



First-principles study of electronic and dynamic properties of AgMg and AgZn

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ABSTRACT

The structural, electronic, and phonon properties of AgMg and AgZn in the cesium-chloride phase have been investigated using the density functional theory (DFT) within the local density approximation (LDA). The calculated ground state properties such as lattice constant and bulk modulus agree well with the previous theoretical calculations. The electronic band structure is also presented for AgMg and AgZn. The calculated DOS at the Fermi energy are $0.49 \frac{\text{states}}{\text{eV cell}}$ for AgMg and $0.43 \frac{\text{states}}{\text{eV cell}}$ for AgZn. A linear-response approach to the density functional theory is used to derive phonon dispersion curves and the total and partial density of states for AgMg and AgZn. The high-frequency region of AgMg is mainly due to the vibrations of Mg atoms.

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1. Introduction

The binary AgMg and AgZn alloys have received extensive attention over the past decades because of their technical promise as high-temperature structural materials. It is well known that they exhibit a high corrosion resistance to oxidizing environments at high temperatures [1,2]. They have also been found to be operating under increasingly demanding conditions in the power engineering industry, the automobile industry, and the aerospace industry for lightweight materials. The structural, electronic, elastic, optical, and phase transition properties of these materials have been studied extensively using different theoretical and experimental methods [3–17]. The present work focuses on the theoretical study of the structural and electronic properties of B2 AgMg and AgZn, with particular emphasis on phonon dispersion, by employing the density of functional theory (DFT). The optical and electronic properties of AgZn studied by Shreder et al. [18], who determined the structural transformation of $\text{CsCl} \rightarrow \text{hcp}$, lead to the emergence of a new absorption band in the optical spectrum. An X-ray diffraction study using diamond anvil cell (DAC) by Iwasaki et al. [7] reported $\text{hcp} \rightarrow \text{B2}$ phase transition at 3 GPa for AgZn. Amar et al. [14] and Harrison et al. [9] reported the band structure calculations of AgZn by using the Khon–Rostoker (K–R) and SCF-LMTO methods, respectively. The experimental study and first-principle calculations on the electronic structure of AgMg

were performed by several groups [12,13,16]. Inelastic neutron scattering data for AgZn have been reported only for acoustic branches [19]. The current work focuses on the theoretical study of the structural and electronic properties of AgMg and AgZn in the B2 phase, with particular emphasis on phonon properties, by employing the DFT. The phonon properties are necessary for a microscopic understanding of the lattice dynamics. The knowledge of the phonon spectrum plays a significant role in determining various material properties such as phase transition, thermodynamic stability, transport and thermal properties. The band structure has been obtained by applying the plane-wave pseudopotential method within the local density approximation (LDA). These results are then used, within a linear-response approach, to calculate the phonon dispersion curves and the density of states.

2. Method

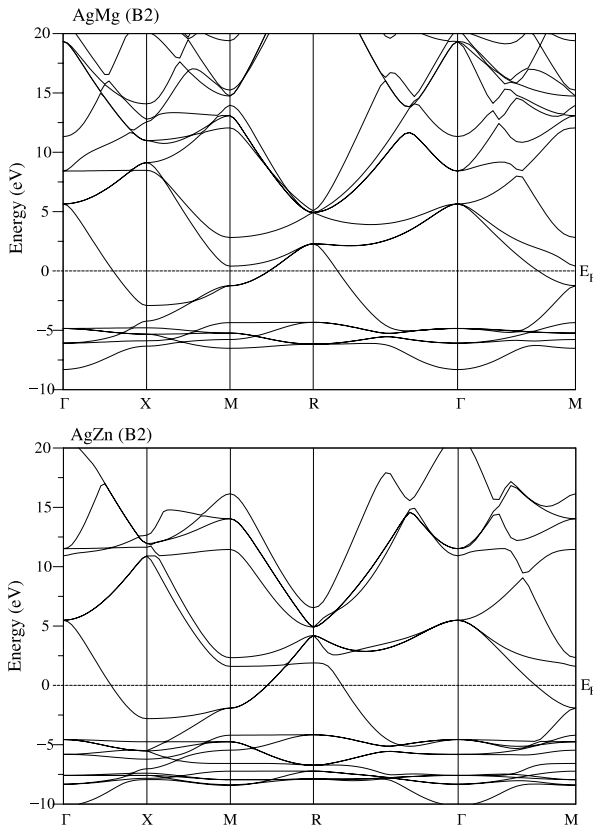
For our calculations, we use the local density approximation (LDA) in the scheme of Perdew and Zunger [20] with a plane-wave pseudopotential approach, using the implementations in the Quantum-ESPRESSO package [21]. The wave functions were expanded into plane waves with kinetic energies of up to 40 Ryd. Self-consistent solutions of Khon–Sham equations were obtained by employing a set of 60 k -points within the irreducible part of the Brillouin zone. Eight dynamical matrices were calculated on a $4 \times 4 \times 4$ q -point mesh obtain complete phonon dispersions and vibrational density of states. The dynamical matrices at the arbitrary wave vectors were evaluated using the Fourier deconvolution on this mesh.

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Table 1

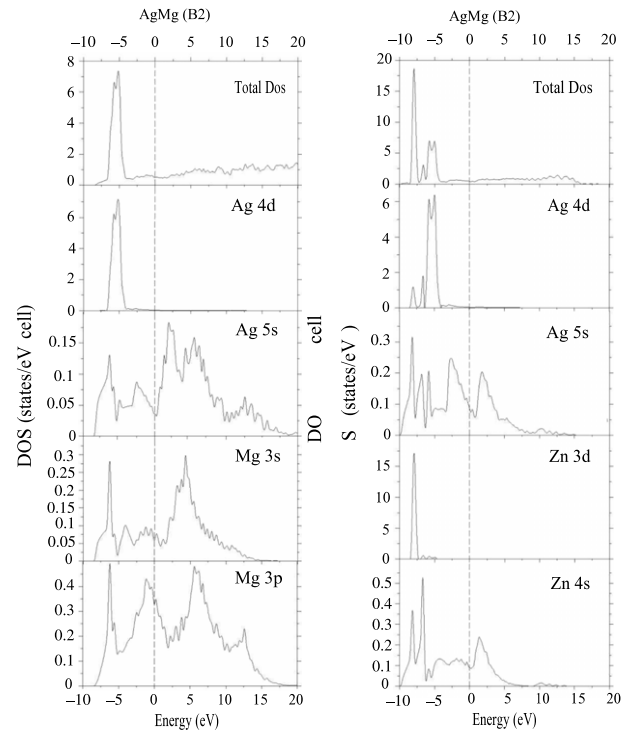
Calculated lattice constants (Å), bulk modulus (in Mbar), and pressure derivative of the bulk modulus dB/dP for AgMg and AgZn in the B2 structure.

Materials	Reference	a	B	dB/dP
AgMg	This work	3.247	0.696	4.54
	SCF-LMTO-ASA(LDA) [13]	3.243	0.89	–
	Theory [8]	3.305	–	–
	Theory [5]	3.28	0.66	–
	Theory [16]	3.239	0.91	–
	Exp. [16]	3.3125	–	–
	Exp. [11]	3.314	–	–
AgZn	This work	3.082	1.098	5.29
	Theory [17]	3.947	1.23	–
	Exp. [7]	3.155	–	–
	Exp. [23]	3.147	–	–

**Fig. 1.** Calculated electronic band structure for AgMg and AgZn in the B2 phase.

3. Results

The AgMg and AgZn crystallize in the CsCl (B2)-type structure with the Pm3m space group. The two atoms have coordinates $\tau_{Ag} = (0, 0, 0)$ and $\tau_{Mg,Zn} = (0.5, 0.5, 0.5)$. The theoretical lattice constants and bulk modulus in this section are obtained through fitting the total energy data with the Murnaghan equation of state [22]. The calculated structural properties (lattice constant a , bulk modulus, and the pressure derivative of the bulk modulus, dB/dP) of AgMg and AgZn are summarized in Table 1. For AgMg and AgZn, the resulting lattice constant, $a = 3.247$ and 3.082 Å, and bulk modulus, $B = 0.696$ and 1.080 Mbar, agree well with previous theoretical calculations. However, our calculated lattice constants for these materials are about 1% lower than the experimental values [7,11,12,23]. The band structures of the B2 phase of AgMg and AgZn as well as the high symmetry directions in the simple cubic Brillouin zone (BZ), calculated by using the local density

**Fig. 2.** Calculated partial and total DOS for AgMg and AgZn in the B2 phase along several lines of high symmetry in the Brillouin zone.

approximation (LDA), are shown in Fig. 1, in which $E_F = 0$ is taken. The overall band profiles are quite similar to those of AgMg and AgZn alloys, and they are in good agreement with the earlier works [9,12–14,18]. The character of the band states for these alloys has been identified by calculating their total and partial densities of states (DOS) (in Fig. 2). It is seen that there is no gap at the Fermi level and the total density of state (DOS), which is 0.49 and $0.43 \frac{\text{states}}{\text{eV cell}}$ for AgMg and AgZn, respectively. Due to the odd number of valence electrons per unit cell, the system is metallic. Jordan et al. [13] reported that the $n(E_F)$ for AgMg was $0.525 \frac{\text{states}}{\text{eV cell}}$. The results indicate that the predominant contributions of the density of states at the Fermi level come from the Ag 5s and Mg 3s and 3p states for AgMg, whereas they originate from both the Ag 5s and Zn 4s states. From the calculated total DOS of AgMg alloys, it can be seen that there is one peak below the Fermi level. This peak is centered 5.15 eV, which is mainly dominated by the Ag 4d state. On the other hand, for AgZn, the total DOS contains two peaks below the Fermi level. These peaks are situated between -7.95 and -5.40 eV, respectively. The characters of these peaks are dominated by the Zn 3d and Ag 4d states. The calculated phonon dispersion curves for AgMg and AgZn along the high-symmetry directions and the phonon density of states (partial and total) are illustrated in Fig. 3. The primitive cell of AgMg and AgZn contains two atoms, leading to a total of 6 phonon branches. Due to the symmetry, the distinct number of phonon branches is reduced along the principal symmetry directions Γ -X and M -R- Γ . All phonon frequency both materials are positive that there are no phonon branches with dispersion that dip toward the zero frequency. This indicates that the both of the materials are dynamically stable. Owing to the mass ratio of Ag and Mg, there is a band gap between the acoustic and optic branches for AgMg. The value of the band gap between the acoustic and optic branches of AgMg is about 3.213 THz at the point X. From the phonon partial density of states for AgMg, we can conclude that the optical frequency region is mainly caused by Mg atoms, whereas the acoustic frequency region is mainly caused by Ag and

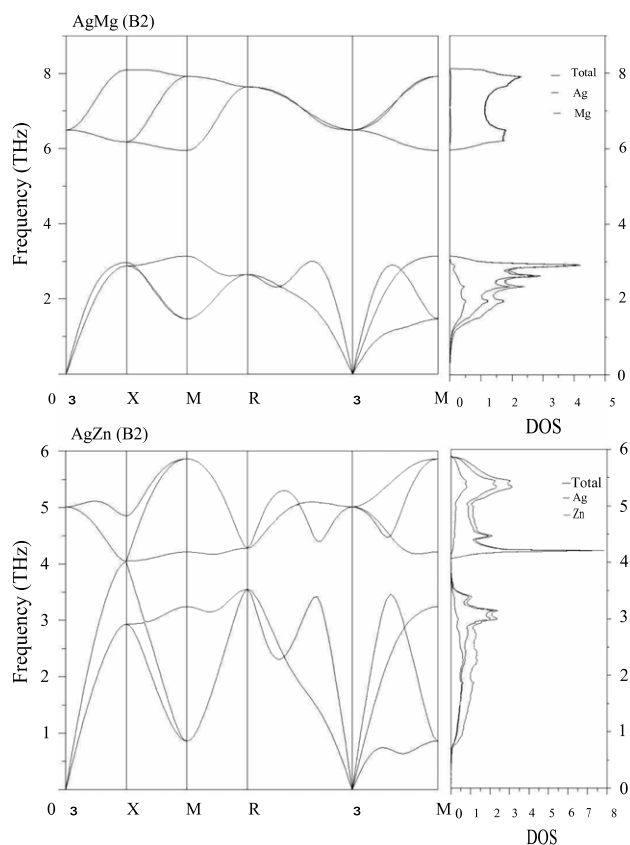


Fig. 3. Calculated phonon dispersion curves and phonon densities of states for AgMg and AgZn in the B2 phase along several lines of high symmetry in the Brillouin zone.

Mg atoms. At the acoustic region for AgMg there is a relatively sharp peak at about 3.00 THz, which corresponds to LA phonons. The total phonon density of states of AgZn in Fig. 3 shows that there is a peak at around 4.2 THz in the optical region which is due to an extremely flat branch along the X-M-R symmetry directions. In the acoustic frequency range for AgZn, there is a large peak at about 2.87–3.27 THz, which belongs to the LA and TA phonons. Our acoustic phonon results for AgZn are shown to be in agreement with inelastic neutron experiments [19]. The phonon spectra of these materials has similar characteristics to the spectra of FeAl [24]. General trends of these materials phonon dispersion curves consistent with the earlier work [24]. In this study, the optical frequency at the zone center point is 6.495 and 5.012 THz

for AgMg and AgZn, respectively. The phonon calculations of both materials will certainly be useful for the interpretations of future theoretical and experimental studies.

4. Conclusion

In this article, the structural, electronic, and phonon properties of AgMg and AgZn have been studied, using the *ab initio* pseudopotential method, within the LDA of the DFT. Our main results and conclusions can be summarized as the calculated structural properties (equilibrium lattice constant and bulk modulus) in the B2 (cesium chloride) phase, which are in good agreement with the values reported in the literature. The electronic band structures were calculated for both materials, in the B2 phase. The phonon spectrum and density of states in the B2 phase along several lines of high symmetry in the Brillouin zone (BZ) were calculated using the density-functional perturbation theory.

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