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Ab initio study of structural, electronic and dynamical properties of MgAuSn

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Abstract. The structural and electronic properties of MgAuSn in the cubic AlLiSi structure have been studied, using density functional theory within the local density approximation. The calculated lattice constant for MgAuSn is found to be in good agreement with its experimental value. Our calculated electronic structure is also compared in detail with a recent tight-binding. A linear-response approach to density-functional theory is used to calculate the phonon spectrum and density of states for MgAuSn.

PACS. 63.20.Dj Phonon states and bands, normal modes, and phonon dispersion – 71.15.Mb Density functional theory, local density approximation, gradient and other corrections

1 Introduction

Ternary and quaternary coloured compounds have received considerable attention, due to their fundamental and technological importance [1–3]. The electronic and optical properties of MgAuSn are interesting because it shows a purple colour. For the $Mg_{0.36}Au_{0.10}Sn_{0.54}$ ternary alloy, both theoretical and experimentally measured optical and electronic properties have been reported recently by Lee et al. [3]. To the best of our knowledge, the structural and electronic properties of this material have not been studied using density functional theory. However, results obtained from this method [4–7] are in good agreement with experimental results. Thus, the first aim of this work is to investigate structural and electronic properties of MgAuSn by employing the plane-wave pseudopotential method. The calculated lattice constant is compared with a recent experimental value [3]. The second aim of this work is to obtain vibrational properties of this material, since they play a significant role in determining various material properties such as phase transitions, electron-phonon interactions, and transport coefficients. Thus, linear-response theory [5] is used in the calculation of the phonon dispersion curves and density of states of MgAuSn. The frequencies of zone-center phonon modes are found to be 142.9 cm^{-1} and 213.4 cm^{-1}. We also present atomic displacement patterns of optical phonon modes at the X point. From these displacement patterns, we observe that the highest optical phonon mode is characterised by the vibration of Mg atoms due to large mass differences between Mg and Au(or Sn).

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2 Theory

The calculations have been performed using a first-principles density functional pseudopotential method [8]. The calculation is carried out with the ab initio program PWSCF [9] using a linear combination of atomic orbitals as the basis set, and norm-conserving Troullier-Martins pseudopotentials [10]. Electron-electron interaction was considered within the local density approximation (LDA), with the correlation scheme of Ceperley and Alder [11]. Single particle wave functions are expanded in a plane-wave basis set up to the kinetic energy cut-off 50 Ry. The number of **k** points in the irreducible Brillouin zone (BZ) used in the self-consistent calculations is 120 [12]. Integration up to the fermi surface is done with a smearing technique [13] with the smearing parameter $\sigma = 0.02$ Ry. The lattice dynamical properties are calculated within the framework of self-consistent density functional perturbation theory [5]. We have calculated eight dynamical matrices. A Fourier interpolation has been used to obtain complete phonon dispersion curves of MgAuSn.

3 Results

MgAuSn crystallizes with the well-known AlLiSi structure, with three atoms per unit cell. The positions of atoms

Table 1. Calculated structural lattice constant, bulk modulus and the pressure derivative of bulk modulus of MgAuSn compared with previous experimental results.

	a (Å)	B (kbar)	$B^{'}$
This work	6.38	8.31	5.38
Experiment [1]	6.41		
Experiment [3]	6.42		

in the unit cell are $\mathrm{Mg} = (0, 0, 0)$, $\mathrm{Au} = (0.25, 0.25, 0.25)$ and $\mathrm{Sn} = (0.50, 0.50, 0.50)$. The equilibrium lattice parameter has been determined by minimizing the crystal total energy calculated for different values of the lattice parameter. The resultant energies have been fitted to the Murnaghan equation of state [14] in order to obtain the lattice constant, the static bulk modulus at zero pressure B and the first-order pressure derivative of the bulk modulus $B^{'}$. The calculated lattice constant, bulk modulus and its pressure derivative are listed in Table 1. Our calculated lattice constant is in good agreement with experiment [3] to within 0.5%. Figure 1 displays the electronic band structure of MgAuSn along various symmetry directions. The bands are quite dispersive near the Fermi level, with a Fermi velocity of 1.65×10^6 ms^{-1}. Our calculated Drude plasma energy [15] for MgAuSn of 10.05 eV is in fairly good agreement with the previous theoretical value [3] of 8.17 eV. Along the [110] and [100] directions, two bands crosses the Fermi level while only one band cross the Fermi level along the [111] direction. This picture clearly indicates the metallic nature of this material. The direct interband energy differences close to the K and X point (marked solid arrows in Fig. 1.) are found to be 2.8 and 4.1 eV. These values are smaller then the corresponding theoretical values [3] of 2.9 and 4.2 eV, respectively. From this comparison, it is clear that the effect is due to LDA errors. The occupied and unoccupied states are well separated along the X-W direction. A similar observation was made in the tight-binding linear muffin-tin orbital (TB-LMTO) work of Lee et al. [3].

The electron distribution in any energy spectrum is described by the density of states and this is also shown in Figure 1. In this figure, the peaks below the Fermi level are labelled from P^1 to P^7. The lowest peak P^1 at -8.0 eV mainly arises from the Sn $5s$, Au $5d$ and Mg $2p$ states. In previous theoretical work [3], the contribution of Sn $5s$ states to this peak was not reported. The cluster of peaks (from P^2 to P^4) between -6.5 eV and -4.5 eV are due to Au $5d$ states with a contribution from Sn $5p$ states. The energy peak structure (P^5) is centred around -4.0 eV and is composed mainly of electrons from the Au $5d$ and $6p$ states. The peak P^5 compares well with previous theoretical partial densities of states for Au d-states [3]. The theoretical data [3] for the partial densities of states for p-states peaks below the Fermi level are at -1.5 eV and -2.8 eV, respectively, which are close to the present results (P^6, P^7). The last two peaks are related to the Sn $5p$ and Au $6p$ states. Finally, the density of states at the Fermi level is found to be 1.02 $\frac{\text{states}}{\text{eV.cell}}$ in good agreement with a previous theoretical value of

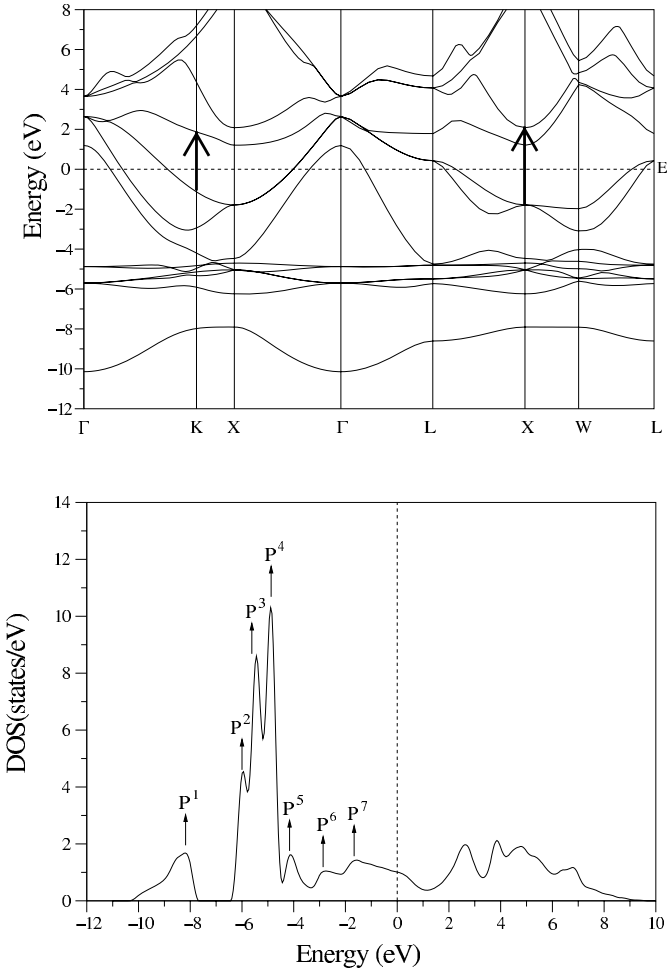

Fig. 1. Calculated electronic band structure and corresponding density of states for MgAuSn. The peaks below the Fermi level are labelled from P^1 to P^7 in the density of states.

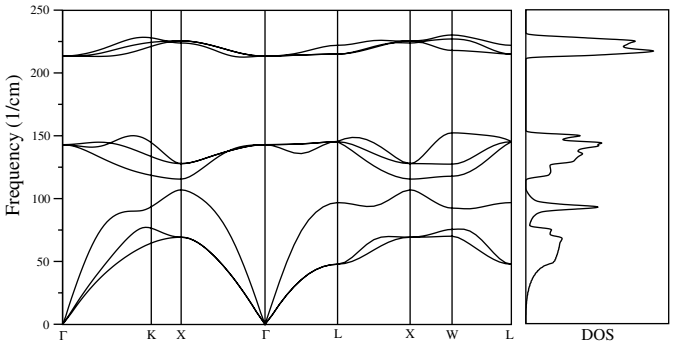

Fig. 2. Calculated phonon dispersions and density of states for MgAuSn.

0.95 $\frac{\text{states}}{\text{eV.cell}}$ [3]. In this material, the contribution of the Sn $5p$ states to the density of states at the Fermi level is about 50% while the Au $6p$ states contributes 25% to this. The Mg $2p$ and Au $5d$ states also contribute to the density of states at the Fermi level. These contributions indicate that the p bands of Sn and Au play a more active role in the properties of this material. The lowest occupied bands

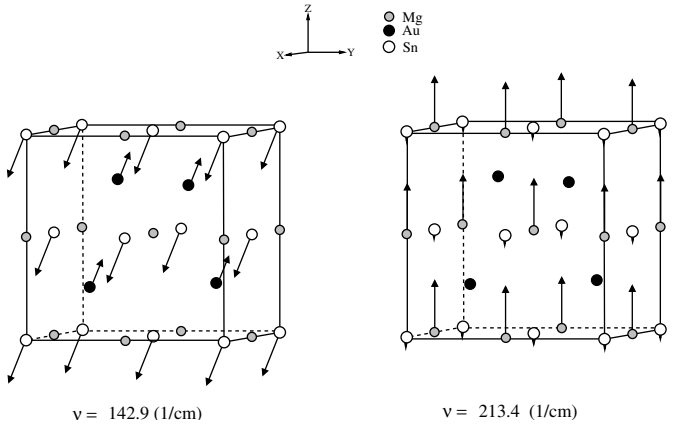

Fig. 3. Schematic eigendisplacements of zone-center phonon modes in MgAuSn.

for RAuSn (R = rare-earth elements) compounds are primarily the *d*-states of Au and p-electron states of the R elements [16–18].

The phonon dispersion curves and the density of states curves for MgAuSn are plotted in Figure 2. There is a band gap between acoustic and optical frequencies in the phonon spectrum due to the heavy Au atoms. In addition to the acoustic-optical gap, there is a optical-optical gap in the phonon spectrum due to the light Mg atoms. The sharp peak at 85 cm^{-1} in the phonon density of states results from the flatness of the longitudinal acoustic branch along the W-L direction. There are clear optical phonon peaks at 120 cm^{-1}, 132 cm^{-1}, 139 cm^{-1}, 145 cm^{-1}, 216 cm^{-1} and 225 cm^{-1} due to the flatness of the optical phonons along the selected symmetry directions. The frequencies of the zone-center phonon modes are found to be 142.9 cm^{-1} and 213.4cm^{-1}. The polarization characteristics of these phonon modes are presented in Figure 3. The lower mode results from the opposing motion of Au and Sn atoms while the higher one is mainly localised on the Mg atoms due to a large mass difference between Mg and Au (or Sn) atoms. Along the lowest symmetry direction [110] (Γ-K), the phonon branches are in general non-degenerate. All the nine phonon branches show an appreciable amount of dispersion along this direction. At the zone edge of X, there are four optical phonon modes with frequencies of 115.5 cm^{-1}, 127.8 cm^{-1}, 223.8 cm^{-1} and 225.5 cm^{-1}. The eigendisplacement of these optical frequencies are given in Figure 4. We note that the frequency difference between the third and highest optical phonon modes is very small because they are both localised on the Mg atoms. For the lowest optical phonon mode, Mg and Sn atoms vibrate while the second optical phonon mode includes atomic vibrations from all atoms in the unit cell.

4 Summary

The present paper reports a study on the structural, electronic and phonon properties for the cubic AlLiSi phase

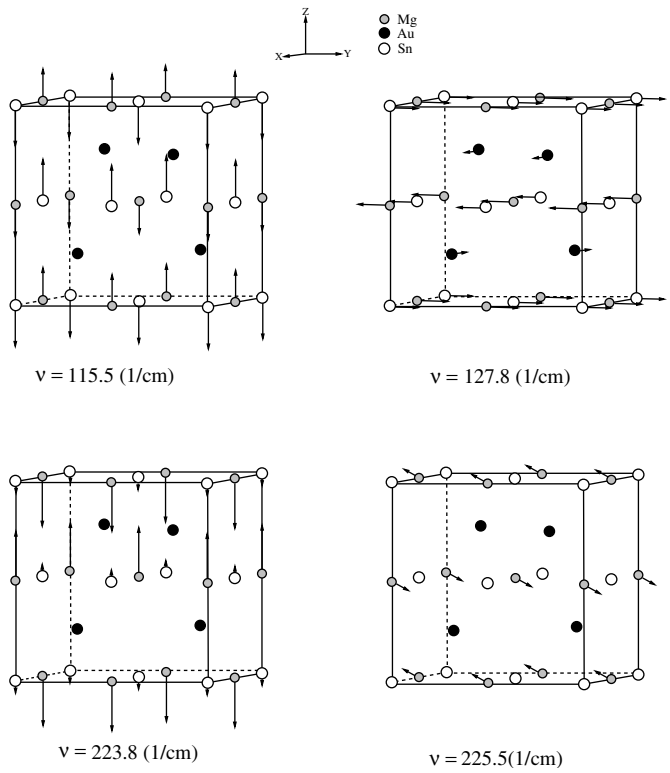

Fig. 4. Schematic eigendisplacements of the optical phonon modes in MgAuSn at the X point.

of MgAuSn using a plane-wave pseudopotential method within the framework of density functional theory. The calculated equilibrium lattice constant of MgAuSn compares very favourably with the experimental value. Our electronic results indicate that the peaks near the Fermi level are mainly due to the Sn 5*p* and Au 6*p* states. The main contributions to the density of states at the Fermi level come from these electronic states. From these findings, one can say that the *p* bands of Sn and Au play a very important role in the properties of this material. Moreover, we have calculated the phonon spectrum and density of states for MgAuSn using a density functional perturbation method. These shows two phonon gaps due to mass differences between atoms in this material. Finally, we have presented a discussion on the location and polarization of zone-center and zone-edge phonon modes in this material.

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