Local electronic structure of ordered Li-X (X=Na, Mg, Al) alloys under high pressure

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Abstract. The present work extends our previous studies of Li–X (X=Na, Mg, Al) alloys to some local electronic properties of the alloys using the optimized structure data obtained. The electronic band structure of the alloys is determined using the self-consistent-field LMTO method in order to analyse the local phenomena induced by solute atoms, such as the changes in the average charge density of atomic Wigner–Seitz spheres and in the electronic density of states (DOS). The results obtained for the Li alloys show that charge transfer occurs from the solute atoms to the solvent Li atoms as the volume of the alloy decreases. The charge transfer is found to follow a universal curve as a function of volume. The details of the DOS curves indicate that the charge transfer is directed mainly to the bottom of the Li p band. This phenomenon can be related to the orthogonality property of the valence and core states and the missing p states in the Li core.

1. Introduction

Li–Mg and Li–Al alloys are interesting, both in physical and technological respects, because of their strength and low density. In recent years, a number of experimental [1–9] and theoretical [10–18] investigations have been performed on these alloys. In alloy design it is important to understand the mechanical and electronic properties of materials and how these properties depend, for example, on alloying and external pressure. In our previous investigations of Li alloys [19, 20] the lattice distortion induced by solute atoms was studied using the first-principles structural optimization technique [21–24]. This technique enables one to optimize the crystal structure thus making it possible to investigate the effects of lattice distortion on the physical properties of alloys. The present paper extends our previous studies to certain local electronic properties of the alloys closely related to the local partial density of states, which could not, however, be determined with the molecular dynamics program at our disposal.

Although the first-principles structural optimization method is an accurate and convenient way to calculate the geometric and electronic structure of alloys, it is a computationally heavy method and this significantly restricts its applicability especially in the case of non-metals and transition metals. The LMTO–ASA method was used in the present investigation to analyse the local electronic effects, since it gives a useful background for investigating alloying processes in transition metals using large supercells. In the present paper, the average charge density of atomic Wigner–Seitz spheres and the electronic density of states (DOS) are considered. Of course in the case of alloys the Wigner–Seitz cells are not uniquely defined but anyhow they are useful concepts in studying, for instance, relative charge transfers between these cells at different pressures.

2. Methods of calculations

The calculational method used is described in [25–27]. The Wigner–Seitz radii of Li and X atoms were taken to be equal. We made a test calculation for $Li_{15}Mg$ in which the ratio of the atomic Wigner–Seitz radii (R) was taken to be $R_{Mg}/R_{Li} = 1.04$. The results of this test for normalized valence charge ρ/ρ_0 (= valence charge of the atomic sphere divided by its value at equilibrium volume) of the Mg sphere were found to differ by less than 2% from the results shown in this paper. The calculations for Li_{16} and $Li_{15}X$ were made with a 16-atom supercell containing of eight conventional BCC cells with the solute-atom-induced lattice distortion taken from the first-principles structural optimization calculations [20]. There are five different shells of neighbouring atoms surrounding the solute atom in the unit cell. All the neighbouring atoms excluding the first neighbours were treated as equivalent atoms, since this choice led to the best agreement with the total DOS obtained from our previous pseudopotential calculations [19, 20]. Furthermore, any different choice to equivalent and inequivalent atoms led to only a minor change in the charge distribution. The k-space integrations were done using 35 k-points in the irreducible wedge of the simple cubic Brillouin zone.

3. Results and discussion

Our previous investigation of the solute atom induced lattice distortion and its pressure dependence in BCC Li [20] revealed that this distortion depends crucially on the type of the solute atom. In the present paper, the effects of these atomic distortions on the local electronic properties of the corresponding alloys are reported.

Although the solute atoms investigated are different in several respects, the volume dependence of the charge transfer between the solute and solvent atoms was found to follow approximately a universal curve (figure 1). All the solute atoms investigated lose part of their valence charge to surrounding Li atoms as pressure increases, showing also a distinct correlation between the induced charge transfer and the change in volume. As figure 1 shows, the relaxation of the Li atoms around the solute atom has the effect that the data points fall with better statistics on the same universal curve.

Analysing the pressure-induced charge transfer in more detail shows that the solute atom loses s- and p-type charge. The solvent Li atoms lose s-type charge and gain p-type charge (figure 2). Since the total amount of d-type charge is small in the alloys investigated only s- and p-type charges are considered in the present work. This kind of charge transfer may be explained by the mutual orthogonality property of the valence and core states. These orthogonality relations put an extra restriction on the deformations of the wave functions as volume decreases. Since there are no p states in the core of a Li atom, this restriction does not exist for p valence states in Li and they can relax more freely as volume decreases. Due to this, the increasing pressure increases the energy of the Li p states less than the energy of the other s and p states in these alloys which means that the net charge flow to Li p states lowers the total energy of the system.

The local partial density of states provides a tool for investigating the predicted charge transfer in the energy space. The DOS figures are shown only for $Li_{15}Mg$ alloy since it serves as a good example of the DOS of the alloys investigated. In figure 3, the occupied parts of the partial density of states are shown for the Mg atom and its nearest neighbours, Li atoms, in $Li_{15}Mg$ with two different lattice parameters. As we have already stated, in compressing the lattice, part of the valence charge of $Li_{15}Mg$ is transferred from Mg s and p
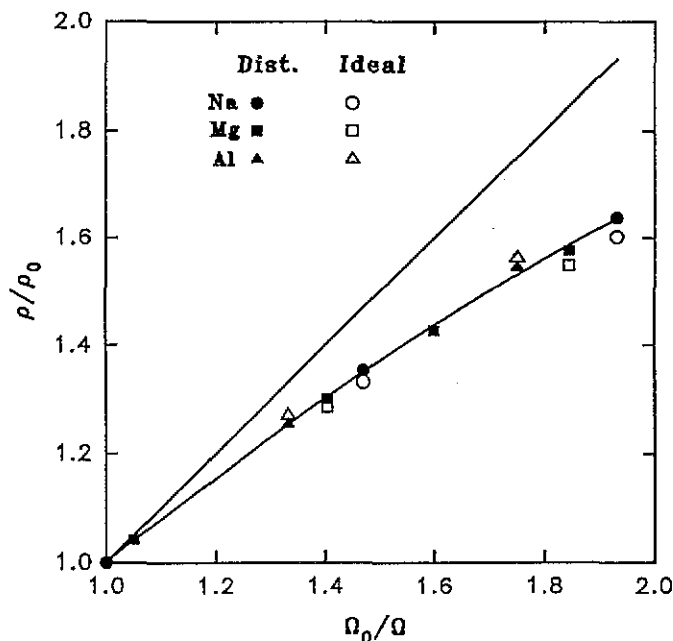
Figure 1. Normalized valence charge ρ/ρ_0 ($\rho = Q/\Omega$) for the impurity atom X in $Li_{15}X$ alloy. Black and white symbols correspond to distorted and ideal structures, respectively. Ω_0 corresponds to the equilibrium volume of each alloy.

states and from Li s states to Li p states. This charge transfer is also discernible in the DOS curves, like those shown in figure 3. In the following, the general features of the changes in the partial DOS of $Li_{15}Mg$ with decreasing lattice parameter are considered. Whereas the elongation of the DOS over the whole occupied energy region is common to all the partial DOS of $Li_{15}Mg$, the intensity of the DOS curve behaves in a characteristic way in various cases. The Mg and Li s DOS decrease over the whole occupied energy region but for Li s DOS this decrease is smaller in the lower-energy region than in the higher-energy one. The Mg p DOS increases at the bottom of the band and decreases elsewhere. The Li p DOS increases also at the bottom of the band but has approximately constant intensity elsewhere, contrary to what is found in the Mg case. While figure 2 shows that part of the valence charge flows mainly to the Li p states as the volume of the alloys decreases, figure 3 reveals that this charge goes mainly to the bottom of the Li p band. Although the detailed structure of the partial DOS of $Li_{15}Na$ and $Li_{15}Al$ is different from that of $Li_{15}Mg$, the general changes in the partial DOS, as well as the charge transfer effects of alloying as a function of lattice parameter, are similar to those in $Li_{15}Mg$ discussed above.

The partial DOS is an essential quantity if one wants to know how charge distribution changes in energy space. Another important quantity is the total DOS at the Fermi level since a large number of physical properties depend on that quantity. Thus, it is important to find out how much the total DOS at the Fermi level for ideal and optimized structures differ from each other. Our results for $Li_{15}X$ alloys are shown in table 1, which shows that in $Li_{15}Na$, $Li_{15}Mg$ and $Li_{15}Al$ the total DOS of optimized structures differ by 4% ($a = 11.5$ au), 7% ($a = 10.5$ au) and 14% ($a = 11.5$ au), respectively, from those of ideal structures. Hence, it seems that the results may differ from each other quite a lot depending on whether the ideal or optimized structure is used in the calculations.
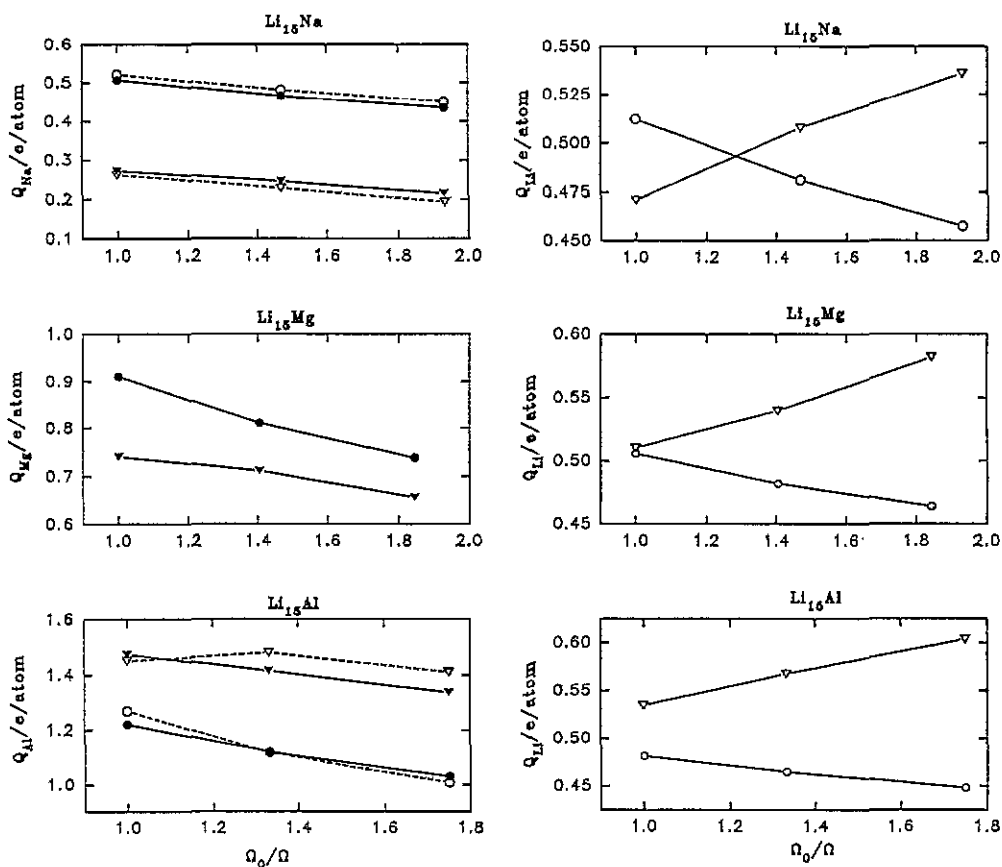
Figure 2. Partial charge Q (in units of electrons/atom) for Na, Mg, Al and Li atoms in $Li_{15}X$ alloy. Circles and triangles correspond to s and p partial charges, respectively. In addition solid and broken curves correspond to distorted and ideal structures, respectively.

4. Conclusions

In the Li alloys investigated charge transfer occurs from the solute atoms to the solvent Li atoms as the volume of the alloy decreases. This charge transfer was found to follow a universal curve as a function of volume. If the solute-atom-induced lattice distortion is taken into account the data points fall with better statistics on the same universal curve. A detailed investigation showed that this charge transfer is directed mainly to the bottom of the Li p band. This kind of behaviour of the Li p states can be attributed to the orthogonality property of the valence and core states and the missing p states in the Li core. This peculiarity of Li appears also in a relatively deep p pseudopotential and localized p states as compared to those of Na, Mg and Al. The effect of this orthogonality property can be seen also in the DOS of Li [28–30] and in compressibility and spin susceptibility as a function of pressure [31]. In the cases investigated the solvent element Li dominates the volume induced charge transfer. Thus, it would be important and interesting to further investigate the charge transfer and related properties of Li–Be alloys since the charge transfer from Al to Li and Be in Al–Li and Al–Be alloys, respectively, is almost the same [12].
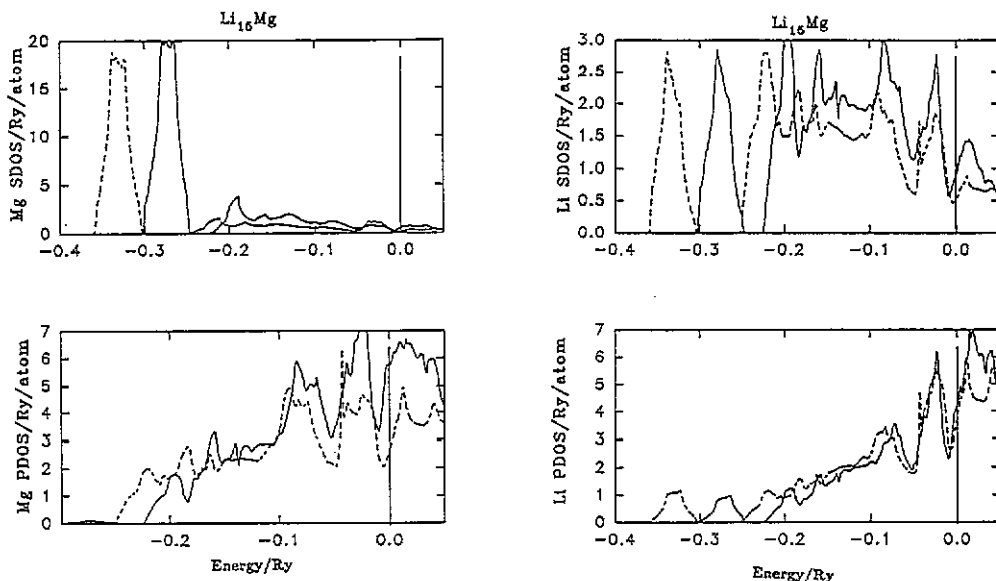
Figure 3. Partial density of states of Mg and Li atoms in $Li_{15}Mg$. Solid and broken curves correspond to lattice parameters 12.9 au and 10.5 au, respectively. The Fermi energy is shown by the vertical line.

Table 1. Total DOS at the Fermi level and pressure in $Li_{15}X$ alloys (X=Na, Mg, Al).

Alloy	a (au)	Total DOS (states Ryd^{-1}/atom)		Pressure (kbar)	
		Ideal	Optimized	Ideal	Optimized
	13.07	4.20	4.32	21	24
$Li_{15}Na$	11.50	5.15	4.93	160	170
	10.50	4.99	4.93	390	410
	12.88	6.13	6.31	53	53
$Li_{15}Mg$	11.50	4.71	4.75	230	240
	10.50	4.09	3.84	550	550
	12.65	6.27	6.12	43	43
$Li_{15}Al$	11.50	4.51	5.23	190	220
	10.50	4.28	4.67	540	570

Acknowledgment

References

[1] Mason J F, Warwick C M, Smith P J, Charles J A and Clyne T W 1989 *Mater. Sci.* **24** 3934–46
[2] Gonźales-Doncel G, Wolfenstine J, Metenier P, Ruano O A and Sherby J 1990 *J. Mater. Sci.* **25** 4535–40
[3] Siedersleben M E and Taylor G 1989 *Phil. Mag.* A **60** 631–47
[4] Siedersleben M E, Naito S and Taylor G 1993 *Phil. Mag.* B **67** 3–23
[5] Crisp R S 1991 *J. Phys.: Condens. Matter* **3** 5761–8

[6]   Zhao J, Qian Y J, Yu Z-Z, Haerle M L, Yin S, Sato H, Pratt W P Jr, Schroeder P A and Bass J 1989 *Phys. Rev.* B **40** 10 309–21

[7]   Lavernia E J and Grant N J 1987 *J. Mater. Sci.* **22** 1521–9

[8]   Boukos N and Papastaikondis C 1993 *Phys. Rev.* B **47** 13 147–50

[9]   de Diego N, Segers D, del Rio J, Dorikens-Vanpraet L and Dorikens M 1991 *J. Phys.: Condens. Matter* **3** 5415–23

[10] Vaks V G and Trefilov A V 1988 *J. Phys. F: Met. Phys.* **18** 213–35

[11] Benedek R, Yang L H, Woodward C W and Min B I 1992 *Phys. Rev.* B **45** 2607–12

[12] Masuda-Jindo K and Terakura K 1989 *Phys. Rev.* B **39** 7509–16

[13] Podloucky R, Jansen H J F, Guo X Q and Freeman A J 1988 *Phys. Rev.* B **37** 5478–82

[14] Rahman S M M and Karaoglu B 1993 *J. Phys.: Condens. Matter* **5** 851–60

[15] Mehl M J 1993 *Phys. Rev.* B **47** 2493–500

[16] Abrikosov I A, Vekilov Yu H, Korzhavyi P A, Ruban A V and Shilkrot L E 1992 *Solid State Commun.* **83** 867–70

[17] Grammatikakis J G, Eftaxias K, Patapis S and Hadjicontis V 1988 *J. Phys. Chem. Solids* **49** 965–7

[18] Franck W, Breier U, Elsässer C and Fähnle M 1993 *Phys. Rev.* B **48** 7676–8

[19] Salo P T and Kokko K 1993 *J. Phys.: Condens. Matter* **5** 3325–32

[20] Kokko K, Salo P T and Mansikka K 1994 *Comput. Mater. Sci.* **2** 261–9

[21] Car R and Parrinello M 1985 *Phys. Rev. Lett.* **55** 2471–4

[22] Williams A R and Soler J 1987 *Bull. Am. Phys. Soc.* **32** 562

[23] Kobayashi K 1990 *PhD Thesis* University of Tokyo

[24] Morikawa Y 1994 *PhD Thesis* University of Tokyo

[25] Andersen O K 1975 *Phys. Rev.* B **12** 3060–83

[26] Skriver H L 1984 *The LMTO Method (Springer Series in Solid State Sciences, vol 41)* ed M Cardona and P Fulde (Berlin: Springer)

[27] Kokko K, Ojala E and Mansikka K 1990 *J. Phys.: Condens. Matter* **2** 4587–93

[28] Papaconstantopoulos D A 1986 *Handbook of the Band Structure of Elemental Solids* (New York: Plenum) p 34

[29] Schülke W, Schulte-Schrepping H and Schmitz J R 1993 *Phys. Rev.* B **47** 12 426–36

[30] Schülke W, Nagasawa H, Mourikis S and Lanzki P 1986 *Phys. Rev.* B **33** 6744–57

[31] Takada Y 1993 *Phys. Rev.* B **47** 3482–94