

## Pressure-induced charge transfer in Li and Al alloys

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In pure metals, the  $s, p, d, \dots$  bands have different energy shifts as the metals are compressed. Changes that are produced in this way in the amount of  $s, p, d, \dots$  type valence charge affect, e.g., the bonding properties of the atoms, which in turn can lead to structural phase transitions at high pressures. In alloys, the band shifts can produce complex changes in the electronic structure. The present work deals with the pressure-induced charge transfer in alloys. In Li- $X$  alloys ( $X = \text{Be, Na, Mg, Al, Si, P, Ca, Sr}$ ) the number of Li valence electrons is found to increase along with increasing pressure. This is attributed to the properties of Li  $p$  states. A similar type of charge transfer is also found in Al- $X$  alloys ( $X = \text{Ti, Zr, Hf, Cu, Ag, Au}$ ). The effects of fully occupied and partially occupied  $d$  bands can be studied by considering Al alloyed with noble metals and transition metals. The electronic structure of the alloys is calculated with the linear muffin-tin orbital atomic sphere approximation method. To check the magnitude of the possible computational errors involved in our results we also performed pseudopotential plane-wave calculations for Li-Mg alloys. [S0163-1829(96)05120-X]

In our previous investigations of Li alloys<sup>1-4</sup> we studied local lattice distortions and charge transfers as a function of pressure. The results obtained show that a part of the valence electrons are transferred from the solute atoms to the solvent Li atoms as the volume of the alloy decreases. The solvent element Li seems to determine both the direction and the amount of the pressure-induced charge transfer. The charge transfer was found to follow approximately a single curve for all investigated solute elements (Na, Mg, Al).<sup>4</sup> The fact that the pressure-induced charge transfer between the solute and solvent atoms seems to be independent of the type of the solute atom is even more surprising since the induced lattice relaxation depends crucially on the type of the solute atom.<sup>3</sup>

A more detailed analysis of the pressure-induced charge transfer<sup>4</sup> showed that the solute atom loses both  $s$ - and  $p$ -type charge. The solvent Li atoms lose  $s$ -type charge and gain  $p$ -type charge. The amount of the  $d$ -type charge transfer is small due to the small  $d$  contribution in the valence charge of the investigated elements. This kind of charge transfer effect was suggested to be due to 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 the 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 the 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. This peculiarity of Li also appears as a relatively deep  $p$  pseudopotential and localized  $p$  valence states of Li as compared to those of, i.e., Na, Mg, and Al. The effect of this orthogonality property can also be seen in the density of states (DOS) of Li (Refs. 5-7) and in its compressibility and spin susceptibility as a function of pressure.<sup>8</sup>

The investigation of Li-Be alloys would shed more light on the obtained pressure-induced charge-transfer phenomenon since Li and Be are expected to have the same kind of electronic effects in alloys. As Li, Be has only  $s$  states in the

core. And, moreover, the calculated charge transfers in both Al-Li and Al-Be alloys at zero pressure are almost the same.<sup>9</sup> The results obtained for Li alloys suggest that a similar pressure-induced charge transfer could exist in other alloys as well. Al alloyed with transition metals is a good candidate for a charge-transfer system. From the experimental point of view, aluminum and transition metals are not as difficult materials as alkali and alkaline earth metals are.

In the present study we concentrate on the following three questions. (1) Does the core or the valence electron configuration of the solute atom have an effect on the pressure-induced charge transfer in Li alloys? To answer this question we extend our previous investigation on Li alloys<sup>4</sup> to contain solute atoms such as Be, Si, P, Ca, and Sr. (2) Does the pressure-induced charge-transfer effect exist in other alloys too? As an example we consider Al alloyed with solutes from Ti and Cu groups. (3) Does the calculational method used here have an effect on the calculated pressure-induced charge transfer in alloys? To check this we investigate the Li<sub>15</sub>Mg alloy using both the linear muffin-tin orbitals (LMTO) and the pseudopotential plane-wave methods.

The self-consistent-field LMTO method used here is described in Refs. 10-12. The calculations for Li<sub>15</sub> $X$  alloys are made with a 16-atom simple cubic supercell consisting of eight conventional bcc cells with the atoms fixed at their ideal bcc lattice sites. Al<sub>3</sub> $X$  alloys are calculated with the  $L1_2$  structure. All the solvent atoms are treated equivalently and the Wigner-Seitz (WS) radii of different component atoms of the alloys are taken to be equal. The  $k$ -space integrations are done with 35 and 120  $k$  points in the irreducible wedge of the simple cubic Brillouin zone for Li<sub>15</sub> $X$  and Al<sub>3</sub> $X$  alloys, respectively. The LMTO calculations are made with the atomic sphere approximation (ASA). In the plane-wave pseudopotential method the potential around the atoms is not restricted by the spherical symmetry requirement as in the LMTO-ASA method. The pseudopotential plane-wave method used here is described in Ref. 2.

Investigations of pure metals showed that at a sufficiently high pressure the crystal structure of even simple third-

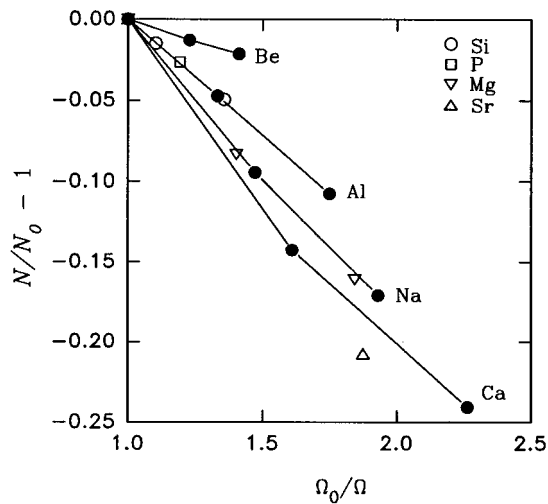


FIG. 1. The normalized number of valence electrons ( $N/N_0 - 1$ ) in Wigner-Seitz spheres of solute atoms as a function of the inverse of the normalized average atomic volume ( $\Omega_0/\Omega$ ) in Li-based alloys. The subscript 0 refers to the zero pressure value. The solute element in question is shown by its symbol. The points refer to the calculated results, curves are only to guide the eye.

period metals such as Na, Mg, and Al is controlled by  $d$  electrons.<sup>13</sup> At least in Mg and Al this is due to the lowering and partial filling of the initially unoccupied  $3d$  band as the metals are compressed. In the case of Al it was shown that the number of  $s$  electrons decreases, but the number of  $p$  and  $d$  electrons increases as the volume is compressed.<sup>14</sup> Part of the valence electrons from  $s$  and  $p$  states were found to transfer to  $d$  states in Cr, Mo, and W as the volume of the metal is decreased.<sup>15</sup> The obtained pressure-induced changes in the electronic structure of metals can be understood by considering the simple energy band picture of solids. Under compression the energy bands rise in the energy scale due to the increased overlap between the states belonging to different atoms. The spatially extended  $s$  and  $p$  states feel more compression than the more localized  $d$  states, and therefore the  $sp$  band rises faster than the  $d$  band, which leads to the electron transfer from the higher-lying  $sp$  levels to the lower-lying  $d$  levels. In alloys, the pressure-induced band shifts are different for different atomic types, leading to more complex phenomena than in pure metals. Both intrasite and intersite effects in the electronic structure are expected to occur as the volume of the alloy changes.

In Figs. 1 and 2 the normalized number of valence electrons ( $N/N_0 - 1$ ) of the solute atom is plotted as a function of the inverse of the normalized average atomic volume ( $\Omega_0/\Omega$ ) of the alloy.  $N$  is the number of valence electrons inside the WS sphere centered at the solute atom site and  $\Omega$  is the volume of the WS sphere. Here the subscript 0 refers to the case corresponding to the zero external pressure.

In Fig. 1 two trends of the pressure-induced charge transfer in Li alloys can be found. For solute atoms belonging to the same group in the Periodic Table the charge transfer per volume change increases with the increasing atomic number (Be, Mg, Ca, Sr). Within the same period (Na, Mg, Al, Si, P) the charge transfer is more efficient for alkali metal and alkaline earth solutes than for other solutes. However, the ob-

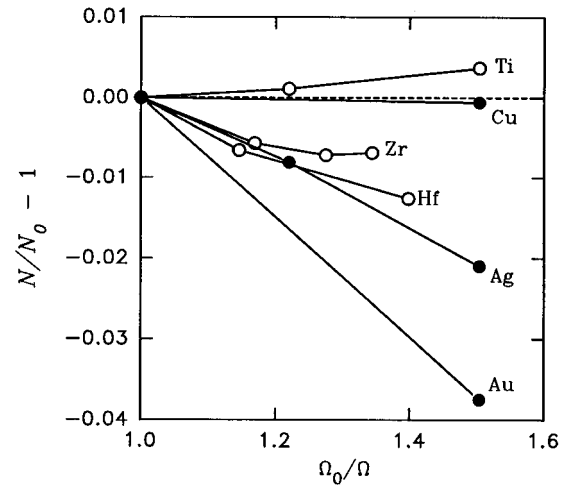


FIG. 2. Same as Fig. 1, but for Al-based alloys.

tained difference in the pressure-induced charge transfer between the different cases is expected to decrease if the solute-atom-induced lattice relaxation were taken into account.<sup>4</sup> Figure 2 shows that there exists a pressure-induced charge transfer in Al alloys too. In this case a trend of increasing charge transfer per volume change with the increasing atomic number of the solute atom is also obtained.

As mentioned before, Li-Be alloys are interesting because both atoms have an identical core electron configuration and, at zero external pressure, they induce practically the same charge transfer when alloyed in Al.<sup>9</sup> In  $Al_7X$  ( $X=Li, Be$ ) systems the Al atoms were found to lose about 0.05 electron compared to pure Al. The volume derivative of this electron transfer is positive for both Li and Be, which means that the number of electrons in Al atoms will decrease as the alloys are compressed. This is in accord with our results for the  $Li_{15}Al$  system. Because the volume derivative is larger for Li than for Be, one can expect that in Li-Be alloys Be should lose electrons as the volume of the alloy decreases. As shown in Fig. 1 this is what actually happens. Masuda-Jindo and Terakura<sup>9</sup> also calculated the volume derivative of the charge transfer in  $Al_7X$  with  $X$  being Na, Mg, Ca, and Cu. Their results show that this derivative decreases linearly from Li to Ca. This implies that the slope of the charge-transfer curves in Fig. 1 should decrease progressively when going from Be to Ca solutes. This actually happens, but the slopes in Na and Mg cases are very close to each other.

Figure 2 shows the results for Al alloys with two different type of solutes. The solutes of the Ti group have a partially occupied  $d$  band whereas the solutes of the Cu group have a completely occupied  $d$  band. For the Ti group solutes the  $d$  band effects are expected to be significant in the pressure-induced charge transfer. Ti as a solute is found to be exceptional because electrons are transferred from Al to Ti under compression. This is suggested to be due to the fact that there are no  $d$  states in the core of Ti atoms and therefore the Ti  $d$  states feel less compression under pressure than the  $d$  states in Zr and Hf. There are no  $d$  states in the core of Cu atoms either, but in Cu the  $d$  states lie below the Fermi level, which means that they can affect the pressure-induced charge transfer only indirectly. The difference of the solutes belonging to Ti and Cu groups is also shown by the curvatures of

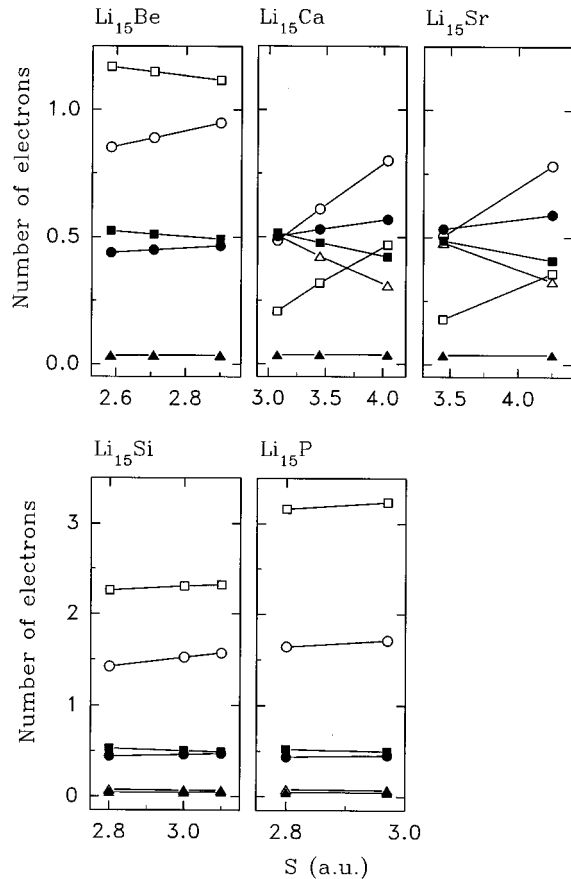


FIG. 3. The partial number of valence electrons in Wigner-Seitz spheres in Li-based alloys as a function of the WS radius  $S$ . Filled symbols refer to Li and open symbols to the solute atoms. Circles, squares, and triangles refer to  $s$ ,  $p$ , and  $d$  electrons, respectively.

the charge-transfer curves. For the Ti group the charge transfer curve has an upward curvature whereas for the Ag solute it has a downward curvature.

The obtained results for the pressure-induced charge transfer in alloys can be analyzed in more detail by plotting the partial valence charges of the component atoms as a function of the WS radius. In the case of Li alloys the following trends with the decreasing volume are found (Fig. 3). In Li atoms the number of  $s$  electrons is decreased and the number of  $p$  electrons increased. In solute atoms the number of both  $s$  and  $p$  electrons is decreased except for Be solutes where the number of  $p$  electrons is increased. Because there are no  $p$  states in the core of Li and Be atoms, the  $p$  valence states of these atoms feel less compression under pressure than the other states in the alloys, which means that the energies of the  $p$  states of Li and Be rise more slowly than the energies of the other states as the volume of the alloy is decreased. The number of  $d$  electrons in  $\text{Li}_{15}\text{X}$  alloys is small except for  $\text{X}=\text{Ca}$  or  $\text{Sr}$ . In Ca and Sr solutes the number of  $d$  electrons is increased under compression. This is because in these metals the bottom of the unoccupied  $d$  band is not far from the Fermi level at zero pressure. The trends of the charge transfer under compression in Al alloys are the following (see Fig. 4). In the Al site the number of  $s$  electrons decreases and the number of  $p$  and  $d$  electrons increases in all cases investigated. In Ti, Zr, and Hf solutes the

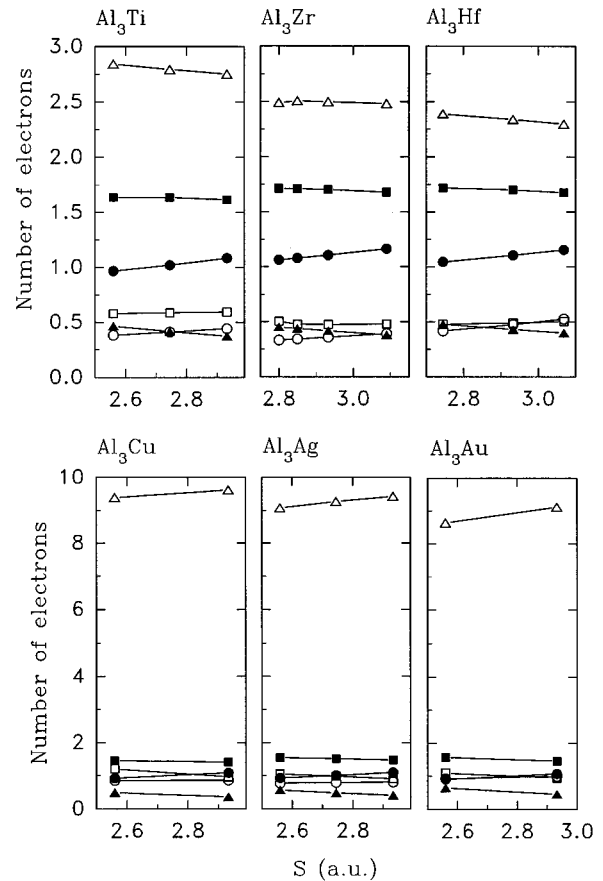


FIG. 4. Same as Fig. 3, but for Al-based alloys. Filled symbols refer to Al.

number of  $s$  and  $p$  electrons is decreased and the number of  $d$  electrons is increased. However, at high pressures in the case of Zr the number of  $p$  electrons starts to increase and the number of  $d$  electrons starts to decrease. For Cu, Ag, and

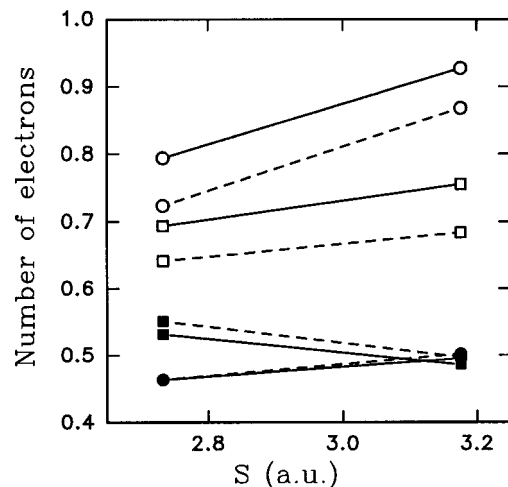


FIG. 5. The partial number of the valence electrons in the WS sphere of Li (filled symbols) and Mg (open symbols) in  $\text{Li}_{15}\text{Mg}$ . Solid and dashed lines represent the LMTO-ASA and pseudopotential calculations, respectively. Circles and squares refer to  $s$  and  $p$  electrons, respectively.

Au solutes the number of  $s$  and  $d$  electrons decreases and the number of  $p$  electrons increases.

To estimate the magnitude of the possible computational errors involved in our calculations we also performed pseudopotential plane-wave calculations for the  $\text{Li}_{15}\text{Mg}$  alloy (Fig. 5). Although the number of electrons in the Mg sphere is larger in the LMTO-ASA calculations than in the pseudopotential calculations the obtained pressure-induced charge transfers are quite similar in both cases. This means that the investigated phenomenon is not very sensitive to the calculational method and the results are expected to be reliable in that respect.

To summarize briefly, we have shown that in Li alloys the valence electrons have a tendency to transfer from solute atoms to Li atoms as the volume of the alloy is decreased. This tendency is attributed to the missing core-valence orthogonalization of the Li  $p$  valence states. For solute atoms belonging to the same group in the Periodic Table the pressure-induced charge transfer becomes more efficient with the increasing atomic number of the solute atoms. This is in accord with the increasing core-valence orthogonalization effects as the number of core states of the solute atom is increased. A similar type of pressure-induced charge-transfer phenomenon was also found in Al alloys.

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