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The first-principles study on Zr_3Al and Sc_3Al in $L1_2$ structure

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ABSTRACT

The elastic, electronic, and phonon properties of the intermetallic compounds Zr_3Al and Sc_3Al in the $L1_2$ structure have been investigated in detail by employing an *ab initio* pseudopotential method and a linear-response technique within a generalized gradient approximation (GGA) of the density-functional theory (DFT) scheme. The calculated ground-state properties such as lattice constants and bulk modulus agree well with the previous theoretical calculations. The numerical first-principles calculations of the elastic constants have been used to calculate C_{11}, C_{12}, and C_{44} for Zr_3Al and Sc_3Al. The electronic band structures of Zr_3Al and Sc_3Al show that at the Fermi level, a major part of the contribution comes from Zr 4d (Sc 3d) states. The phonon-dispersion curves and phonon total and partial density of states based on the linear-response method have been investigated for both materials. Temperature variations of specific heat capacity in the range of 0–500 K are obtained using the quasi-harmonic model.

1. Introduction

The ordered $L1_2$-structured intermetallic alloys Zr_3Al and Sc_3Al have received interest as potential candidates for structural application because of their relatively high melting point, good corrosion properties, low absorption cross section for thermal neutrons, pand otentially useful high temperature strength [1–3]. Thus, several studies have been performed to investigate the structural, mechanical, elastic, thermodynamic, superconductor, and electronic properties of Zr_3Al and Sc_3Al [4–24]. For Zr_3Al, Clouet and Sanchez [4] calculated elastic properties by using the full-potential linear muffin-tin orbitals (FP-LMTO) method. Guan et al. [5] have conducted a systematic investigation of the structural, elastic, and electronic properties of Zr_3Al with the help of the vienna *ab initio* simulation package (VASP) based on the DFT. Ravindran and Asokamani [6] realized the self-consistent linear muffin-tin orbitals (LMTO) electronic band structure calculation for Zr_3Al. The electronic structure calculations for Sc_3Al have been determined by Wiendlocha et al. [7], using the KKR method. Paljević and Ban [8] studied the oxidation behavior of Zr_3Al in the dry oxygen at a temperature of 647–1050 K. The Zr_3Al and Sc_3Al crystallize in the Cu_3Au ($L1_2$)-type structure with the Pm-3m space group. The phonon properties of solids play a major role in determining various fundamental solid-state properties, such as thermal expansion, specific heat, electron–phonon interaction, heat conduction, and phase transition. The entire phonon properties of Zr_3Al and Sc_3 Al have not yet been studied by using any theoretical or experimental method. The present article aims at investigating the ground-state properties such as lattice constants, bulk modulus, elastic constants, and band structure as well as the phonon properties of both materials by the density-functional theory (DFT). The linear-response method has been used to determine the phonon-dispersion curves and the total and partial density of the states.

2. Method

The *ab initio* calculations have been performed with the plane-wave pseudopotential method, density-functional theory (DFT) within the generalized gradient approximation (GGA) using the scheme of Perdew–Burke–Ernzerhof (PBE) [25] parameterization for the exchange-correlation potential, and the Quantum-ESPRESSO code [26]. The electron–ion interaction was described by ultrasoft Vanderbilt pseudopotential [27]. The single-particle functions were expanded in a plane-waves basis set up to the kinetic energies cut off 40 Ry, which is sufficient to fully converge all properties relevance. The electronic charge density was evaluated up to the kinetic energy cut-off 400 Ry. The number of **k**-points in the irreducible Brillouin zone (BZ) used in the self-consistent calculations is 60. Integration up to the Fermi surface is done with a smearing technique [28] with the smearing parameter $\sigma=0.02$ Ry. Eight dynamical matrices have been calculated on a $4\times4\times4$ **q**-point mesh to obtain complete phonon dispersions and vibrational density of states. The dynamical matrices at arbitrary wave vectors were evaluated by using the Fourier

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Table 1
Calculated lattice constants (Å), elastic constants (GPa), bulk modulus (GPa), shear modulus (GPa) and pressure derivative of the bulk modulus dB/dP and B/G_H for Zr_3Al and Sc_3Al.

Materials	Reference	a	C_{11}	C_{12}	C_{44}	B	dB/dP	G_H	B/G_H
Zr_3Al	This work	4.375	132.155	81.981	70.586	98.706	2.830	48.767	2.024
	VASP (GGA-PW91) [5]	4.381	148.653	79.387	70.834	102.476	3.480	53.400	1.919
	FP-LMTO(LDA) [4]	–	163.8	79.3	86.5	107.67	–	–	–
	LMTO [6]	4.556	–	–	–	87	–	–	–
	Theory [15]	4.380	–	–	–	65	–	–	–
	Theory [16]	4.372	–	–	–	–	–	–	–
	Exp. [24]	4.392	–	–	–	–	–	–	–
	Exp. [3]	4.374	–	–	–	–	–	–	–
	Exp. [1]	4.370	–	–	–	–	–	–	–
	Exp. [12]	4.290	–	–	–	–	–	–	–
Sc_3Al	This work	4.427	105.494	42.492	53.169	63.493	3.100	36.14	1.756
	Theory [7]	4.312	–	–	–	–	–	–	–

deconvolution on this mesh. Specific heat and Debye temperature are calculated at various temperature from the phonon frequencies obtained through the quasi-harmonic Debye model (QHA) [29]. Within the Debye approximation, the Helmholtz free energy at low temperature is:

$$F = E_{static} + RT\left[\frac{9}{8}\left(\frac{\theta_D}{T} + 3\ln(1-e^{-\theta_D/T})1 - D\left(\frac{\theta_D}{T}\right)\right)\right], \quad (1)$$

$D(\theta_D/T)$ is the Debye function written as:

$$D\left(\frac{\theta_D}{T}\right) = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{z^2 dz}{e^z - 1}. \quad (2)$$

3. Results

The lattice constants and the pressure derivatives of the bulk modulus have been obtained by fitting the total energy data with the Murnaghan equation of state [30]. The calculated values for a, B, C_{11}, C_{12}, C_{44}, dB/dP, G_H, and B/G_H of Zr_3Al and Sc_3Al have been summarized in Table 1. The present calculated lattice constants for Zr_3Al are in good agreement with the available theoretical and experimental results. In the available literature, there are no experimental data reported for the lattice constant of Sc_3Al, while there is a theoretical value for the lattice constant of Sc_3Al. The elastic constants are important parameters that describe how a material behaves under stress. In the case of cubic crystals, there are three independent elastic constants (C_{11}, C_{12}, and C_{44}), and the mechanical stability conditions are $C_{11}+C_{12}>0$, $C_{44}>0$, and $C_{11}-C_{12}>0$. I have used the formulas and procedures for the calculation of elastic constants and bulk modulus in a previous publication [31]. The experimental values of the elastic constants of both materials are not available in the literature. For the bulk modulus, elastic constant C_{44}, and C_{11} of Zr_3Al, the calculated values are less than the values calculated by Clouet and Sanchez [4] and Guan et al. [5]. Thus, further experimental studies are needed to compare with these calculated results for Zr_3Al and Sc_3Al. In order to investigate the ductility and brittleness properties of Zr_3Al and Sc_3Al, the ratio of bulk modulus to shear modulus, B/G, has been calculated. This ratio can be considered as an empirical criterion of the extent of the fracture range in the materials [32]. If the ratio of B/G is higher than 1.75, then the material behaves in a ductile manner. If it is less than 1.75, then that material demonstrates brittleness. The B/G values are 2.024 and 1.756 for Zr_3Al and Sc_3Al, respectively. The B/G values of Zr_3Al and Sc_3Al indicate the ductile nature of the materials. The electronic band dispersions are presented along high symmetry directions in Fig. 1, in which E_F=0 have been taken. According to

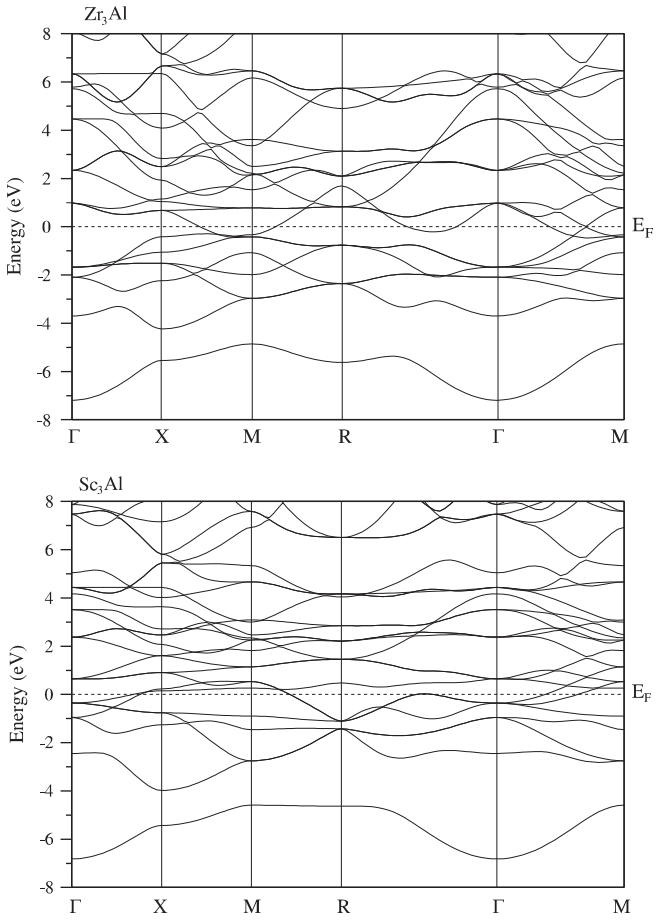

Fig. 1. Calculated electronic band structure of Zr_3Al and Sc_3Al along several lines of high symmetry in the Brillouin zone.

Fig. 1, there is no band gap at the Fermi level. Valance and conduction bands overlap significantly at the Fermi level. Consequently, Zr_3Al and Sc_3Al exhibit a metallic character. The overall bands profiles and DOS for these compounds are in good agreement with previous theoretical results [5–7]. The character of the band states for these alloys has been identified by calculating their total and partial densities of the states (DOS) (in Fig. 2). According to the band structures, the peaks in the total and partial density of the states have been found: three peaks, which are above and below the Fermi level are mainly due to the Zr 4d states for Zr_3Al, Sc 3d for Sc_3Al and smaller contributions from the other states of the Zr (Sc) and Al atoms. In both the materials, the

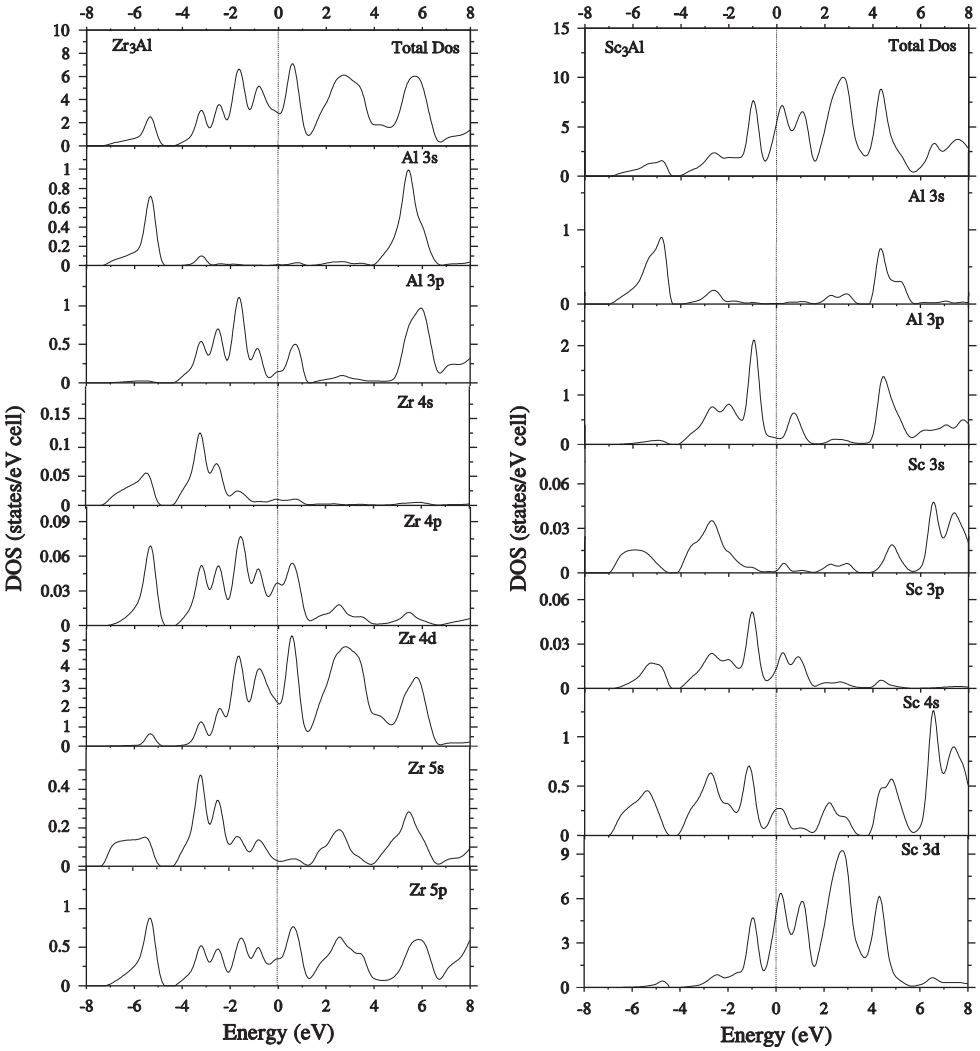

Fig. 2. Calculated partial and total DOS for Zr_3Al and Sc_3Al. The Fermi level is set at 0 eV.

lowest lying bands around −5.7 eV for Zr_3Al, 4.7 eV for Sc_3Al stemmed mainly from the Al 3s states and Zr 5p states for Zr_3Al, Al 3s states and Sc 4s states for Sc_3Al, and the Zr 4s, 4p, and 5s (Sc 3s and Sc 3p) with smaller contributions. These alloys have four atoms per primitive cubic unit cell: there are a total of 12 phonon branches, due to symmetry, the distinct number of phonon branches is reduced along the principal symmetry direction Γ–X and M–R–Γ in the $L1_2$ phase. The experimental data on the phonon spectra of these materials are not yet available. The phonon-dispersion curves and the density of states (partial and total) curves for Zr_3Al and Sc_3Al have been plotted in Fig. 3. The spectrums of Zr_3Al and Sc_3Al indicate that these compounds are mechanically stable, as phonon frequencies ω along all directions are positive. For Zr_3Al, the highest three optical branches are separated from the rest of the phonon branches, by looking at the phonon density of states. This gap has been calculated to be 24.020 cm^{-1}. For Zr_3Al, it is found that the phonon density of states is mostly composed of Al states above the phonon band gap, as its atomic mass is lighter than the mass of the element Zr. The partial density of states of both materials indicates that the density of states is mostly composed of Al states at a high frequency and Zr (Sc) states at a low frequency. There is an overlap between the optical and acoustical phonon branches along all the directions for Sc_3 Al. The mass ratios of Al and Sc are responsible for the overlap between the acoustic and optical branches of Sc_3Al. The zone center optical phonon modes for Zr_3Al (Sc_3Al) have been calculated to be 168.9 cm^{-1} (182.21), 186.41 cm^{-1} (214.42), and 235.43 cm^{-1} (243.13), respectively. Fig. 4 shows the calculated specific heat capacity at constant volume (C_v) of Zr_3Al and Sc_3Al alloys as a function of temperature. The C_v increases rapidly in the range 0–500 K before it starts to saturate. Calculated specific heat capacity C_v is very close to the Dulong–Petit limit [33], which is commonly satisfied with all solids at high temperatures. For all materials, the C_v functions flatten out as the temperature increases above 500 K. The optic and acoustic modes have large efforts on the heat capacity.

$\theta_D(T)$ was at obtained at temperature T by solving Eq. (1). Fig. 5 shows the Debye temperature as a function of temperatures.

4. Conclusion

In this article, the structural, elastic, electronic, and phonon properties of Zr_3Al and Sc_3Al, using the *ab initio* pseudopotential method within the GGA of the DFT have been studied. The Zr_3Al and Sc_3Al lattice constants, bulk modulus, and elastic constants have been calculated and compared with the available literature. In the band structure of Zr_3Al and Sc_3Al, it has been found that the Zr 4d (Sc 3d) states mainly contribute to the density of the states that are very close to the Fermi level. The GGA calculations show

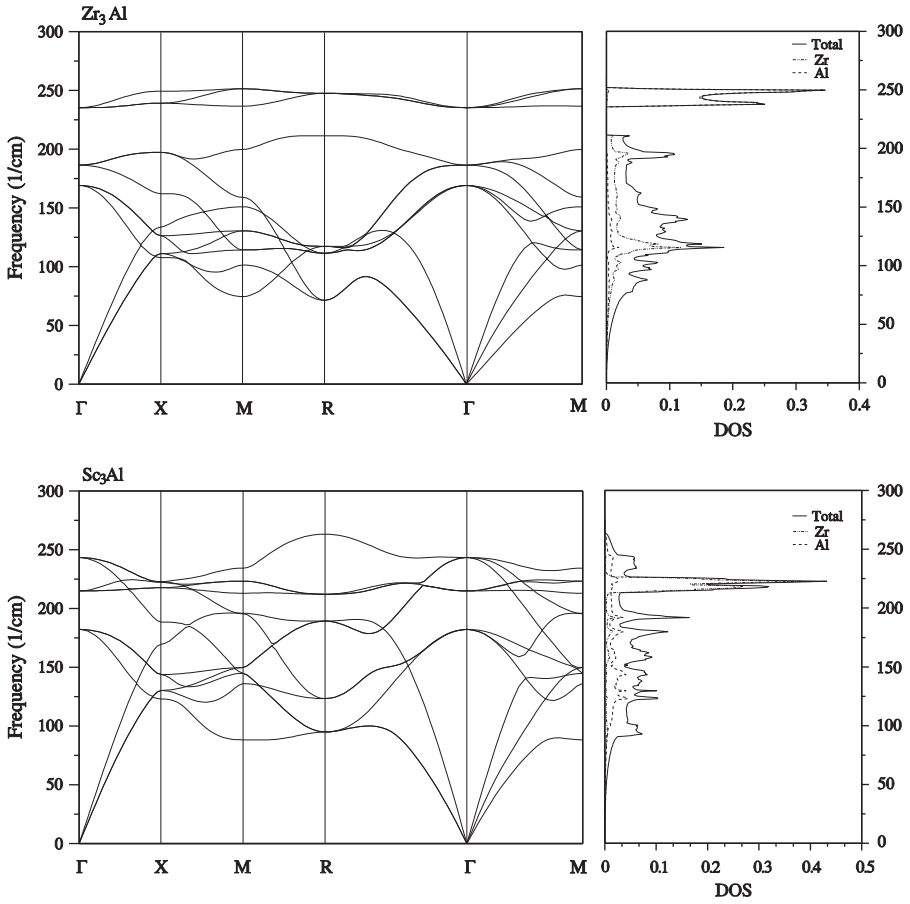

Fig. 3. Calculated phonon dispersion curves and phonon densities of states of Zr_3Al and Sc_3Al along several lines of high symmetry in the Brillouin zone.

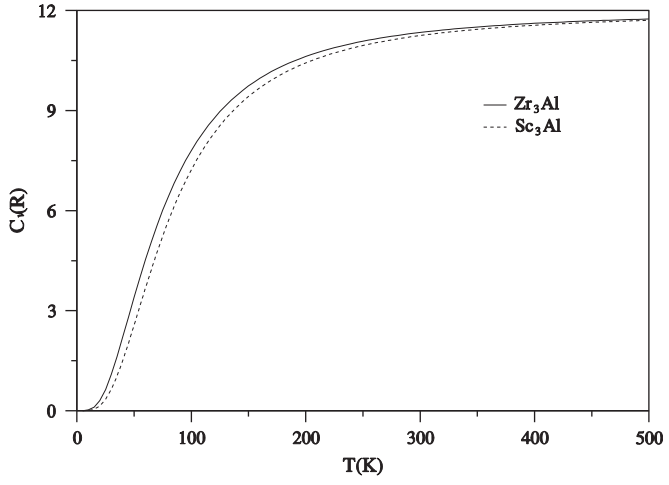

Fig. 4. The calculated specific heats at constant volume *versus* temperature of Zr_3Al and Sc_3Al alloys.

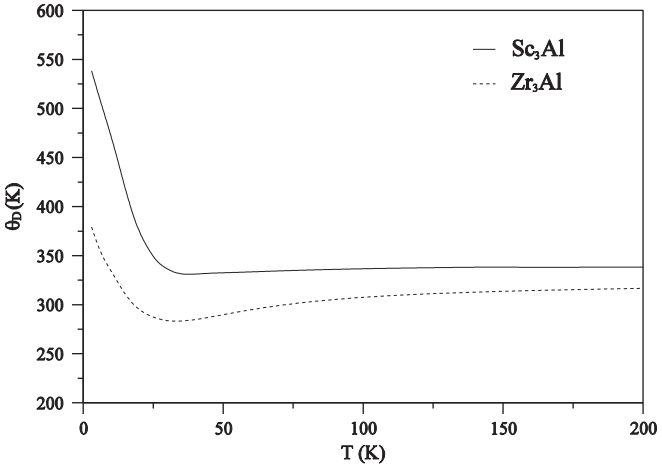

Fig. 5. Debye temperature variation with temperature for Zr_3Al and Sc_3Al alloys.

that Zr_3Al and Sc_3Al are metallic compounds for the $L1_2$ structure. The phonon-dispersion curves and the density of states of Zr_3Al and Sc_3Al in the several lines of the high symmetry of the Brillouin zone have been calculated using the density-functional perturbation theory (DFPT). The current phonon calculations of Zr_3Al and Sc_3Al will certainly be useful for the interpretations of future experiments and theoretical studies. Finally, the specific heat capacity at constant volume *versus* temperature and Debye temperature have also been reported.

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