 2b), the s peak is pulled down by 0.8 eV whereas the p peak remains unaffected. The contributions from IE for s and the p bands are now 69% and 84%, respectively. The p state is more delocalized as compared to the s state. Figure 2c shows the total density of states for LiAl. The s state goes further down due to greater attractive potential with the increase in central ion nuclear charge. Our theoretically calculated density of states for LiAl is similar to the linear muffin tin orbital electronic structure calculations of Asada *et al* (1981) where they find a dominant s -like peak in the total density of states. Such a trend is also obtained for a 9 atom LiAl cluster by Ellis *et al* (1977) using discrete variational method. Zunger (1978) from his population analysis study finds a strong Al $3s$ and Li $2s$ hybridization at the bottom of the valence band close to -8.3 eV as compared to our calculated value of -10.5 eV. The Al $3p$ and Li $2p$ hybridization shows up at -6.2 eV. The central peak has approximately equal contribution from s and p for LiAl alloy at about -5.5 eV. The photoionization efficiency curve for LiNa with ultraviolet light (Kappes *et al* 1986) finds the ionization potential to be at 5.05 eV. This is in very good agreement with the present calculated value of 5.5 eV. The calculated ionization potential for LiMg is 5.58 eV whereas the corresponding value for LiAl is 4.8 eV.

4. Conclusion

We have performed, for the first time, a detailed calculation of electronic structure, charge distribution and the density of states of NaLi, LiMg and LiAl alloys using a

multiple scattering X_α self-consistent method. Covalency in these materials is studied using a charge transfer diagram. As we move from NaLi to LiAl via LiMg, covalency increases owing to greater overlap between the cation and anion electrons. NaLi shows no ionic character. The ionic bond strength is larger for LiAl as compared to LiMg. The density of states for LiAl show similar trend as also seen in other band structure and cluster calculations. The theoretically calculated ionization potentials are found to be in good agreement with experimental results. We conclude with the hope that the present work has contributed to our knowledge of bonding characteristics in these alloys.

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