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AB INITIO STUDY OF PHONON DISPERSION AND ELASTIC PROPERTIES OF $L1_2$ INTERMETALLICS Ti_3Al AND Y_3Al

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In this paper, the structural, elastic and phonon properties of Ti_3Al and Y_3Al in $L1_2(Cu_3Al)$ phase are studied by performing first-principles calculations within the generalized gradient approximation. The calculated lattice constants, static bulk moduli, first-order pressure derivative of bulk moduli and elastic constants for both compounds are reported. The phonon dispersion curves along several high-symmetry lines at the Brillouin zone, together with the corresponding phonon density of states, are determined using the first-principles linear-response approach of the density functional perturbation theory. Temperature variations of specific heat in the range of 0–500 K are obtained using the quasi-harmonic model.

Keywords: *Ab initio* calculations; elastic constant; density functional theory; Ti_3Al intermetallic compound.

1. Introduction

Ti_3Al and Y_3Al has been a subject of immense research interest in high-temperature and structural applications.[1–7] Ti_3Al possess several interesting characteristics, *viz.*, low density, good high-temperature strength, high thermal conductivity, high melting temperature, and oxidation resistance at elevated temperatures.[5–19]

Electronic structure, thermodynamic properties, phase transformations, and structural stability of Ti_3Al in $L1_2$ phase are studied either by experimental techniques or by theoretical methods.[10–14]

The phonon density of states for Ti_3Al in $L1_2$, were investigated using the linear response approach based on DFPT.[5] The electronic structure and phase stability of Ti_3Al in $L1_2$ and $D0_{19}$ were reported using the tight-binding linear muffin tin orbital method (TB-LMTO) within atomic sphere approximation (ASA).[11] The structural and electronic properties of Ti_3Al are studied by the linear muffin-tin orbitals (LMTO) and the full-potential linearized augmented plane-wave (FLAPW) methods within the local density approximation.[14] On the other hand, studies for characterization of Y_3Al are scarce.[16–19] The structural properties of Y_3Al including heat of formation, ΔH, and lattice constant in both $L1_2$ and BiF_3 phases were also reported.[17]

The phonon dispersion curves in Ti_3Al and Y_3Al are necessary for understanding the lattice dynamics. The knowledge of phonon spectrum plays a significant role in determining different material properties, including phase transition, thermodynamic stability, transport and thermal properties. The aim of this paper is to study the dynamic properties of Ti_3Al and Y_3Al in the $L1_2$ phase using the density functional theory (DFT) within generalized gradient approximation (GGA).

2. Method

Calculations were carried out with pseudopotential method based on the DFT[20,21] as implemented in the Quantum-ESPRESSO software package.[22] Ultrasoft pseudopotentials were used, and the cut-off energy for the plane wave basis set was 40 Ry. The exchange-correlation potential was treated with the GGA parametrized by Perdew–Burke and Ernzerhof.[23] 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. This number of k-points is sufficient to lead better convergence on the total energy and elastic moduli. The integrals over the Brillouin zone are performed up to $12 \times 12 \times 12$ mesh in the irreducible Brillouin zone. The self-consistent calculations are considered to be converged when the phonon frequencies of the system is stable within 0.05 THz. Eight dynamical matrices were calculated on a $4 \times 4 \times 4$ q-point mesh to obtain a complete phonon dispersion and vibrational density of states. The dynamical matrices at the arbitrary wave vectors were evaluated using the Fourier deconvolution on this mesh. Specific heat at constant volume versus temperature was calculated using the quasi-harmonic approximation (QHA).[24]

Elastic constants were obtained by calculating the total energy as a function of volume-conserving strains that break the cubic symmetry. Bulk modulus B, C_{44} and shear modulus $c = (C_{11}C_{12})/2$ were 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.[25] Hence, B was

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 as a result of an applied strain with vector $e = (e_1, e_2, e_3, e_4, e_5, e_6)$. The shear modulus c is

$$\frac{\Delta E}{V} = 6C'\delta^2 + 0\delta^2 \,. \tag{2}$$

The two expressions above yield $C_{11} = (3B + 4c)/3$, $C_{12} = (3B - 2c)/3$ and C_{44} is given by

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

The details on the calculation of elastic constants have been described in our previous paper.[26]

3. Results

Ti_3Al and Y_3Al have face-centered cubic crystal lattices, with Cu_3Au-type ($L1_2$) structure belonging to space group Pm-$3m$. The equilibrium lattice parameter is determined by minimizing the total energy with respect to different values of the lattice parameter. These energy values are fitted to the Murnaghan's equation of state[27] in order to obtain the lattice constant a, and the first-order pressure derivative of the bulk modulus, dB/dP. The computed values of a and dB/dP for Ti_3Al and Y_3Al are listed in Table 1. Lattice parameters agree well with other calculations.

The calculated elastic constants C_{11}, C_{12}, C_{44}, bulk modulus and shear modulus are also quoted in Table 1. In view on this table, one can notice that the unidirectional elastic constant C_{11} is much higher than the C_{44} indicating that these compounds present weaker resistance to pure shear deformation compared to

Table 1. Calculated lattice constants (in Å), bulk modulus (in GPa), second order elastic constants (in GPa) and pressure derivative of the bulk for Ti_3Al and Y_3Al in the $L1_2$ structure.

	Ref.	a (Å)	B (GPa)	dB/dP	C'	C_{11}	C_{12}	C_{44}
Ti_3Al	This work	4.046	112.157	3.42	26.085	146.936	94.767	88.432
	TB-LMTO-ASA[11]	3.991	159.000	—	—	—	—	—
	LDA[5]	4.115	—	—	—	—	—	—
	TB-LMTO[2]	4.098	125.800	—	—	—	—	—
Y_3Al	This work	4.768	49.957	2.75	27.537	86.673	31.600	37.100
	Exp.[15]	4.785	—	—	—	—	—	—
	Exp.[18]	4.818	—	—	—	—	—	—
	FLASTO[17]	4.729	—	—	—	—	—	—

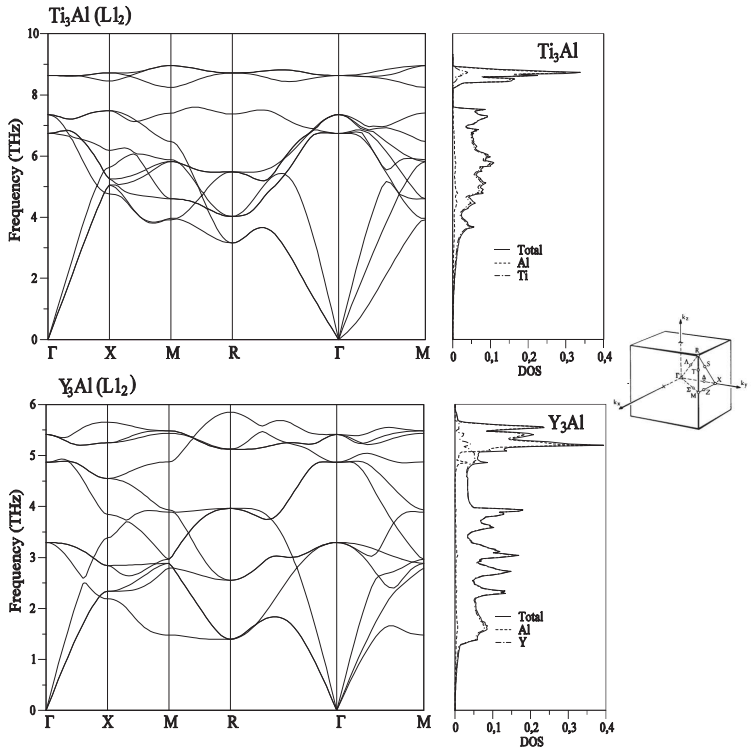

Fig. 1. Calculated phonon dispersion curves and phonon densities of states for Ti_3Al and Y_3Al in the $L1_2$ structure along several lines of high symmetry in Brillouin zone.

resistance to unidirectional compression. The traditional mechanical stability conditions of the elastic constants in cubic crystals are known to be $C_{44} > 0$, $C_{11} > 0$ and $C_{11} > C_{12}$. Our results for elastic constants in Table 1 satisfy these stability conditions meaning that the herein studied compounds are elastically stable. To the best of our knowledge no reported experimental or theoretical data on the elastic constants for Ti_3Al and Y_3Al compounds in $L1_2$ phase. Our calculated bulk modulus value of Ti_3Al is slightly underestimated compared to LMTO calculations.[2,11] There are no experimental results available to us to check our results.

Phonon dispersion curves, including the partial and total density of states for Ti_3Al and Y_3Al, along the high-symmetry directions are shown in Fig. 1. The primitive cell of Ti_3Al and Y_3Al contains four atoms, leading to total 12-phonon branches. In our previous paper, we have reported that the phonon branches reduce some symmetry directions.[28] There are two acoustic and two optical modes along the principal symmetry directions Γ-X and M-R-Γ due to degeneracy of the transverse modes in both acoustic and optical modes. We did not observe any imaginary phonon frequency for any of modes for both compounds. This supports the dynamical stability of both compounds.

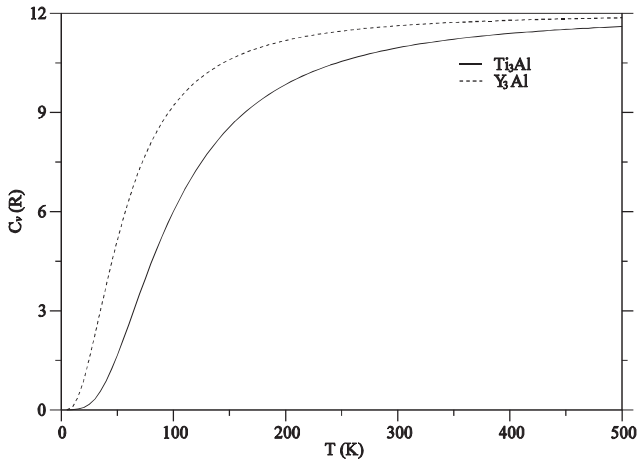

Fig. 2. Calculated lattice specific heat at constant volume as functions of temperature for Ti_3Al and Y_3Al in the $L1_2$ structure.

From partial density of states, it can be inferred that the vibration modes are mostly excited by Al atoms in high frequencies, while Ti and Y contribute a major part to the modes with lower frequencies. For Ti_3Al, energy gap exist between high frequency optical modes and lower frequency optical modes. In phonon density of states, the energy band gap is around 1.002 THz. For Y_3Al, there is no gap between acoustical and optical phonon branches (see Fig. 1), since there is a considerable overlap between the transverse optical (TO) and longitudinal acoustical (LA) phonon branches. The zone-centered optic phonon modes are found as 6.727, 7.334 and 8.688 THz for Ti_3Al and at 3.308, 4.876 and 5.408 THz for Y_3Al. The calculated density of states for Ti_3Al has a similar shape compared with previous theoretical calculations.[5]

The calculated specific heat capacity at constant volume C_v versus temperature of Ti_3Al and Y_3Al in $L1_2$ phase is shown in Fig. 2. The C_v values of both compounds increased smoothly with temperature in the range 0–300 K. At high temperature C_v is close to a constant value which is the so-called Dulong–Petit limit,[29] which is common to all solids at high temperatures. For both compounds, the C_v functions flatten out as temperature increases above 300 K. The optic and acoustic modes have large effects on heat capacity.

4. Conclusion

Structural, elastic and phonon properties of Ti_3Al and Y_3Al in $L1_2$ phase were evaluated from first principles. The predicted lattice constant and bulk modulus of these compounds are in good agreement with theoretical results. We also calculate the phonon frequencies along high-symmetry directions. We found using GGA that our phonon density of states for Ti_3Al exhibit the same trend as previous theoretical

curves. Finally, using the calculated phonon density of states, the specific heat at constant volume versus temperature was determined within QHA.

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