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Phonon and elastic properties of AlSc and MgSc from first-principles calculations

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ABSTRACT

First principle calculations of structural, electronic, elastic, and phonon properties of the intermetallic compounds like MgSc and AlSc in the B2 (CsCl) structure are presented in this study, using the pseudo-potential plane waves approach based on the density functional theory, within the generalized gradient approximation. The calculated lattice constants, bulk modulus, and first-order pressure derivative of the bulk modulus are reported for the B2 structure and compared with the earlier experimental and theoretical calculations. The numerical first principles calculation of the elastic constants were used to calculate C_{11}, C_{12} and C_{44} for these compounds. The present results concur with the earlier theoretical calculations. Electronic band structures and densities of states have been derived for MgSc and AlSc and subsequently, a linear-response approach to the density functional theory is used to derive the phonon frequencies and densities of states.

1. Introduction

Sc is one of the typical transitional metals which forms a very stable intermetallic compound with Mg and Al alloys. MgSc and AlSc alloys are widely used in the automotive, aircraft and aerospace industries and interest in their applications is increasing. There are several reasons to study binary intermetallic MgSc and AlSc alloys. Sc is known to be the most effective modifier and recrystallizator, a small addition of which to the Mg and Al alloys increases the strength and raises the ductility [1]. For example, the addition of Sc (0.3%) to Al increases the ultimate rupture strength of annealed Al sheets from 55 to 240 MPa. Sc added to Mg increases the creep resistance and improves the high temperature stability. Recently, extensive literature has been added on the elastic, mechanical, thermodynamic and defect properties of MgSc and AlSc alloys [2–8]. Lattice parameters, residual electrical resistivities and microhardness values have been measured [9] for AlSc. Further, electrical resistometry has been used to measure [10] the phase transformation of the Al–Sc based alloys. Besides these experimental studies, there have been considerable advancements in the theoretical description of the structural, electronic and thermodynamic properties of MgSc and AlSc. The tight-bonding linear muffin-tin orbital (TB-LMTO) method [8], the scaler relativistic all-electron Blöchl's projector augmented wave (PAW) approach [3,4,11], first-principles density functional calculations within the local density approximation [12], the analytic modified embedded atom method (MEAM) [5], full-potential linear muffin-tin orbitals (FP-LMTO) method [7] and a Scheil model [7] have been used to investigate the structural, elastic, electronic, and thermodynamic properties of these materials.

Despite much study on the structural and electronic properties of these compounds the dynamical properties are relatively less studied in the literature. Phonon properties of solids are significant as they are closely associated with various fundamental solid-state properties, such as thermal expansion, specific heat, electron–phonon interaction and thermal conduction of the lattice. To date, the phonon frequencies of B2-AlSc along the main symmetry directions have been calculated by Asta and Ozoliņš [1] using the Vienna *ab initio* simulation (VASP) code in the local-density approximation (LDA). To the best of the knowledge of the authors, the phonon properties of MgSc and AlSc have not been completely studied using any theoretical or experimental method. Thus, we have performed a study of the structural, elastic, electronic and dynamical properties of MgSc and AlSc, to provide a better basis for further experimental and theoretical investigations.

In this paper we investigated the structural, electronic, elastic, and phonon properties of MgSc and AlSc by applying the density functional theory. The band structure was obtained by applying the plane-wave pseudopotential method within the generalized

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gradient approximation (GGA). These results were then used, within a linear-response approach, to calculate the phonon dispersion curves and the densities of states. The MgSc [13] and AlSc [2] phases were treated as part of an ordered B2 type of CsCl structure.

2. Method

We have employed a plane-wave pseudopotential method in the framework of the density functional theory with the generalized gradeient approximation (GGA) using the Perdew and Wang [14] parametrization for the exchange-correlation potential. The electron–ion interaction was described by ultra soft pseudopotential [15]. The wave functions were expanded in a plane-wave basis set with a kinetic energy cut-off of 40 Ry. The electronic charge density was evaluated up to the kinetic energy cut-off 400 Ry. Brillouin-zone integrations were performed using a $10 \times 10 \times 10$ **k**-points mesh. Integration up to the Fermi surface was performed using the smearing technique [16] with smearing parameter $\sigma = 0.02$ Ry. 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 [17,18]. To obtain complete phonon dispersions and density of states, eight dynamical matrices were calculated on a $4 \times 4 \times 4$ **q**-point mesh. The dynamical matrices at arbitrary wave vectors were evaluated using Fourier deconvolution on this mesh. All calculations have been made by using the code PWSCF [19].

3. Results

First, calculations were done to determine the equilibrium lattice parameters of the B2 phase of MgSc and AlSc. The total energy was calculated for different values of the lattice constant, and equilibrium corresponded to the lowest value of the total energy. In the next step, these energy values were fitted to the Murnaghan equation of state [20] to obtain the lattice constants, a and the first-order pressure derivative of the bulk modulus, dB/dP.

Elastic constants are significant parameters of a material, and often provide valuable information on the structural stability. A cubic system has three independent elastic constants C_{11}, C_{12} and C_{44}. These elastic constants and bulk modulus can be obtained by calculating the total energy as a function of volume-conserving strains that break the cubic symmetry. The bulk modulus B, C_{44} , and shear modulus $C' = (C_{11} - C_{12})/2$ are calculated from hydrostatic pressure $e = (\delta, \delta, \delta, 0, 0, 0)$, tri-axial shear strain $e = (0, 0, 0, \delta, \delta, \delta)$ and volume-conserving orthorhombic strain $e = (\delta, \delta, (1+\delta)^{-2} - 1, 0, 0, 0)$, respectively [21]. Thus, B can be obtained from

$$\frac{\Delta E}{V} = \frac{9}{2} B \delta^2 \tag{1}$$

where V is the volume of unstrained lattice cell, and ΔE is the energy variation resulting from an applied strain with vector $e = (e_1, e_2, e_3, e_4, e_5, e_6)$. C' can be calculated from

$$\frac{\Delta E}{V} = 6C'\delta^2 + O\delta^3 \tag{2}$$

The two expressions above yield $C_{11} = (3B + 4C')/3$ and $C_{12} = (3B - 2C')/3$, and C_{44} is expressed as,

$$\frac{\Delta E}{V} = \frac{3}{2} C_{44} \delta^2 \tag{3}$$

In this study, we calculated 21 sets of $\frac{\Delta E}{V}$ by varying δ from -0.02 to 0.02 in jumps of 0.002. Then, we fitted these data to a parabola, and the elastic constants were obtained from the quadratic coefficients. We have also calculated the average shear modulus G_H from the bulk modulus and elastic constants data, by the following equation [22]:

$$G_H^3 + \frac{9B + 2(C_{11} - C_{12})}{8} G_H^2 - \frac{3C_{44}(B + 2(C_{11} - C_{12}))}{8} G_H - \frac{3C_{44}(C_{11} - C_{12})B}{8} = 0. \tag{4}$$

The calculated values for a, B, C_{11}, C_{12}, C_{44}, dB/dP, G_H and B/G_H for MgSc and AlSc are listed in Table 1. Our results have been compared with the available theoretical and experimental results in this table. The calculated lattice parameters reasonably concur with experimental and earlier calculations for both materials. The values of the calculated bulk modulus are smaller than the previous theoretical results for both materials [1,3,8,11,12]. For cubic crystals, the mechanical stability requires the elastic constants to satisfy the well-known Born stability criteria [23]:

$$C_{44} > 0, \quad C_{11} - C_{12} > 0 \text{ and } C_{11} + C_{12} > 0 B > 0.$$

From our calculated elastic constants shown in Table 1, it is clear that the B2 structure of both materials is mechanically stable. Unfortunately, we have not been able to find any experimental data for the elastic constants of these materials. For comparison, we have presented previous theoretical results from Refs. [3,7,11,12] in this table. In general our results for both materials are in good agreement with experimental data. In particular, we identify that the deviations vary between 1% and 16% for the elastic constants of MgSc. The elastic constants for MgSc can also be extracted from the slopes of the acoustic phonon branches for small wave vectors [24]. We obtain the sound velocities $V_{TA}^{[001]} =$

Table 1
Calculated lattice constants (Å), elastic constants (in GPa), bulk modulus (in GPa), shear modulus (in GPa) and pressure derivative of the bulk modulus and B/G_H for MgSc and AlSc in B2 structure.

Materials	Reference	a	C_{11}	C_{12}	C_{44}	B	dB/dP	G_H	B/G_H
MgSc	This work	3.592	62.052	43.611	53.100	49.75	3.5	27.25	1.825
	VASP (LDA) [12]	3.593	70.77	43.11	55.65	52.33	–	38.92	1.344
	VASP (PAW-GGA) [11]	3.5801	63.86	45.09	52.62	51.35	–	27.30	1.881
	Exp. [27]	3.597	–	–	–	–	–	–	–
								–	–
AlSc	This work	3.371	87.976	70.246	82.724	76.156	4.05	36.44	2.089
	FP-LMTO(LDA) [7]	3.390	90	63	98	72	–	–	–
	VASP(PAW-GGA) [3]	3.372	91.65	74.05	87.99	79.92	4.05	37.96	2.105
	VASP(LDA) [1]	3.32	–	–	–	84	–	–	–
	TB-LMTO(LDA) [8]	3.315	–	–	–	92.9	–	–	–
	Exp. [27]	3.388	–	–	–	–	–	–	–
	Exp. [28]	3.45	–	–	–	–	–	–	–

4672 m/s and $V_{LA}^{[001]} = 5248$ m/s for TA and LA branches along the [0 0 1] direction, respectively. Then C_{11} and C_{44} are calculated from these sound velocities. The calculated sound velocity of the LA phonon branch along the [1 1 0] direction is $V_{LA}^{[110]} = 6538$ m/s. We then used $V_{LA}^{[110]}$, C_{11} and C_{44} to obtain the C_{12}. From our phonon dispersion curves, C_{11}, C_{44} and C_{12} are found to be 68.80, 54.40 and 38.70 GPa, respectively. These values are in good agreement with our *ab initio* results in Table 1. It is an important to note that a similar observation has been made for the elastic constants of AlSc.

A simple relationship was proposed by Pugh [25], empirically linking the plastic properties of the materials and their elastic moduli. A high B/G value thus indicated a tendency toward ductility, while a low value indicated a tendency toward brittleness. The critical value separating ductile materials from the brittle ones was calculted as equal to 1.75. Table 1 shows that B/G is greater than 1.75 for both materials, indicating the ductile nature of these materials. Energy band structures and total density of states for MgSc and AlSc calculated at equilibrium lattice parameters in high symmetry directions of the Brillouin zone are shown in Fig. 1, assuming that $E_F = 0$. The band structures were calculated using the density functional theory, within a generalized gradient approximation. The calculated electronic structures clearly revealed the metallic nature of both materials. For AlSc the lowest valance band, barring R point separated from the other valence bands, is the Al 3s character, strongly hybridized with the Sc 4s state. In the B2 structure at the Fermi level, the electronic DOS for MgSc and AlSc are noted to be 2.51 and 0.8 $\frac{states}{eVcell}$, respectively. For MgSc, the density of states at the Fermi level, is mainly from the Sc-3d and Mg-3p states. The Sc 3d states contribute 70% to the DOS at the Fermi level, while the Mg-3p states contribute 22% of DOS at the Fermi level.

The phonon dispersion curves and phonon density of states for the B2 MgSc and AlSc along the high-symmetry directions are plotted in Fig. 2. The phonon properties of MgSc and AlSc were calculated within the generalized gradient approximation in the CsCl(B2) structure, with space group symmetry Pm3m(221), in which the Mg(Al) atom is positioned at (0,0,0) and the Sc at (0.5,0.5,0.5). These materials contain two atoms per primitive cubic unit cell. Due to the symmetry, the distinct number of branches is reduced along the principal symmetry directions Γ–X and M–R–Γ in the B2 phase. The mass ratio of Mg(Al) and Sc is responsible for the band gap between the acoustic and optic branches, for both materials. The band gaps between the acoustic and optic branches of MgSc and AlSc are around 25 cm^{-1} and 5 cm^{-1}, respectively. The zone center optical phonon modes for MgSc and AlSc are calculated to be 251.8 cm^{-1} and 274.7 cm^{-1}, respectively. An interesting feature is seen from the phonon dispersion curves of MgSc and AlSc, in the direction of Γ–R symmetry. At about $\mathbf{q} = \frac{2\pi}{a}$ (0.26,0.26,0.26), the LA branch crosses the TA branches. Such phenomena have been observed in the phonon spectra of LaTe in B2 structure [26]. The peaks were observed to be distributed mainly around five frequency ranges in of the total DOS in MgSc. First, the peak located between 78 cm^{-1} and 106 cm^{-1} is due to the transverse acoustic (TA) phonon modes. Second, the peak between 106 cm^{-1} and 137 cm^{-1} is also obtained mainly from the longitudinal acoustic (LA) and TA phonon modes. The next peak, at about 150 cm^{-1} is significantly stronger and corresponds to the LA branch which is quite flat along the X–M and M–R directions. The sharp peak centered at 225 cm^{-1} is due to the flatness of the transverse optic (TO) phonon modes. The last peak, between 231 cm^{-1} and 262 cm^{-1} is mainly a result of the longitudinal optic (LO) phonon

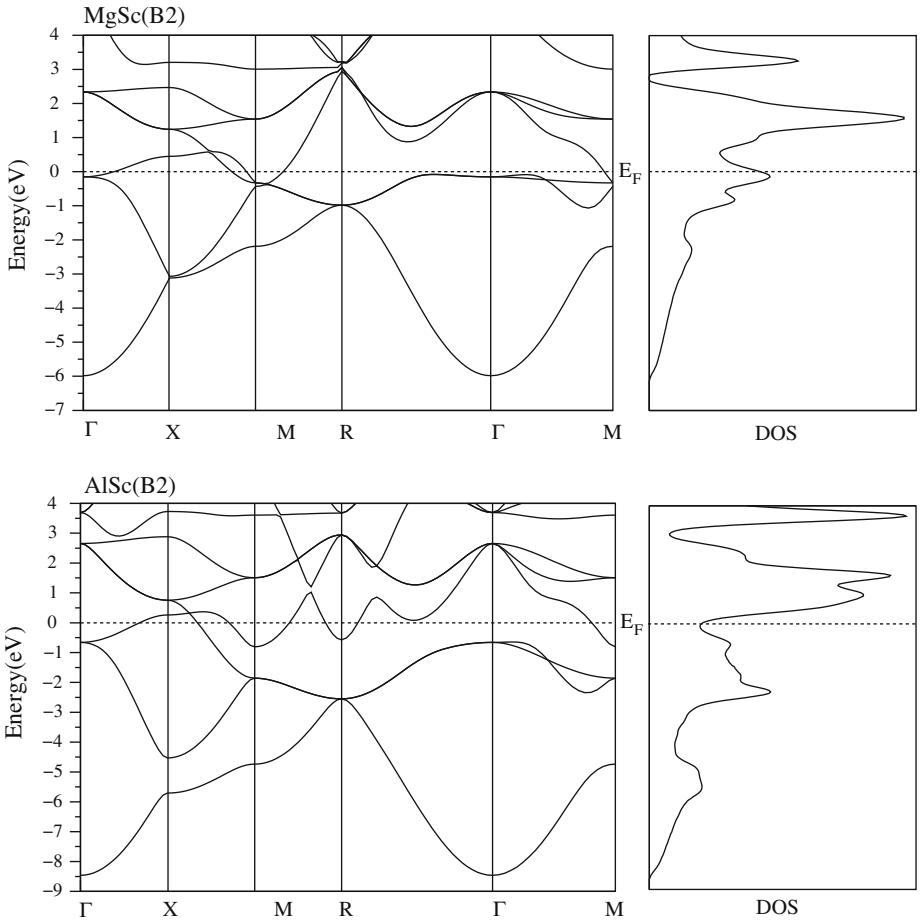

Fig. 1. Calculated electronic band structure and total density of states for MgSc and AlSc in the B2 phase.

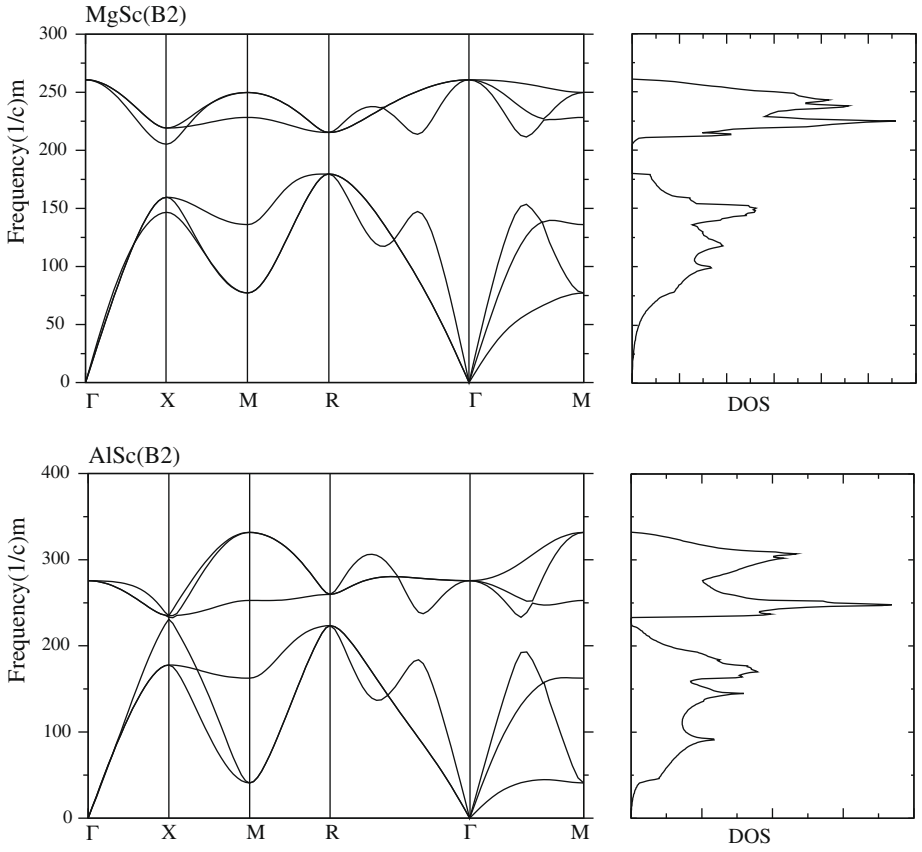

Fig. 2. Calculated phonon dispersion curves and phonon densities of states for MgSc and AlSc in the B2 phase along several lines of high symmetry in Brillouin zone.

modes. The phonon frequencies of the AlSc are compared with LDA predicted values [1]. The calculated phonon frequencies are less than those of the LDA calculations, by about 8%. The differences between the two calculations is due likely to the employed generalized gradient and the pseudo-potential approximations. The phonon dispersion curves of MgSc and AlSc in B2 structure could not be compared with experimental works; therefore, no comment can be unequivocally made on the success of this *ab initio* method. The current phonon calculations of the MgSc and AlSc will certainly be very useful in interpreting future experiments.

4. Conclusions

In this work, the structural, electronic, elastic and dynamic properties of MgSc and AlSc in the B2 (CsCl) structure have been calculated, using the *ab initio* pseudopotential method, within the GGA of the density functional theory. The lattice parameters compared well with the experiments. Three independent elastic constants, bulk modulus, shear modulus and pressure derivative of the bulk modulus concurred excellently with the other works in the literature. The B/G ratio values for the MgSc and AlSc compounds are higher than the critical values which distinguish brittle behavior from ductile. Hence, these compounds are ductile. The electronic band structures were calculated for both materials, in the B2 structures. The phonon frequencies and phonon densities of states in the B2 phase in several lines of high symmetry of the Brillouin zone, were obtained using the density-functional perturbation theory.

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