

***Ab initio* investigation of the electronic, lattice dynamic and thermodynamic properties of ScCd intermetallic alloy**

B. I. Adetunji^{*,†,¶}, A. S. Olayinka[§], J. B. Fashae[†] and V. C. Ozebo[‡]

^{*}*Department of Physics,
University of Agriculture, Abeokuta, Nigeria*

[†]*Department of Physical Sciences,
Bells University of Technology, Ota, Nigeria*

[‡]*Department of Physics,
University of Lagos, Akoka, Nigeria*

[§]*Department of Physics,
Benson Idahosa University,
Benin City, Nigeria*

[¶]*adetunji@physics.unaab.edu.ng*

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The electronic structures, lattice dynamics and thermodynamic properties of rare-earth intermetallic ScCd alloy are studied by the first-principles plane-wave pseudopotential method within the generalized gradient approximation in the framework of density functional perturbation theory. The band structure, density of states, phonon dispersion frequencies, vibrational free energy F_{vib} , specific heat capacity C_V and entropy are studied between 0 K and 1500 K. Finally, using the calculated phonon density of states, the thermodynamic properties are determined within the quasi-harmonic approximation and a value of 47.9 (J/mol · K) at 300 K for specific heat capacity of ScCd is predicted.

Keywords: Lattice dynamics; thermodynamics properties; electronic structure; heat capacity.

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1. Introduction

In recent years, intermetallic compounds have received extensive attention because of their potential promise as high temperature structural materials with anisotropic properties.¹ Rare-earth intermetallic compounds represented as RM (where R is a rare-earth element and M is a main group or transition metal element) has been

[¶]Corresponding author.

discovered to be ductile at room temperature.² Some of these RM intermetallics are promising high-temperature structural materials in industrial and engineering applications such as; superconductors, permanent magnets, catalysts, electrocatalysts and hydrogen storage systems.^{3,4} ScCd which crystalizes in *B2* structure (CsCl-type structure) is a member of the rare-earth intermetallic compounds with a space group of *Pm3m* (No. 221). Experimentally, it had been confirmed by Indelli *et al.*⁵ that these compounds are stable in *B2* phase at ambient conditions using X-ray diffraction technique. Also, the phase diagram of Sc–Cd system has been investigated using differential thermal analysis, metallographic analysis, X-ray diffraction and electron microscopy by Palenzona *et al.*⁶ Recently, Hansa *et al.*⁷ used full-potential linearized augmented plane-wave (FP-LAPW) method within the density functional theory (DFT) to investigate the electronic and high pressure elastic properties of ScCd and other notable intermetallic compounds. However, the dynamical and thermodynamic properties of ScCd intermetallic alloy are still not available in the literatures. The knowledge of the full phonon properties plays a key role in studies of a wide range of physical properties of solids, such as phase-transition thermodynamic stability, thermal expansion, electron–phonon interaction, and lattice thermal conductivity.⁹ Also, the study of the thermodynamic properties of materials is important so as to understand the specific behavior of materials under severe constraints of high pressure and high temperature.⁸ This is in line with the advent of modern technologies (geophysics, astrophysics, particle accelerators, fission and fusion reactors, etc.), from which new advances and innovations in material science to reach higher performances is always expected. The objective of this work is to investigate the electronic, dynamical and thermodynamic properties of ScCd intermetallic alloy at zero pressure using DFT^{10,11} and density functional perturbation theory (DFPT).¹²

The rest of this paper is organized as follows: in Sec. 2, we present the computational methods; in Sec. 3, we present our numerical results and their discussion. Finally, the major conclusions are given in Sec. 4.

2. Computational Method

Our numerical calculations were performed using the Quantum Espresso package¹³ with projector augmented-wave (PAW) within the generalized gradient approximation (GGA)¹⁴ with Sc and Cd PAW datasets from the PSLibrary project.¹⁵ The wavefunctions and the charge density were expanded in a plane-wave basis up to a kinetic energy cutoff of 80 and 360 Ry which are sufficient to obtain converged results. The Brillouin zone integrations were performed using $6 \times 6 \times 6$ Monkhorst–Pack mesh of *k*-points.¹⁶ The tetrahedron method of Brillouin zone integration had been used to calculate the density of state. The phonon band structure is calculated using DFPT via the linear response approach,¹² in which second-order derivatives of the total energy with respect to the phonon displacement of atoms are calculated to obtain the dynamical matrix. Using linear response approach, the uses of supercell

can be avoided and dynamical matrix at any wave vector in the Brillouin zone can be calculated. The thermodynamic properties including the phonon contribution to the Helmholtz free energy, the contribution to the internal energy, the entropy and the constant volume specific heat are calculated within the quasi-harmonic approximation (QHA).

3. Results and Discussion

3.1. *Electronic and structural properties*

We have performed the structural optimization for the lattice constants of ScCd intermetallic alloy through energy minimization. The obtained total energies and lattice constants data are then fitted to third-order Birch–Murnaghan equation of state,¹⁷ the equilibrium lattice parameter (a_0), bulk modulus B_0 and pressure derivative of the bulk modulus B' were obtained. In Table 1, we summarize our calculated structural properties: lattice constant, bulk modulus and its pressure derivative of ScCd at ambient pressure together with available theoretical and experimental data. Our results for the structural properties as observed from Table 1, are in good agreement with the reported theoretical and experimental data.^{5,7} The electronic band structure along the high symmetry direction of the Brillouin zone for ScCd intermetallic alloy is shown in Fig. 1, where the conduction and valence bands are seen overlapping at the Fermi level (E_f). This overlapping is an indication of the metallic nature of the ScCd intermetallic alloy. We also observed from the band structure shown in Fig. 1, that states dominated by d -states of Cd which lies between the energy range of -8.5 to -8.9 eV and between the energy range 0.0 to -7.0 eV, there are hybridization of s -, p - and d -states of (Sc and Cd). However, the bands that cross the Fermi level are mainly the d -states of Sc atom. These features are also observed in Fig. 2 where we presented the density of states showing up and down spins of ScCd intermetallic alloy.

3.2. *Dynamical properties*

The dynamical properties are calculated using the DFPT. At arbitrary points in the Brillouin zone, the dynamical matrices can be obtained with the help of a

Table 1. Calculated lattice constant (a), bulk modulus (B) and pressure derivative (B') of ScCd rare-earth intermetallic at ambient condition.

Alloy	Ref.	$a(\text{\AA})$	$B(\text{GPa})$	$B'(\text{GPa})$
ScCd	Present	3.540	66.00	4.41
	Cal. ^a	3.5419	66.64	4.69
	Exp. ^b	3.510	—	—
	Exp. ^c	3.514	—	—

^aHansa *et al.* (2015),

^bPalenzona *et al.* (1996),

^cIndelli *et al.* (1965).

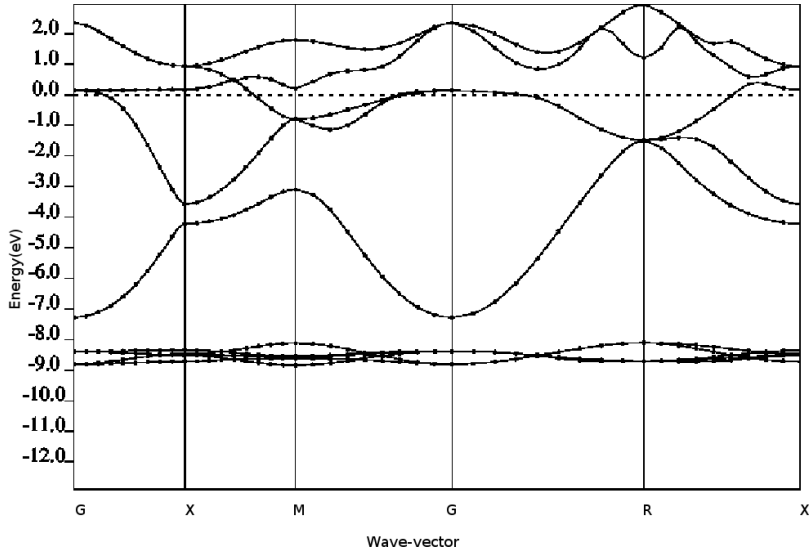


Fig. 1. The band structure of ScCd along high symmetry points.

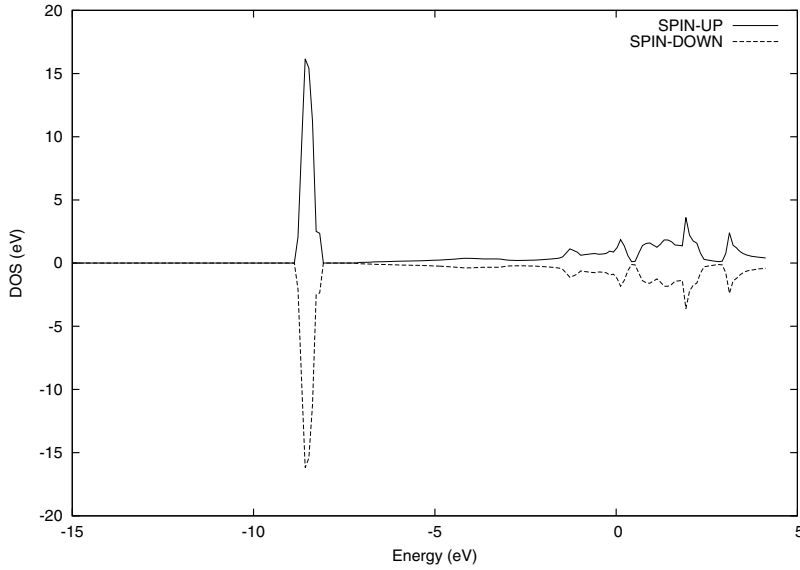


Fig. 2. The density of states for ScCd.

Fourier deconvolution procedure. Based on lattice vibration theory, the relationship between vibration frequency ω and wave vector q in a three-dimensional lattice is known as the dispersion relation $\omega = \omega_j(q)$. The vibration frequency ω is a function of both the direction of the wave vector q and its magnitude. The branch index is denoted by the subscript j . In a crystal lattice with N number of atoms per unit

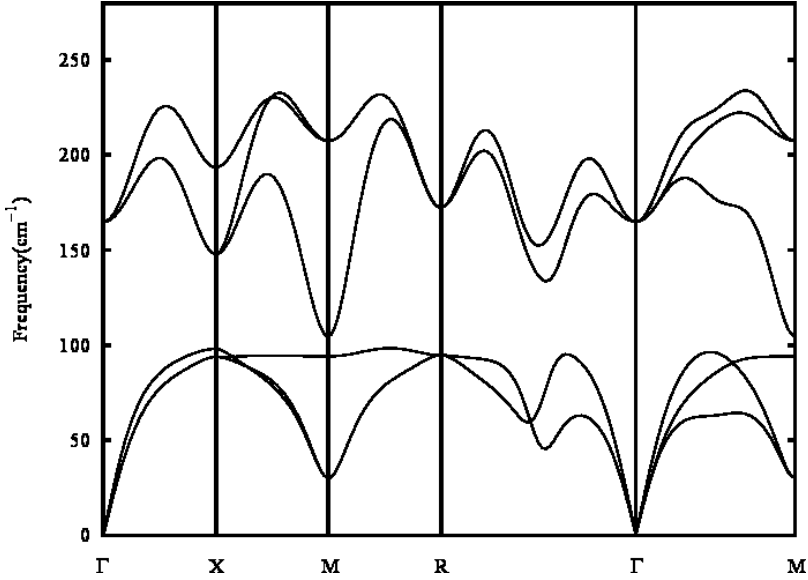


Fig. 3. The phonon frequencies along some high symmetry points for ScCd.

cell, there are $3N$ branches per crystal lattice, three of which are acoustic and the others are optical. In q -space, the dispersion curve displays symmetry properties. The translational symmetry $\omega_j(q+G) = \omega_j(q)$ allows us to contemplate on the first Brillouin zone only, while the inversion symmetry $\omega_j(-q) = \omega_j(q)$ and the rotation symmetry establish the relation between various regions of the Brillouin zone.¹⁸ The phonon dispersion curves along the high symmetry points in the Brillouin zone are plotted in Fig. 3. We observed from the phonon dispersion curves that $B2$ -phase of ScCd intermetallic alloy is a stable state since throughout the Brillouin zone, all phonon frequencies are positive. Also, there is a gap of about 8.1 cm^{-1} between the optical and acoustic modes which is due to mass difference between Sc and Cd atoms. At the zone-center along Γ to M , both the optical and acoustic modes degenerate into six branches.

3.3. Thermodynamic properties

In the QHA, the Helmholtz free energy is given by^{19,20}

$$F(V, T) = U_{\text{stat}}(V) + k_B T \sum_{q\lambda} \ln \left\{ 2 \sinh \left[\frac{\hbar \omega_{q\lambda}(V)}{2k_B T} \right] \right\} + F_{\text{el}}(V, T), \quad (1)$$

where the first term on the right-hand side is the static internal energy at volume V and can be easily determined from standard DFT calculations. The second term is the vibrational free energy which comes from the phonon contribution. The sum is over all phonon branches λ and over all wave vectors \mathbf{q} in the first Brillouin zone, \hbar is the reduced Planck constant, and $\omega_{q\lambda}(V)$ is the frequency of the phonon with

wave vector \mathbf{q} and polarization λ , evaluated at constant volume V . The last term is the thermal electronic contribution to free energy. Usually, it is assumed that the electronic contribution to total free energy can be negligible.^{20,21} The vibrational specific heat C_V at constant volume in the QHA is given as

$$C_V^{\text{vib}} = \sum_{q\lambda} k_B \left(\frac{\hbar\omega_{q\lambda}(V)}{2k_B T} \right)^2 \cosh^2 \left(\frac{\hbar\omega_{q\lambda}(V)}{2k_B T} \right). \quad (2)$$

The electronic specific heat can be obtained from

$$C_V^{\text{el}} = T \left(\frac{\partial S_{\text{el}}}{\partial T} \right)_V \quad (3)$$

and the total specific heat at constant volume is then $C_V = C_V^{\text{ph}} + C_V^{\text{el}}$. The specific heat at a constant pressure, C_p , is different from the specific heat at a constant volume due to anharmonicity. C_V goes to a constant which is given by classical equipartition law: $C_V = 3Nk_B$, where N is the number of atoms in the system. Hence, the vibrational contribution to the entropy of the crystal is given by

$$S_{\text{vib}} = -k_B \sum_{q\lambda} \left[\ln \left(2 \sinh \frac{\hbar\omega_{q\lambda}(V)}{2k_B T} \right) - \frac{\hbar\omega_{q\lambda}(V)}{2k_B T} \coth \frac{\hbar\omega_{q\lambda}(V)}{2k_B T} \right], \quad (4)$$

The knowledge of heat capacity of a substance not only provides essential insight into its vibrational properties but is also mandatory for many applications.⁸ The standard elastic continuum theory has predicted two famous limiting cases.²² The constant volume heat capacity C_V tends to the Petit and Dulong limit at high temperatures²³ and at sufficiently low temperatures, C_V is proportional to T^3 .²² Figures 4–6 displays the calculated F_{vib} , S_{vib} and C_V . As temperature increases, the calculated F_{vib} of ScCd decrease gradually; the calculated S_{vib} increase continually and the calculated constant volume specific heat C_V tend to the asymptotic limit

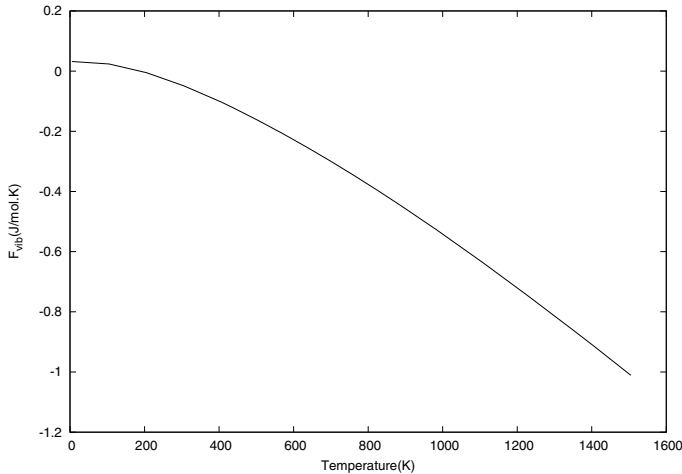


Fig. 4. The calculated phonon contribution to the Helmholtz free energy of ScCd.

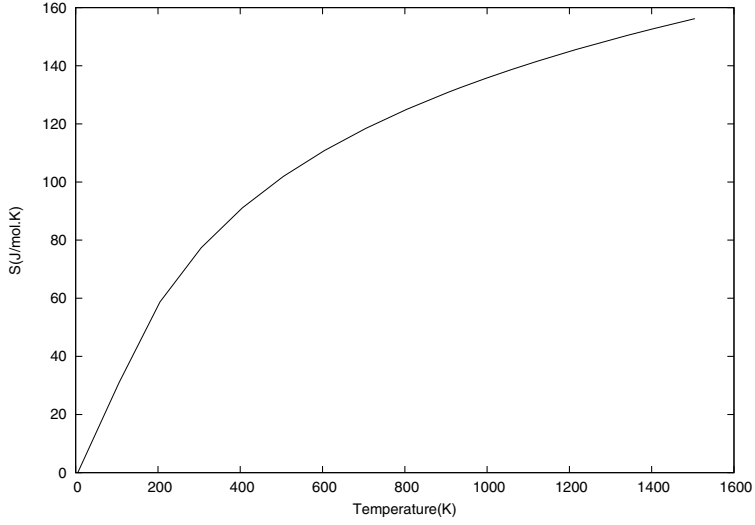


Fig. 5. The phonon contribution to the entropy of ScCd.

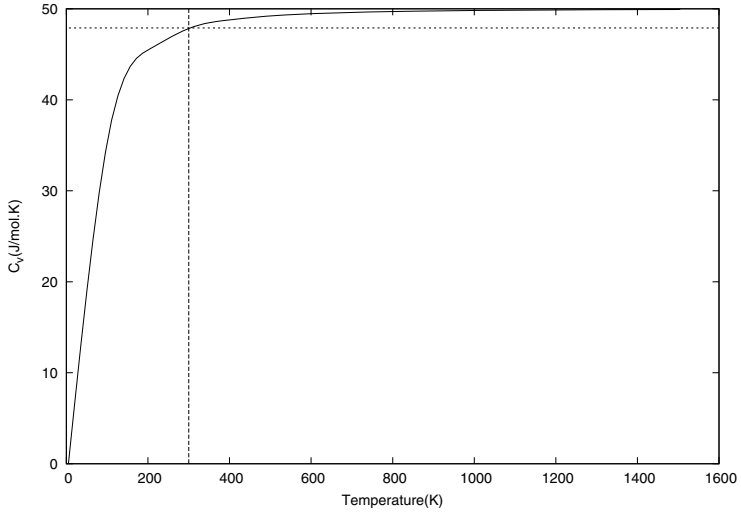


Fig. 6. The constant volume specific heat capacity of ScCd.

of $C_V = 50$ (J/mol · K). Our calculated specific heat capacity for ScCd of 47.9 (J/mol · K) at 300 K is relatively similar to the reported value of 47.78 (J/mol · K) for YCu.²⁴

4. Conclusions

We have performed electronic, lattice dynamics and thermodynamics properties calculations of rare-earth intermetallic ScCd alloy using the first-principle plane-wave

pseudopotential method. Our calculated lattice constant is in good agreement with both theoretical and experimental values. Finally, using the calculated phonon density of states, the thermodynamic properties are determined within the QHA and a value of 47.9 (J/mol · K) at 300 K for specific heat capacity of ScCd is predicted for the first time.

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