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Electronic and phonon properties of Sc-TM (TM = Ag, Cu, Pd, Rh, Ru) compounds

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ABSTRACT

A theoretical study of structural, electronic and phonon properties of the Sc-TM (TM = Ag, Cu, Pd, Rh, Ru) in the B2 phase was presented using the density functional theory within the generalized gradient approximation (GGA). The ground state quantities such as lattice parameter, bulk modulus and first-order pressure derivative of the bulk modulus, were evaluated. The calculated structural and electronic properties were in good agreement with previous theoretical and experimental results. The calculated total density of states showed that they were all metallic. Phonon-dispersion curves were obtained using the first principles linear-response approach of the density functional perturbation theory (DFPT).

1. Introduction

Scandium is the first member of transition metal series and does not have the unpaired 4f electrons unlike other rare-earth metals. The Sc atoms and their 3d electrons are barely important in the Sc-TM (transition metals) compounds. Sc-TM compounds are of interest for applications in the production of material for spacecraft and electronics because of their structural and physical properties [1]. Furthermore, some of the compounds are of interest for the high ductility and high fracture toughness at room temperature. Over the past decade, various studies [2–7] on structure, specific heat, susceptibility, and Knight shift of Sc-TM (TM = Ag, Cu, Pd, Rh, Ru) compounds in B2(CsCl) phase have been carried out. The electronic properties of B2 Sc-TM (TM = Ag, Cu, Pd, Rh, Ru) compounds have been studied by different experimental [3,6] and theoretical [4,8] groups. Experimental studies have shown that large d contributions to the density of states at the Fermi level originate from the Sc site in Sc-TM (TM = Ag, Cu, Pd). In contrast, in ScRu large d contributions to the Ru site are predominant at the Fermi level. ScRh has rather small d contributions but from sites, and the total density of states is smaller for this compound. Detailed theoretical studies of the electronic structure have also been made using a symmetrized version of relativistic Korringa–Kohn–Rostocker (RKKR) (Ref. [4]) and linearized muffin-tin-orbital (LMTO) (Ref. [8]) methods. Although considerable progress has been made in the theoretical description of the structural and electronic properties of Sc-TM (TM = Ag, Cu, Pd, Rh, Ru) compounds, many of their dynamic properties are still not well-established. The full phonon-dispersion curves are necessary for a microscopic understanding of the lattice dynamics. The knowledge of the phonon spectrum plays a significant role in determining various materials properties such as phase transition, thermodynamic stability, transport and thermal properties. The aim of this paper is to study the dynamic properties of Sc-TM compounds in their B2-phase using the density functional theory within the generalized gradient approximation (GGA).

2. Method

The calculations were performed using the Quantum-ESPRESSO program package [9]. The program was based on the density functional theory and plane-wave basis set. The electronic exchange correlation potential was calculated by the generalized gradient approximation (GGA) using the scheme of Perdew–Burke–Ernzerhof (PBE) [10]. Electron–ion interaction was represented by the ultrasoft Vanderbilt pseudopotential [11]. The plane-wave cutoff energy in the self-consistent field calculation was taken equal to 40 Ry. Brillouin-zone integrations were performed using a $10 \times 10 \times 10$ k-point mesh. Integration up to the Fermi surface

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was done using the smearing technique [12] with smearing parameter being 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 [13,14]. 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 can be evaluated by means of a Fourier deconvolution on this mesh.

3. Results

The ground state properties of Sc-TM were studied using their calculated total energies. The calculated total energies were fitted to the Murnaghan equation of state [15] to obtain equilibrium lattice constant and other structural properties. In Table 1, the equilibrium lattice constant (a), the static bulk modulus at zero pressure (B), the first order pressure of bulk modulus (dB/dP) are compared with experimental and previous theoretical results. It is found that current theoretical lattice constants for CsCl (B2) structure overestimate the experimental data by a maximum of 1%. This overestimation is typical from the implementation of GGA. The calculated structural properties are in excellent agreement with the experimental and theoretical data.

The electronic band structures of Sc-TM (TM = Ag, Cu, Pd, Rh, Ru) are obtained using the generalized gradient approximation (GGA) along the higher symmetry direction, and are shown in Fig. 1. The overall band profiles are quite similar to that of Sc-TM compounds, and are in good agreement with the earlier works [8,6,4]. This exhibits normal metallic behavior with bands crossing

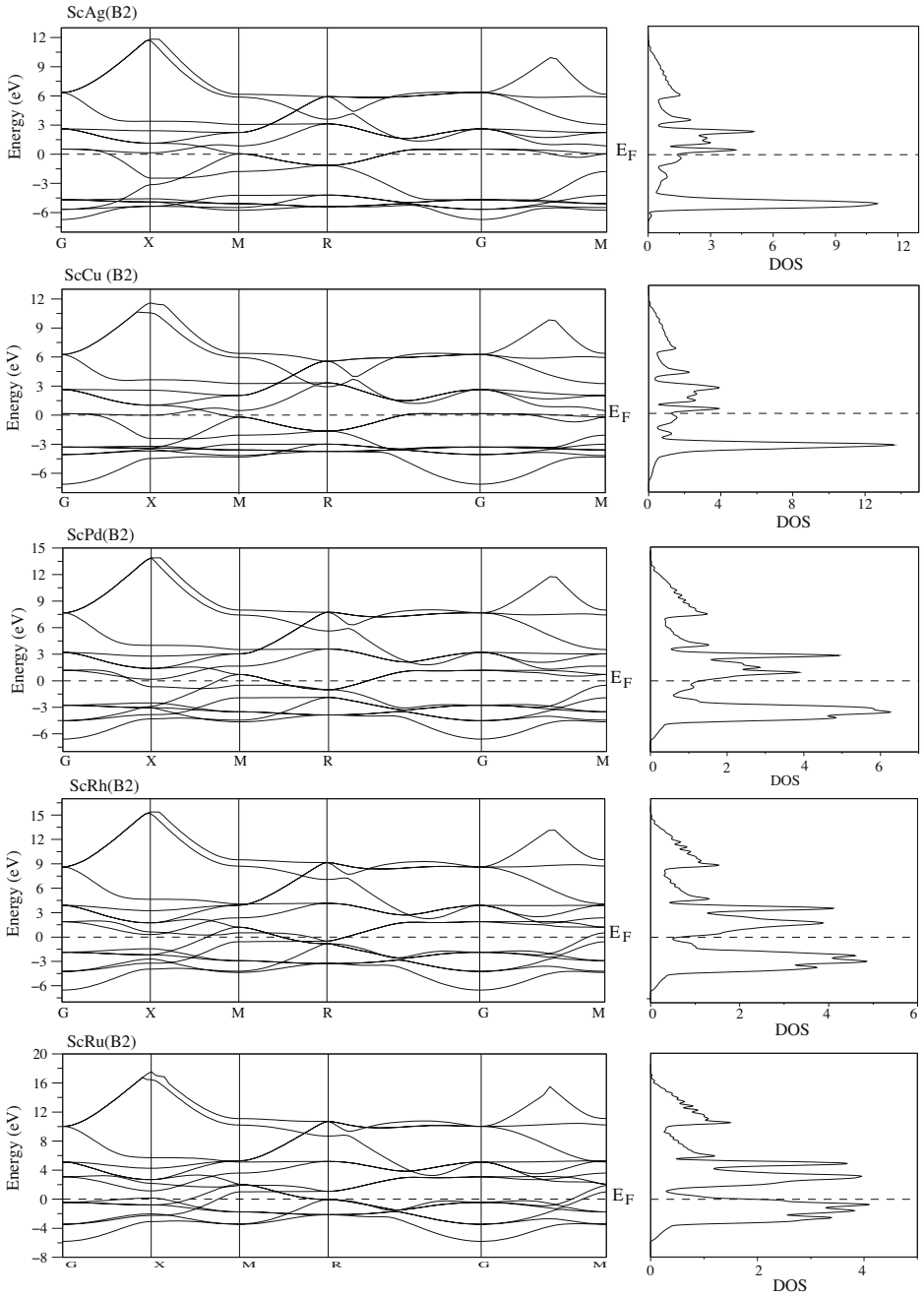

Fig. 1. Calculated electronic band structure and total density of states for Sc-TM (TM = Ag, Cu, Pd, Rh, Ru) in the B2 phase. The zero of energy is defined to be the energy at the maximum of the valence band.

the Fermi level along various directions, which results in a finite DOS at the Fermi level, as shown in Fig. 1 (left panel). To have an explicit understanding of interaction among different orbitals of atoms, the total and projected density of state (DOS) of Sc-TM were shown in Fig. 1 (right panel). The results indicate that the predominant contributions of the density of states at the Fermi level come from the Sc-3d state for Sc-TM (TM = Ag, Cu, Pd), while it originates from both Sc-3d and TM-4d (TM = Rh, Ru) state. There is one sharp peak, the lowest occupied-bands, for Sc-TM (TM = Ag, Cu, Pd). The peak is situated between −5.96 eV and −3.87 eV for ScAg (−6.82 eV to −2.43 eV for ScCu, −6.714 eV to −1.64 eV ScPd) and is due essentially to TM-d states. The lowest peaks below the Fermi level for ScRh and ScRu are quite dispersive.

The experimental data of phonon spectra of these materials are not yet available. Fig. 2 shows the phonon-dispersion curves and DOS for Sc-Tm (TM = Ag, Cu, Pd, Rh, Ru) in the B2 phase. The primitive cell of the Sc-TM contains two atoms, leading to a total 6 phonon branches. Because of the symmetry, the distinct number of phonon branches is reduced along the principal symmetry directions *G–X* and *M–R–G*. The sharp peak at the optical zone in the phonon density of state for all materials results from the flatness of the longitudinal optical branch along the *X–M–R*. For ScAg and ScPd, gaps exist between the acoustical and optical phonon branches. For Sc-TM (TM = Cu, Rh, Ru), there is no gap between the acoustical and optical phonon branches in Fig. 2, since there is a considerable overlap between the transverse optical (TO) and longitudinal acoustical (LA) phonon branches. However, along the *G–X* direction for Sc-TM (TM = Ag, Cu, Pd), the phonon calculations indicate that the frequencies of the twofold-degenerate transverse acoustical (TA) branches are very close than those of the longitudi-

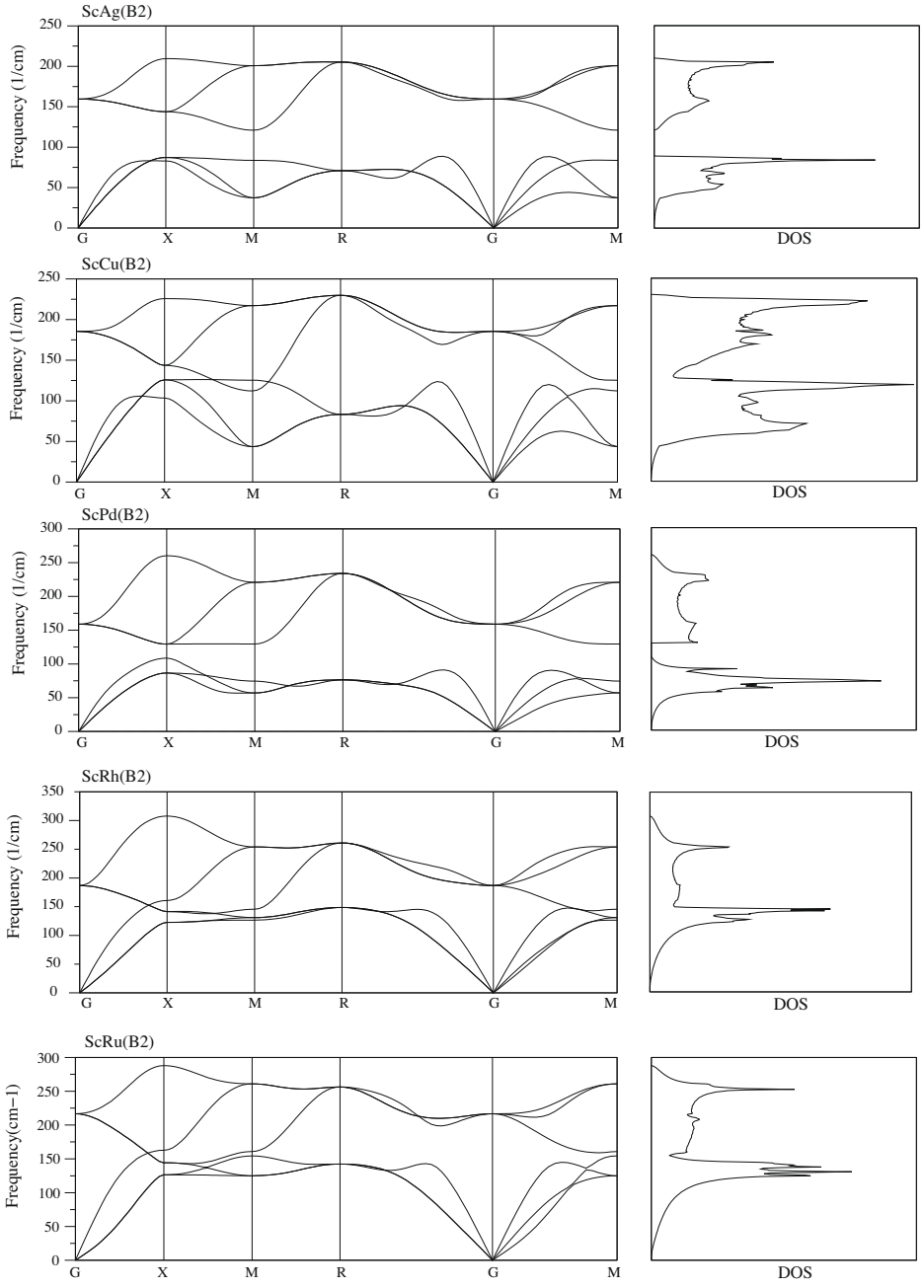

Fig. 2. Calculated phonon-dispersion curves and phonon densities of states for Sc-TM (TM = Ag, Cu, Pd, Rh, Ru) in the B2 phase along several lines of high symmetry in Brillouin zone.

Table 1
Calculated structural parameters of Sc-TM (TM = Ag, Cu, Pd, Rh, Ru) in CsCl (B2) structure.

Materials	Reference	a (au)	B (Mbar)	dB/dP
ScAg	This work	6.500	0.793	4.4
	Expt. [16]	6.448	–	–
	Expt. [17]	6.449	–	–
	Theory [8]	6.50	0.99	–
	Theory [19]	6.652	–	–
ScCu	This work	6.197	0.847	391
	Expt. [17]	6.155	–	–
	Theory [8]	6.153	–	–
	Theory [19]	6.192	–	–
ScPd	This work	6.260	1.115	4.30
	Expt. [16]	6.204	–	–
	Expt. [17]	6.206	–	–
	Theory [8]	6.290	1.480	–
	Theory [19]	6.262	–	–
ScRh	This work	6.103	1.613	6.53
	Expt. [16]	6.058	–	–
	Expt. [18]	6.060	–	–
	Theory [8]	6.150	1.69	–
	Theory [19]	6.158	–	–
ScRu	This work	6.055	1.450	4.77
	Expt. [16]	6.053	–	–
	Expt. [17]	6.054	–	–
	Theory [8]	6.160	1.680	–
	Theory [19]	6.215	–	–

nal branch. In the phonon density of states, the band gap between the acoustic and optic branches of ScAg (ScPd) is around 32.271 (20.309) cm^{-1}. The zone-center optic phonon modes of Sc-TM (TM = Ag, Cu, Pd, Rh, Ru) are calculated to be 159.10 cm^{-1}, 185.01 cm^{-1}, 158.70 cm^{-1}, 185.12 cm^{-1} and 215.82 cm^{-1}, respectively. The four distinct phonon energies are found to be 86.48 cm^{-1} (107.98) (LA), 82.39 cm^{-1} (85.57) (TA), 144.39 cm^{-1} (128.90) (TO), and 208.82 cm^{-1} (259.24) (LO) at the X point for ScAg (ScPd).

4. Conclusions

In this paper, structural, electronic and phonon properties of Sc-TM (TM = Ag, Cu, Pd, Rh, Ru) were studied. Pseudopotential method was used in the framework of the density functional theory (DFT) with the generalized gradient approximation (GGA). The structural properties including lattice constant, bulk modulus and first-order pressure derivative of the bulk modulus were calculated. The electronic structure calculation showed that all materials exhibit metallic character. The analysis of the electronic DOS also revealed that the Fermi energy is mainly composed of Sc-d states (ScAg, ScCu, ScPd); while major contributions are from Sc-3d and TM-d states. Moreover, the phonon dispersion and DOS in B2 phase have also been calculated using the density function perturbation method. From these results, though there is a gap of 32.271 (20.309) cm^{-1} in the acoustic and optic branches for ScAg (ScPd), no clear gap exists in the acoustic and optic branches for Sc-TM (TM = Cu, Rh, Ru).

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