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The effect of martensitic phase transition from cubic to tetragonal on the physical properties of V_3Si superconductor

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ABSTRACT

We report results of ab-initio studies for the structural, electronic, lattice dynamical and electron-phonon interaction properties of cubic and tetragonal phases of V_3Si by using the plane-wave pseudopotential method, the density-functional theory, and a linear-response technique. Our total energy results propose that the martensitic transition from cubic to a tetragonal variant of the A15 structure takes place with a very little change in the unit cell volume and total energy. Thus, the electronic and lattice dynamical properties of both phases look like similar to each other. Our electron-phonon interaction calculations reveal that the phonon properties of V lattice considerably enter into electron-phonon interaction calculations due to noteworthy presence of transition metal d electrons at the Fermi level. Using the calculated value of 1.15 for the average electron-phonon coupling parameter of both phases, the superconducting critical temperature and the electronic specific heat coefficient are evaluated to be 17.3 K and 54.5 $mJ/(\mathrm{mol}K^2)$, respectively, in gratifying agreement with their measured values of 17 K and 53 $mJ/(\mathrm{mol}K^2)$.

1. Introduction

In the last sixty years, A15 intermetallic compounds with the formula A_3B (where A is a transition metal and B is any element) have been very actively studied since many of these compounds display superconductivity at relatively high temperatures [1–61]. Interestingly, some, such as V_3Si, Nb_3Sn and Nb_3Al display the best combination of critical current density, superconducting temperature and critical magnetic field strength [16]. These are important Type II superconductors, with applications of high critical currents for high magnetic field operations. For example, these A15 superconductors can be largely utilized in nuclear magnetic resonance spectroscopy [50] and nuclear fusion reactions [58]. Despite being the first discovered A15 superconductor, V_3Si has received remarkable experimental attention in recent years [62–67]. In particular, this has been reported to be exhibit the superconducting transition temperature (T_c) of 17 K [62]. With this value of T_c, the electron-phonon coupling parameter (λ) has been estimated to be 1.07, confirming that V_3Si is a strongly coupled BCS superconductor [62].

On the theoretical side, noteworthy progress has been made towards the theoretical description of the electronic properties of the A15 compounds [21,22,68–74]. Klein et al. [21] have made self-consistent band structure calculations for V_3X and Nb_3X, X = Al, Ga, Si, Ge and Sn, using the augmented-plane wave (APW) method. This theoretical work indicated that all the investigated materials possess very flat bands near the Fermi level which lead to sharp peaks in their electronic density of states. The linear muffin tin orbital method and related canonical methods [22] are utilized to obtain self-consistent electronic energy band structures for twenty six A15 compounds. In this theoretical work, the electronic density of states for these compounds are presented and discussed. The fully relativistic full-potential linearized augmented-plane-wave (FP-LAPW) calculations have been made to investigate the electronic properties of A15 Nb-based intermetallics Nb_3Rh and Nb_3Ir [68]. This theoretical work [68] confirms that a feature common in the band structures of these A15 materials is the flat behavior of the bands near the Fermi level. Following this theoretical work [68], the FP-LAPW method [69] has been used to analyze the electronic properties of the A15 Nb-based intermetallics Nb_3(Os, Ir, Pt and Au). Although the T_c values for Nb_3Pt (T_c = 10.9 K) and Nb_3Au (T_c = 11.5 K) are much higher than the corresponding values for Nb_3Os (T_c = 0.94 K) and Nb_3Ir (T_c = 1.7 K), similar density of states at Fermi level ($N(E_F)$) have been reported for these four compounds in this

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theoretical work [69]. This observation suggests that the superconducting properties of these four compounds can not be only explained by studying their electronic properties since the electron-phonon coupling constant depends mainly on the phonon properties rather than on the electronic properties of a metal [75]. The FP-LAPW method [70] has been also utilized to calculate the electronic structure of the cubic and tetragonal phases of V_3Si since this A15 compound shows a structural phase transition from cubic to a tetragonal variant of the A15 structure at $T_m = 21.3$ K which is not very far from its transition temperature of 17 K [4,12,62]. This theoretical work [71] reports that the density of states at the Fermi level for both phases of V_3Si is dominated by the d states of V atoms. The band structure and Fermi surfaces of the superconductor A15 compounds V_3B and Nb_3B (B = Ga, Ge and Sn) are reported by utilizing the FP-LAPW method [71]. Although the V-based compounds possess a much lower T_c than the corresponding Nb-based compounds, the V-based compounds have larger density of states at the Fermi level than the corresponding Nb-based compounds [71]. Once again, this theoretical study indicates that phonons in these A15 compounds may play an important role in determining their superconducting properties. Band structure and Fermi surfaces of V_3Co, V_3Rh, V_3Ir and V_3Os have been calculated in the FP-LAPW calculations [72]. In this study it is observed that the density of states at the Fermi level does not change considerably between these materials, except for V_3Os, where a sharp peak is reported at the Fermi level [72]. Furthermore, recent theoretical studies [68–74] confirm that the physical mechanism of superconductivity in the A15 compounds can not be explained clearly by ignoring their phonon properties.

In this study, we present ab-initio numerical results for the structural, electronic, lattice dynamical and electron-phonon interaction properties of cubic and tetragonal phases of V_3Si by employing the plane-wave pseudopotential method, the density-functional theory, and a linear-response technique. The phonon dispersion relations and density of states for both phases are presented and discussed in detail. The linear response method and the Migdal-Eliashberg approach are utilized to obtain the electron-phonon matrix elements for both phases of V_3Si. Then, the Eliashberg spectral functions of these phases are evaluated using the calculated phonon density of states and electron-phonon matrix elements. A comparison of calculated phonon density of states and Eliashberg spectral functions for both phases is made to assess the phonon modes with dominant contribution to the electron-phonon coupling. By integrating the Eliashberg spectral function, the average electron-phonon coupling parameter, and using this the superconducting transition temperature is calculated and compared with the experimental measurement of around 17 K.

The paper is organized as follows. A brief explanation of the theoretical method has been provided in Section 2. The structural and electronic results are given in Subsection 3.1 while the electron-phonon interaction results are presented in Subsection 3.2. A summary of our study is made in Section 4.

2. Theory

In order to investigate the electronic properties of the cubic and tetragonal phases of V_3Si, we use the Quantum-Espresso (QE) program [76] which is based on the density functional theory (DFT), within the plane-wave pseudopotential method. The ultrasoft pseudopotentials of Vanderbilt-type [77] have been used to portray the Coulomb interaction between valence electrons and ionic core. The influences of exchange-correlation interaction are treated within the generalized gradient approximation (GGA) of Perdew, Burke and Ernzrhof (PBE) [78]. The cutoffs for wave functions and charge density are chosen to be 50 Ry and 500 Ry, respectively. Self-consistent solutions of the Kohn-Sham equations [79] are obtained by employing a set of Monkhorst-Pack special $\boldsymbol{k}$ points [80] within the irreducible part of the Brillouin zone. For structural properties of both phases, the Brillouin zone integration has been made using an (8×8×8) $\boldsymbol{k}$ mesh while a (32×32×32) $\boldsymbol{k}$ point mesh is utilized to obtain the electronic density of states for both phases.

The lattice dynamical properties have been investigated by using the linear response method [76]. The dynamical matrices for both phases have been calculated on (4×4×4) $\boldsymbol{q}$ mesh. Then, these dynamical matrices are Fourier-transformed to real space and thus the force constants are determined, which are utilized to obtain phonon frequencies for any chosen $\boldsymbol{q}$-points. Our electronic and vibrational results let us to study the electron-phonon interactions using the linear response method together with the Migdal-Eliashberg approach [81–86]. In this approach, the Eliashberg spectral function $\alpha^2F(\omega)$ is calculated from the below expression;

$$\alpha^2F(\omega) = \frac{1}{2\pi N(E_F)} \sum_{\boldsymbol{qj}} \frac{\gamma_{\boldsymbol{qj}}}{\hbar\omega_{\boldsymbol{qj}}} \delta(\omega - \omega_{\boldsymbol{qj}}), \tag{1}$$

while $N(E_F)$ denotes the electronic density of states at the Fermi level and $\gamma_{\boldsymbol{qj}}$ corresponds the phonon line-width for mode $\boldsymbol{q}$. Also the phonon line-width is determined from the following expression [76,85];

$$\gamma_{\boldsymbol{qj}} = 2\pi\omega_{\mathbf{qj}} \sum_{\boldsymbol{knm}} \left| g^{\boldsymbol{qj}}_{(\mathbf{k}+\mathbf{q})m;\mathbf{k}n} \right|^2 \delta(\varepsilon_{\mathbf{k}n} - \varepsilon_F)\delta(\varepsilon_{(\mathbf{k}+\mathbf{q})m} - \varepsilon_F), \tag{2}$$

where the $\varepsilon_{(\mathbf{k}+\mathbf{q})m}$ and $g^{\mathbf{qj}}_{(\mathbf{k}+\mathbf{q})m;\mathbf{k}n}$ denote the energies of bands and the electron-phonon matrix element, respectively [76,85]. Finally, the Eliashberg spectral function ($\alpha^2F(\omega)$ leads us to obtain the electron-phonon coupling parameter (λ) using the below equation;

$$\lambda = 2\int \frac{\alpha^2F(\omega)}{\omega} d\omega. \tag{3}$$

Finally, it is worthy to mention that a dense (32×32×32) $\boldsymbol{k}$ point mesh is utilized to make the summations in Eqs. (1) and (2).

3. Results

3.1. Structural and electronic properties

The cubic phase of V_3Si belongs to the space group $Pm\bar{3}n$. The Wyckoff positions of the atoms are: (1/4, 0, 1/2) for 6 V atoms and (2a) (0, 0, 0) for 2 Si atoms. As a consequence, the cubic phase of V_3Si is defined by only its lattice parameter a. Using the calculated total energy results, the equilibrium volume (V), the bulk modulus (B) and its pressure derivative (B′) are determined by fitting the numerical data to Murnaghan's equation of state [87]. Our calculated values are presented, together with previous experimental [44,46,52] and theoretical [70] results, in the first part of Table 1. In comparison with the experimental data [52], we find that the calculated cubic lattice constant is slightly smaller than the measured ones, by approximately 1.1%. This feature is not consistent with the usual result that the GGA lattice constants usually exceed the experimental values. However, it is worth mentioning that a previous GGA lattice constant value of 4.7180 Å is also slightly smaller than its experimental value [52] of 4.7530 Å. So far, no bulk modulus and its pressure derivative results are available to

Table 1
The calculated structural parameters for the cubic and tetragonal phases of V_3Si, and their comparison with previous experimental and theoretical results.

Phase	a(Å)	c(Å)	V (Å^3)	B(GPa)	B′
Cubic (present, GGA)	4.7007		103.87	189.6	4.08
Ref. [70] (GGA)	4.7180		105.02		
Experimental [44]	4.7246		105.46		
Experimental [46]	4.7251		105.49		
Experimental [52]	4.7530		107.37		
Tetragonal (present, GGA)	4.6990	4.7089	103.97	192.8	4.02
Ref. [70] (GGA)	4.7010	4.7110	104.42		
Experimental [52]	4.7150	4.7250	105.04		