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Electronic and phonon structures of $AuGa_2$ and $AuIn_2$

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Abstract

We have studied structural, electronic and dynamical properties of $AuGa_2$ and $AuIn_2$ by employing the plane-wave pseudopotential method within the density functional theory. The structural results are in good agreement with previous experimental and other theoretical results. The calculated electronic band structures for both materials have been compared with the angle-resolved photoemission spectroscopy experiment data along the [100] symmetry direction. Phonon dispersion curves and density of states were calculated by employing a density-functional perturbation theory. The calculated zone-centre optical phonon modes for these materials are in good agreement with experimental data.

1. Introduction

In recent years, the binary intermetallic compounds (AuX_2, X = Al, Ga, or In) that crystallize in the cubic fluorite structure have attracted considerable attention. The main reason for this attention is the discovery of the coexistence of the nuclear ferro-magnetism and superconductivity in $AuIn_2$ [1, 2]. This discovery has led to significant interest in the structural and electronic properties of these materials [3–13]. Several experimental techniques have been used to investigate the electronic structures of AuX_2 (X = Al, Ga, and In), such as x-ray [4] and ultraviolet [5] photoemission spectroscopic experiments, optical reflectivity measurements [6], and angle-resolved photoemission spectroscopy (ARPES) [7, 10, 11]. Besides these experimental studies, all-electron full-potential linear augmented-plane-wave method [10], a mixed-basis band-structure interpolation scheme [12] has been used to calculate the electronic structure of these three materials. In addition to these works, first principles density functional theory with the generalized gradient [11] and local density [11, 13] approximations have been applied to these materials.

Despite much work on structural and electronic properties of these materials, their dynamical properties are relatively poorly known in the literature. Raman-scattering experiment and infrared techniques have been used to measure the zone-centre phonon modes of $AuGa_2$ and $AuIn_2$ [14]. On the theoretical side, there exists only one publication presenting phonons for only $AuAl_2$ while no attention has been paid to the lattice dynamical studies of $AuGa_2$ and $AuIn_2$. It is important to perform a true investigation of electronic and vibrational

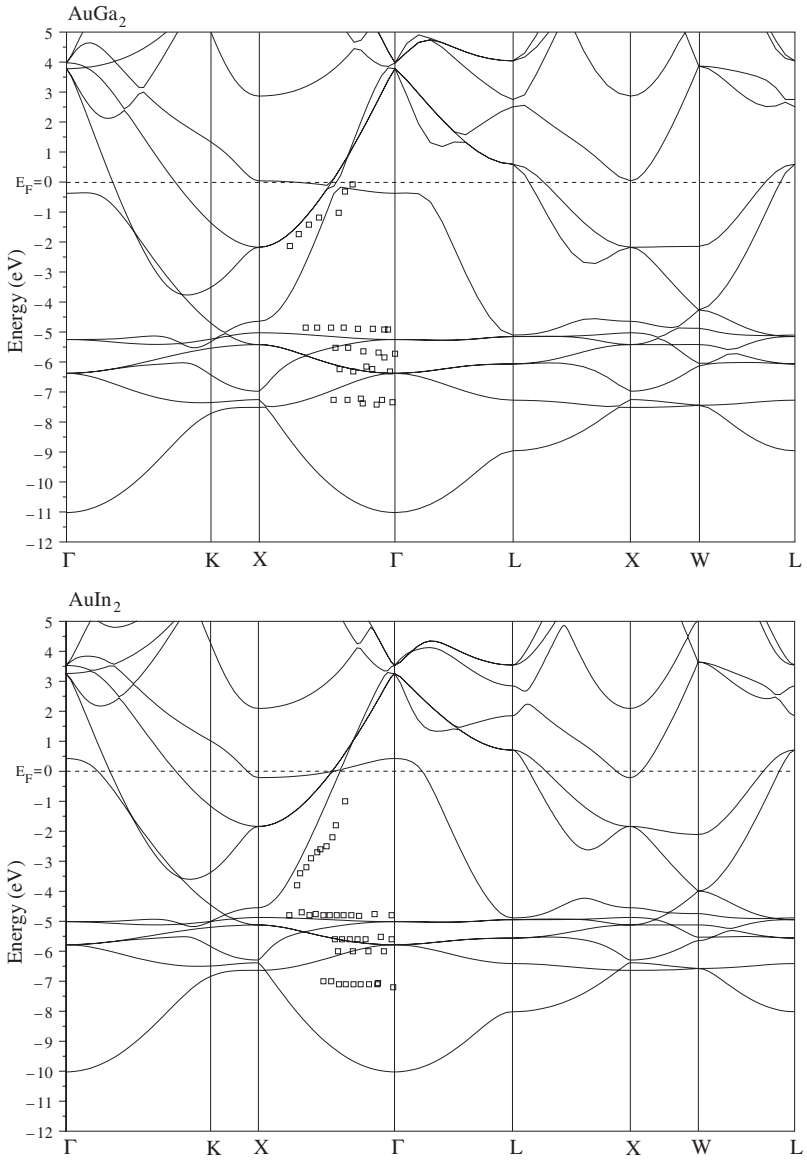

Figure 1. The calculated electronic band structures of $AuGa_2$ and $AuIn_2$ along the main symmetry directions in the fcc Brillouin zone. Experimental results are denoted by open squares [7].

properties of these materials because electrons and phonons in metals play an important role in the superconductivity due to their interactions. In this paper, we present a comprehensive picture of structural, electronic and dynamical properties of the cubic fluorite phase of $AuGa_2$ and $AuIn_2$. To investigate these properties, we performed *ab initio* pseudopotential calculations in the local-density approximation. The calculated structural parameters are compared with previous theoretical calculations and available experimental results. The calculated electronic band structures for both materials have been compared with the angle-resolved photoemission spectroscopy experiment data [7] along the [100] symmetry direction. The calculated zone-

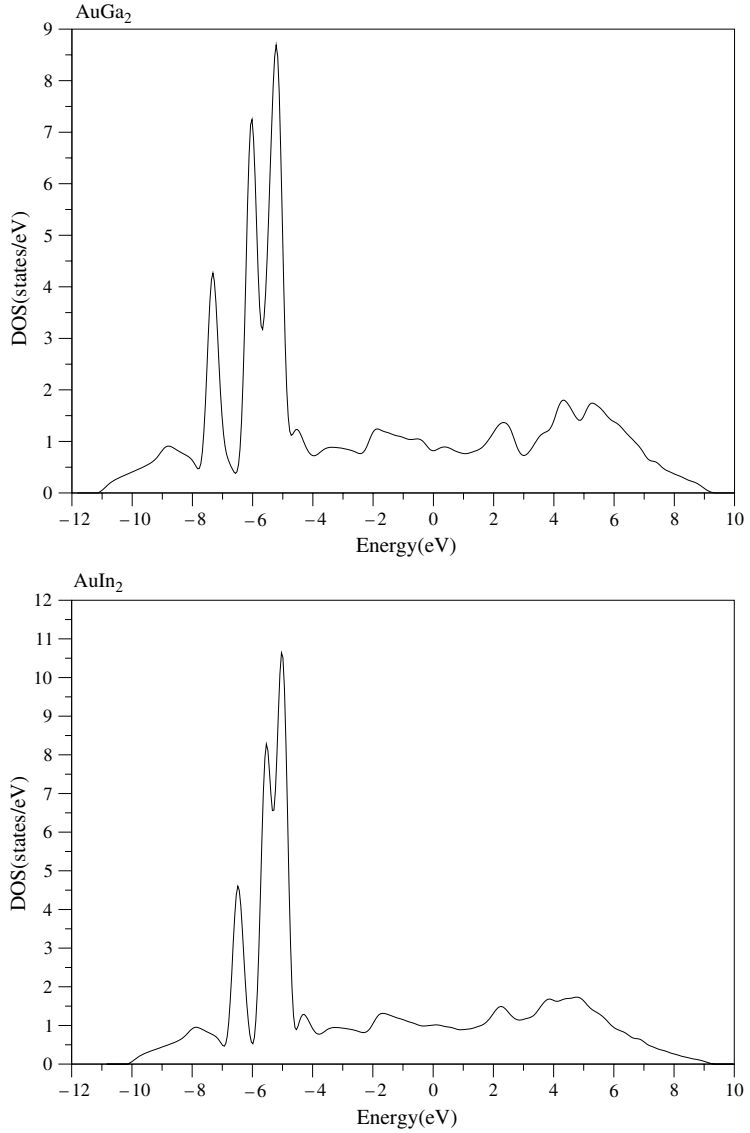

Figure 2. Electronic density of states for $AuGa_2$ and $AuIn_2$. The zero of energy corresponds to the Fermi level.

centre phonon modes are also compared with available experimental results. We have also presented and discussed phonon dispersion curves and density of states for these materials.

2. Theory

The calculations are performed using the plane-wave-pseudopotential approach within the framework of density-functional theory. The *ab initio* norm-conserving pseudopotentials were generated using the method of Troullier and Martins [15]. The electron–electron interaction was considered within the local density approximation of the density functional theory, with the

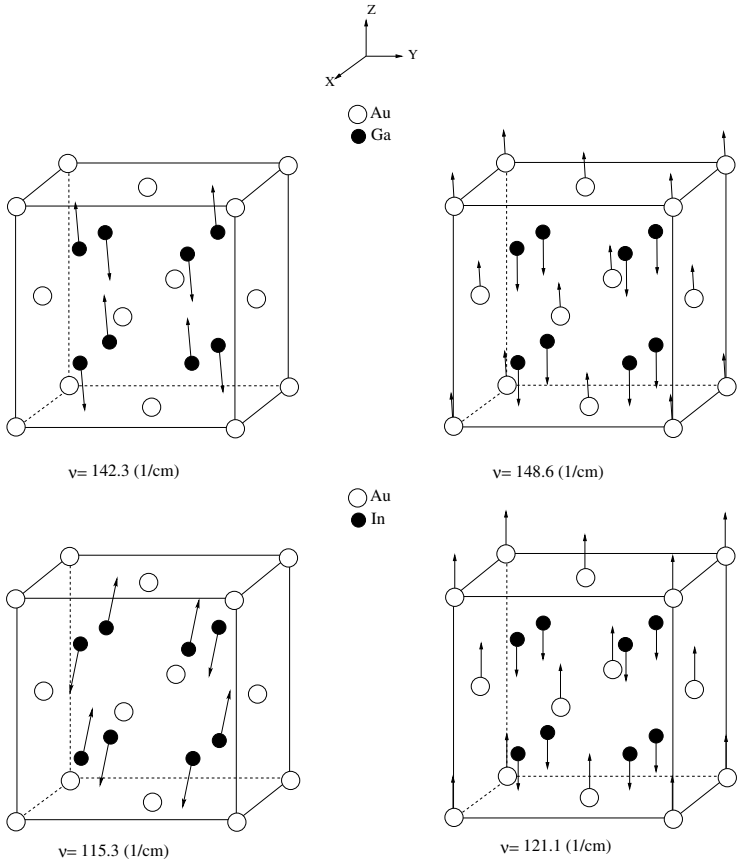

Figure 3. Schematic eigendisplacements of vectors representing optical zone-centre phonon modes for $AuGa_2$ and $AuIn_2$.

correlation scheme of Ceperley and Alder [16]. The Kohn–Sham single-particle functions were expanded in a basis of plane waves, up to the kinetic energy cut-off of 50 Ryd for this material. The electronic charge density is evaluated up to the kinetic energy cut-off 300 Ryd. Self-consistent solutions of the Kohn–Sham equations were obtained by sampling the irreducible part of the Brillouin zone by employing 120 special **k**-points of the Chadi–Cohen type [17]. Integration up to the Fermi surface is done with the smearing technique [18] with the smearing parameter $\sigma = 0.05$ Ryd. Having obtained self-consistent solutions of Kohn–Sham equations, the lattice-dynamical properties were calculated within the framework of the self-consistent density functional perturbation theory [19]. We evaluated eight dynamical matrices on a $4 \times 4 \times 4$ **q**-point mesh, and a Fourier interpolation has been used to obtain complete phonon dispersions and density of states.

3. Results

The crystal structure of $AuGa_2$ and $AuIn_2$ is the calcium fluorite which consists of three interpenetrating face-centred cubic lattices: one lattice of gold ions with origin (0, 0, 0) and two of X (Ga or In) ions with origins at $a/4$ (1, 1, 1) and $3a/4$ (1, 1, 1). Each gold atom occupies

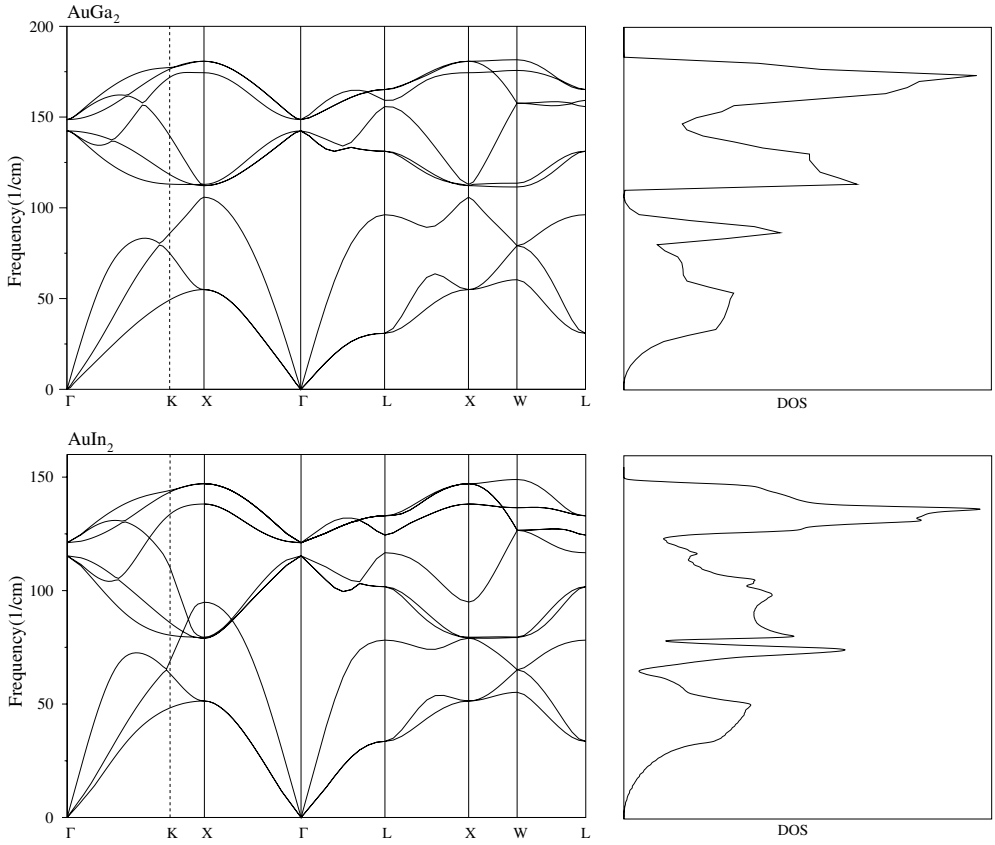

Figure 4. *Ab initio* phonon dispersions and density of states for $AuGa_2$ and $AuIn_2$.

a centre of inversion symmetry and is surrounded by eight X atoms. The ground-state bulk properties of these materials are obtained by minimization of the total energy with respect to the lattice constant. For a given lattice constant, the total energy was calculated. Then, this step was repeated for other lattice constants near the equilibrium one. Finally, the equilibrium lattice constant a, the static bulk modulus at zero pressure B, and the first-order pressure derivative of the bulk modulus B' have been determined by fitting the calculated static total energies as a function of volume to the Murnaghan equation of state [20]. The bulk properties (a, B and B') from the total energy calculations are summarized in table 1 together with previous experimental and theoretical results. The overall agreement with the experimental data for the lattice constants is good. For the bulk modulus B, the agreement with the experimental value for $AuGa_2$ is satisfactory. However, no experimental and theoretical results are available for the pressure derivative of the bulk modulus.

The electronic structures of $AuGa_2$ and $AuIn_2$ are shown in figure 1 along the high-symmetry points in the Brillouin zone for the fcc lattice. The calculated electronic structures show clearly the metallic nature of both materials. Two bands cross the Fermi level along the [110] and [100] symmetry directions. The agreement with experimental data [7] for both materials is not bad along the Γ–X direction. However, experimental results indicate three Au bands at the zone-centre while we have observed only two Au bands. The reason for this difference is that a relativistic effect [10] is not taken into account in our calculations.

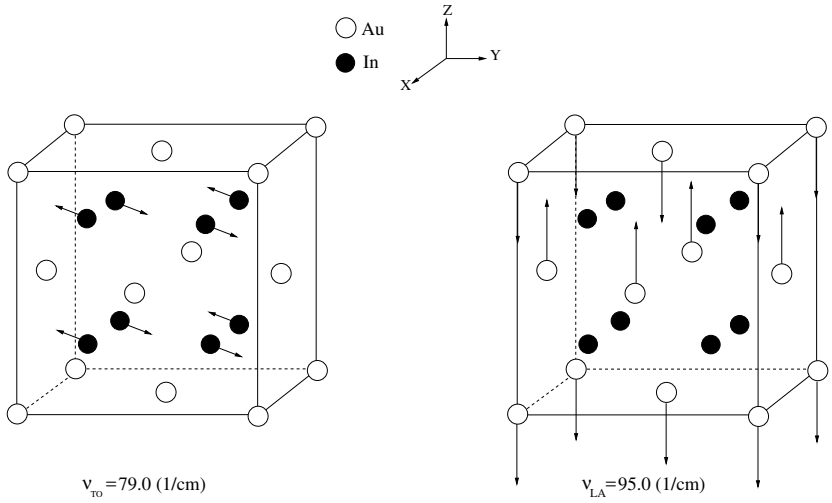

Figure 5. Atomic displacement patterns of LA and lowest TO phonon modes for $AuIn_2$ at the X point.

Table 1. Calculated structural lattice constant a, bulk modulus B and the pressure derivative of the bulk modulus B' of $AuGa_2$ and $AuIn_2$ compared with previous theoretical and experimental results.

Material	Reference	a (Å)	B (Mbar)	dB/dP
$AuGa_2$	This work	6.03	0.874	5.620
	LDA [11]	6.03	0.96	
	GGA [11]	6.22	0.69	
	Exp. [3]	6.074	0.96	
	Exp. [9]	6.08		
$AuIn_2$	This work	6.46	0.741	5.84
	LDA [11]	6.47	0.790	
	GGA [11]	6.68	0.540	
	Exp. [12]	6.50		
	Exp. [9]	6.51		

It is known that a relativistic effect [10] is very important for Au d bands in AuX_2 materials. However, these bands lie well below the Fermi level for both materials and the bands close to the Fermi level play an important role in the properties of materials. In particular, the bands close to the Fermi level are very important for phonons and electron–phonon interactions. The electron distribution in an energy spectrum is described by the density of states (DOS). The densities of states from our calculations for both materials are plotted in figure 2. The DOS curves for $AuGa_2$ include three sharp peaks below the Fermi level, with peaks near -7, -6, and -5 eV. Au 5d states contribute to all three peaks strongly while Ga 4s and Au 6p states contribute only to the peak -7 eV. A small amount of Ga 4p contributes to the middle sharp peak. The highest peaks arises from a band that is extremely flat along the [110] and [111] directions. The density of states at the Fermi level is found to be $0.81\frac{\text{states}}{\text{eV cell}}$, which can be compared with the experimental value of $1.14\frac{\text{states}}{\text{eV cell}}$ [8]. The density of states at the Fermi level mainly comes from Ga 4p and Au 6p states. The contribution of Ga 4p states to the DOS at the Fermi level is as much as 60% while 20% of DOS at the Fermi level comes from Au 6p

Table 2. Phonon frequencies (in cm^{-1}) calculated at the zone-centre for $AuGa_2$ and $AuIn_2$. The results are compared with available experimental results.

Material	Reference	F_{2g}-TO (IR)	F_{1u}-LO (Raman)
$AuGa_2$	This work	142	148
	Exp. [14]	149	
$AuIn_2$	This work	115	121
	Exp. [14]	124	

states. The density of states for $AuIn_2$ also presents three well defined peaks below the Fermi level. The energies of these peaks are -6.5, -5.5 and -5.0 eV. Again all of them include large contributions from Au 5d electrons. The lowest of them has some contribution of In 5s and 5p states while a small amount of In 5p states contributes to the intermediate peak. The sharpest peak of all comes from Au 5d states. Similar to $AuGa_2$, this peak is due to a flat band along the [110] and [111] directions. It is important to note that the energies of these peaks are very close to the corresponding peaks in the density of states for $AuGa_2$. This similarity can be related to 5d electrons of Au atoms. The value of the total DOS at the Fermi level for $AuIn_2$ is calculated to be $0.99\frac{\text{states}}{\text{eV cell}}$, which is slightly higher than the corresponding value for $AuGa_2$. Our calculated value compare well with previous theoretical [11] and experimental values [8] of 1.02 and 1.33 $\frac{\text{states}}{\text{eV cell}}$, respectively. For this material, the density of states at the Fermi level is dominated by In 5p.

As the crystal structure of $AuGa_2$ and $AuIn_2$ materials belongs to the space group $O_h^5(Fm\bar{3}m)$ with three atoms per primitive cubic unit cell, there are a total of nine phonon branches. Due to symmetry, the distinct number of branches is reduced along the principal symmetry directions Γ–X and Γ–L. In accordance with the point group of the lattice, at the zone centre the optical modes are triply degenerate and can be decomposed into two distinct classes. The two irreducible representations are $\Gamma(O_h^5) = F_{1u} + F_{2g}$. F_{1u} is infrared active while F_{2g} is Raman active. The calculated zone centre optical phonon frequencies are presented in table 2. Figure 3 depicts the shapes of these infrared and Raman active modes. A comparison with experimental data [14] is also made in table 2. Our results compare very well with experimental zone-centre frequencies. The calculated phonon dispersion curves along the high-symmetry directions of the Brillouin zone are shown in figure 4. All the optical modes are found to be quite dispersive along the main symmetry directions of [100], [110] and [111]. Due to only a small mass difference between Au and In atoms, there is no clear gap between the acoustic and optic branches for $AuIn_2$. Moreover, the dispersion of the LA phonon branch along the [110] and [100] directions for this material is different from that of $AuGa_2$. For large **q** wavevectors along these symmetry directions the LA phonon branch lies higher in energy than the lowest TO phonon branch for $AuIn_2$. In particular, the frequencies of the lowest TO and LA modes are found to be 79.0 and 94.9 cm^{-1} at the X point. Figure 5 illustrates atomic displacement patterns of these phonon modes for $AuIn_2$. For $AuGa_2$, there is a small optical–acoustic bandgap in the phonon dispersion curves. The bandgap between the acoustic and optic branches of $AuGa_2$ is around 7 cm^{-1}. In the phonon density of states, the lowest peak for both materials is due to transverse acoustic phonon modes. The main difference between their density of states has been found in the second peak. This peak for $AuGa_2$ is totally characterized by the LA branch due to a gap in the phonon density of states. On the other hand, this peak for $AuIn_2$ includes contributions from optical phonon modes because there is no gap in the phonon density of states. The highest optical phonon is flat along the X–W direction for both materials. This flatness leads to a very sharp peak for both materials.

4. Summary

In conclusion, we have presented the structural, electronic and dynamical properties of the $AuGa_2$, and $AuIn_2$ by employing a first-principles scheme, based on the application of the plane-wave pseudopotential method and density functional theory. The calculated lattice constant a and bulk modulus B are in agreement with previous theoretical and available experimental results. The calculated electronic structures for both materials shows good agreement with experimental findings along the Γ–X direction. Our electronic density of states results suggest that the main contributions to the density of states at the Fermi level come from Au 6p and Ga 4p states for $AuGa_2$ and In 5p states for $AuIn_2$ while the Au 5d bands are shifted well below the Fermi level for both materials. From these findings, one can say that the p bands of these atoms play a very important role in the properties of this material. Our calculated phonon-dispersion curves for these materials are in very good agreement with the zone-centre experimental measurements. We have highlighted the main differences in the density of states in both materials.

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