Vibrational stability of $RNiAl_3$ (R=Sc, Y) Compounds

Mehtap Altay[1,2], Haci Ozisik[2], Engin Deligoz[2], Havva Bogaz Ozisik[2]

[1]Ministry of National Education, Yenikent Anatolian High School, TR-68210, Aksaray, Turkey
[2]Dept. of Physics, Faculty of Arts and Sciences, Aksaray University, TR-68100, Aksaray, Turkey
mehtap_altay_@hotmail.com

Abstract: We have used to ab-initio methods for determining the vibrational and thermodynamical properties for the $ScNiAl_3$ and $YNiAl_3$ compounds in orthorhombic Pnma structure (Space Group No: 62). The pseudopotential plane-wave approach is used based on density functional theory and implemented in the VASP package. The present phonon frequencies of $ScNiAl_3$ and $YNiAl_3$ compounds are calculated using the Phonopy code and DFPT methods. Also, the temperature dependent free energy, entropy and heat capacity quantities were calculated and discussed.

Keywords: First Principles, Vibrational Properties, $ScNiAl_3$, $YNiAl_3$

1. Introduction

There are a large number of studies about R-Ni-Al systems, where R is a rare earth metal, because of their glass-forming ability [Pukas, 2010]. The systems belong many structures of the aluminides with different stoichiometry. Pukas et al. were synthesized $RNiAl_3$ (R = Y, Sm, Gd, Tb, and Dy) compounds by arc melting method. Their x-ray diffraction study show that the compounds crystallize with $YNiAl_3$-type structures (SPG Pnma, No: 62) [Pukas, 2010]. Scandium and Yttrium has chemically similar properties to the later lanthanides. The structural and mechanical properties of $ScNiAl_3$ compound, same group element of $YNiAl_3$, were studied by our group [Altay, 2018]. However, there is no information about the vibrational properties of these materials. With this motivation, we have performed the first principles vibrational calculation on the titled compounds for the first time.

2. Method

All calculations have been carried out by using the VASP code [Kresse, 1996] based on the density functional theory (DFT). The electron–ion interaction was considered in the form of the projector-augmented-wave (PAW) method with plane wave up to an energy of 500 eV [Blöchl, 1994], an adequate value for studying the physical properties. Perdew–Burke–Ernzerhof (PBE) type functional [Perdew, 1996] within the generalized gradient approximation (GGA) has been used for the exchange and correlation terms in the electron–electron interaction. 6x11x4 Monkhorstand Pack [Monkhorst, 1976] grid of k-points has been used. The present phonon frequencies of $ScNiAl_3$ and $YNiAl_3$ compounds are calculated using the Phonopy code [Togo, 2015] and DFPT methods. The phonon dispersion curves have been calculated in high symmetry directions using 1x2x1 supercell. Also, the temperature dependent free energy, entropy and heat capacity quantities were calculated and discussed.

3. Results and Discussion

3.1. Structural Properties

Pukas et al. has analyzed the sturucture of $YNiAl_3$ compound and they found that it is in the orthorhombic Pnma structure (Space Group No:62, Z=4) [Pukas, 2010]. This experimental results were used as an input structural parameters for the titled compounds. The data for $ScNiAl_3$ were released in our previous study [Alta, 2018]. The relaxed structural parameters reveal that they are good agreement with x-ray crystallographic data. The present lattice constants, the ground state energy (E_0) and volume (V_0) are given in Table 1 with available experimental data. The relaxed crystal parameters were used to calculate vibrational properties.

Table 1. The calculated lattice parameters a (Å), b (Å), c (Å), energy E_0 (eV/f.u.), volume V_0 (Å^3/f.u.) for $ScNiAl_3$ and $YNiAl_3$ compounds in orthorhombic Pnma structure

Comp.	***A***	***b***	***c***	***E_0***	***V_0***	***Ref.***
$ScNiAl_3$	8.019	3.929	10.393	-25.64	81.88	[Altay,2018]
$YNiAl_3$	8.1574	4.0493	10.6543	-26.16	87.98	Present
	8.1532	4.0426	10.6349			Exp. [Pukas,2010]

3.2. Vibrational Properties

$ScNiAl_3$ and $YNiAl_3$ compounds are considered in the orthorhombic Pnma structure (Space Group No:62, Z=4). The experimental structural parameters of $YNiAl_3$ were used as an input for structural energy minimization. There are 20 atoms in primitive cell and 3N=60 phonon branch (3 optic and 57 acoustic) expected. 1x2x1 supercell (40 atoms in supercell) used to calculate interatomic force constants to determine phonon dispersion curves and the related properties. We were calculated the phonon dispersions and one phonon density of states for $ScNiAl_3$ and $YNiAl_3$ compounds and given in Fig. 1 and Fig. 2.

From Fig. 1-2, there is no imaginary frequency (negative mode) so the compounds vibrationally stable. Partial phonon DOS show that optical and lower acoustic phonon branches dominated by Sc and Y elements. Mid-region vibrations are from Ni atoms, but tops are from Aluminums. This behaviour is expected because of atomic weight difference of atoms contained.

3.3. Thermodynamical properties

The free energy, entropy and Heat capacity (C_v) are calculated in 0-1000 K temperature range and illustrated in Fig. 3. The absolute value of total-free energy rapidly decreases with temperature. In our case the heat capacity approach to the Dulong-Petit limit around 500 K, and at low temperature (<80 K) the $\approx T^3$ behavior is clearly seen. The temperature is limited to 1000 K to minimize the potential influence of anharmonicity in all plots. The calculated room temperature C_v values are 450.8 and

452.1 J/K/mol for $ScNiAl_3$ and $YNiAl_3$ compounds, respectively. The calculated results are similar with little difference.

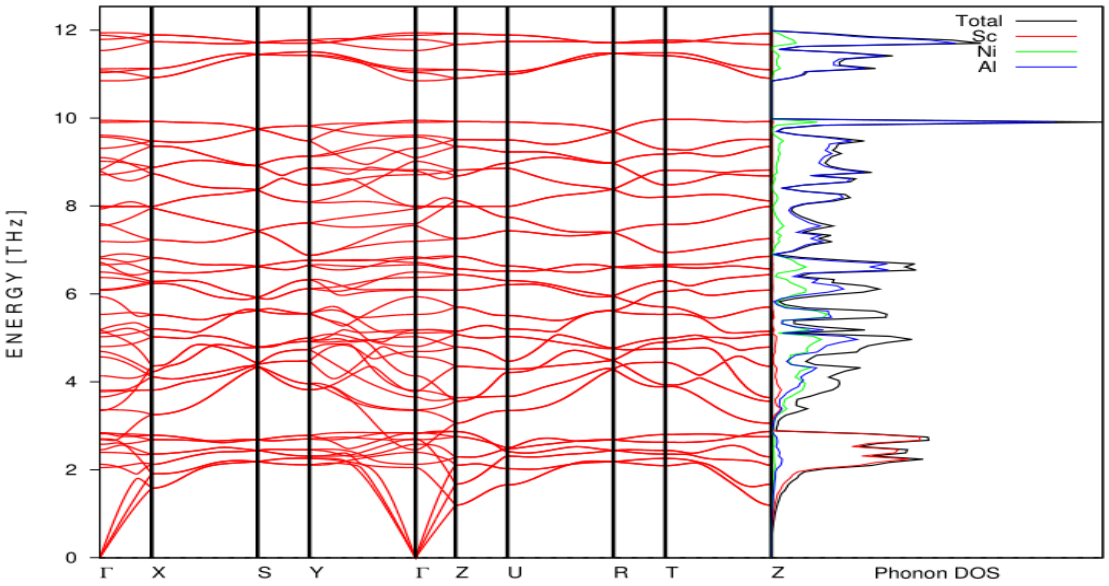

Figure 1. The calculated phonon dispersions and partial density of states for $ScNiAl_3$

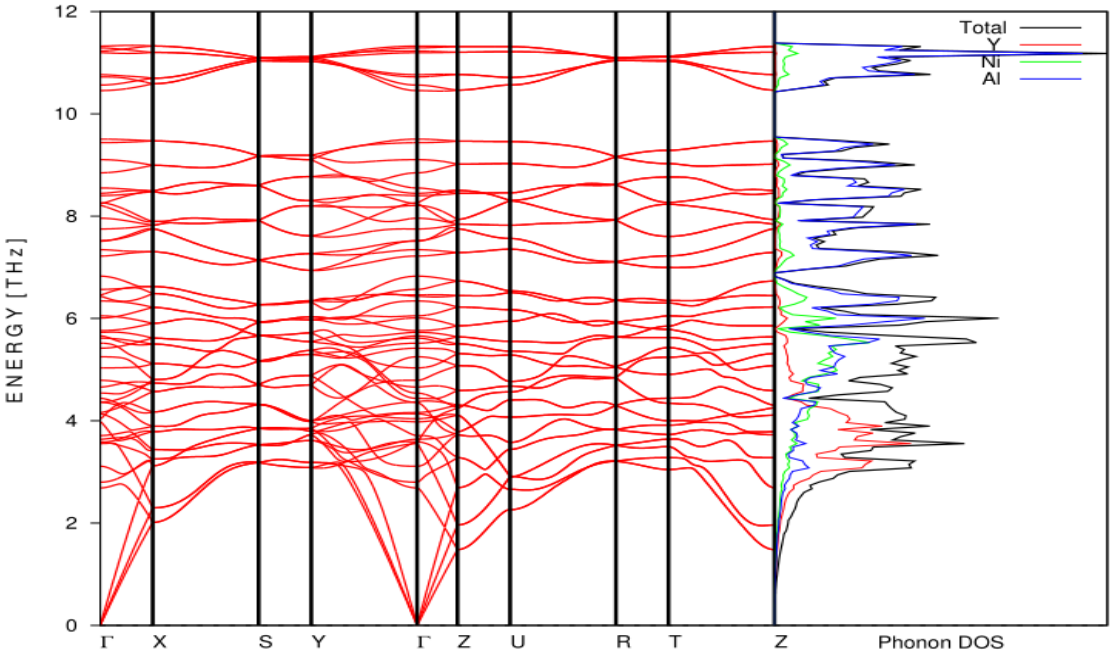

Figure 2. The calculated phonon dispersions and par tial density of states for $YNiAl_3$

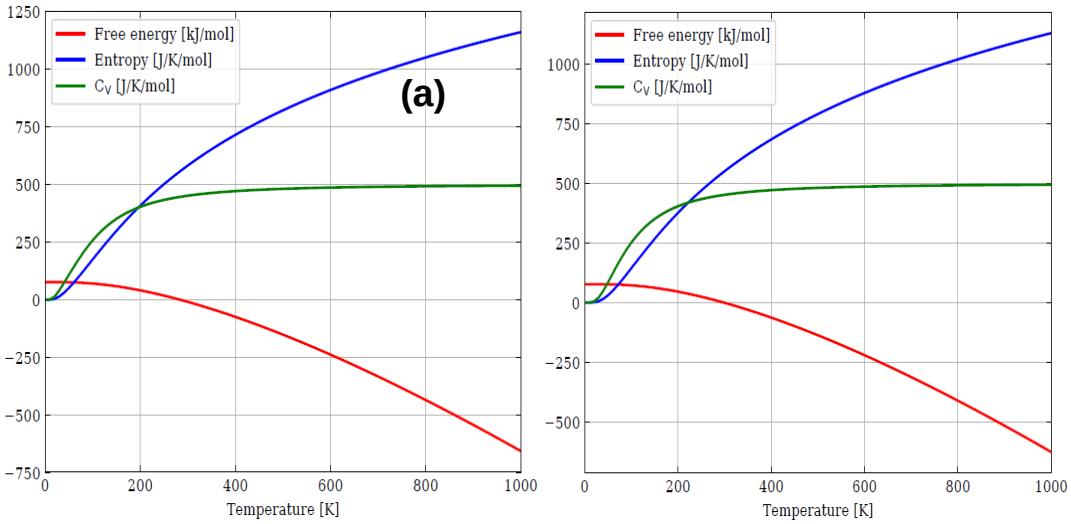

Figure 3. The variation of the free energy, entropy and Heat capacity (C_v) coefficient with temperature for (a) $ScNiAl_3$ and (b) $YNiAl_3$

4. Conclusion

In summary, we have performed the vibrational and thermodynamical calculation for $YNiAl_3$ and $ScNiAl_3$ compounds using the plane-wave pseudopotential approach to the density-functional theory within the generalized gradient approximation. We found that both compounds are vibrationally stable. The calculated phonon dispersion curves and the related thermodynamical properties such as internal energy, free energy, entropy, and heat capacity provide valuable information about the intrinsic character of solids are the other original aspects of the present calculations. We hope that our other predicted results will be serving as a reliable reference for the future experimental and theoretical studies.

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