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Electronic Structure of the A_3B Compounds: $A=Nb$; $B=Al, Ga, Ge, Sn$ and In

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The electronic structure of the A15 compounds A_3B $A=Nb$; $B=Al, Ga, Ge, Sn$ and In is studied by means of fully relativistic full-potential linearized augmented-plane wave (FP-LAPW) calculations within the formalism of the density functional theory. Band structures and densities of states are determined for all the studied compounds. From the calculations are obtained the theoretical lattice constants, the Fermi energy E_F , the density of states at the Fermi level $N(E_F)$ which is used to estimate the electronic specific heat coefficient γ and the electron-phonon coupling parameter λ for the Nb_3In compound. Generally, a good agreement between results of the calculations and experiments is found.

Keywords: Band structure; Density of states; Electronic properties; A-15; Superconductors; FP-LAPW

I. INTRODUCTION

Since the discovery of the superconductivity in compounds with the A-15 structure a challenge still pursued is how to raise the transition temperature T_c within this family. All A-15 phases exist over a range of composition near to the A_3B stoichiometric ratio (the Cr_3Si phase)[1–6]. The high-temperature superconductors of the A-15 structure are known to be strong electron-phonon coupling materials, in which the Fermi level lies in a peak in the density of states (DOS). A comprehensive review of lattice and electronic properties of these compounds have been written by Weger and Goldberg[7], and a review of the critical superconducting parameters has been done by Dew-Hughes[8]. The A atoms have fourteen nearest neighbors (CN14) arranged in a polyhedron, whereas the B atom have a smaller coordination number of 12 (CN12). The A atoms lie on closely spaced linear chains running along each of the three faces of the cubic cell formed by the background bcc lattice of B atoms.

A-15 compounds, such as Nb_3T , $T = Sn, Al, Ge$ and Ga are well known to have relatively high T_c and high critical field among the metallic superconductors. A-15 compound Nb_3Ga is a superconductor with high T_c above 20 K and high H_{c2} above 30 T at 4.2 K. A X-ray photoemission spectra study of the high T_c crystalline and the low T_c amorphous phases of Nb_3Ge indicates a change of the Nb-Ge bonding from covalent to metallic upon the amorphous to crystalline transition. The high T_c superconductivity of Nb_3Ge does not appear to stem only from an unusually high $N(E_F)$ but rather from another property such as a resonant enhancement of the electron-phonon coupling resulting from cation-anion hybridization at the Fermi level[9].

According to experimental results, the substitution of Al with other elements such as Ge, Ga, Be, B and Cu leads to an increase of T_c of the Nb_3Al compound, being that, Ge and Si are especially good at stabilizing the A-15 phase. Some efforts have been concentrated on the addition of Ge, and it is known that at some point there must be a maximum T_c for the $Nb_3(Al, Ge)$ whilst still retaining its high current capability. Otherwise, it still would seem desirable to support the empirical crystal-chemical rules with energetic arguments based on analyzes of the electronic structure of these compounds.

In this contribution is employed the FP-LAPW method[10] to determine the band structure and densities of states of the A_3B compounds: $A=Nb$; $B=Al, Ga, Ge, Sn$ and In to study the electronic properties of these materials. To the best of my knowledge this is the first study on the Nb_3In compound. A minimization of the total binding energy with volume was performed in order to determine the theoretical equilibrium lattice constants. Next is briefly described the calculational procedure.

II. METHOD

In this study the fully relativistic full-potential linearized augmented-plane wave (FP-LAPW) calculations are done within the density functional theory with the generalized gradient approximation (GGA) for the exchange and correlation potentials. In order to separate core and valence states a energy threshold of -6.0 Ry is adopted. The scalar relativistic basis functions are expanded in combinations of spherical harmonics with angular momenta up to $l_{max} = 10$ inside non-overlapping MuffinTin (MT) spheres surrounding the atomic sites. The sphere radii are 2.4 and 2.3 for nontransition elements and Nb, respectively. The plane-wave cut-off for the basis functions is $R_{MT}K_{max} = 9$. A expansion in a Fourier series was used in the interstitial region where plane waves with reciprocal lattice vectors up to $G_{max} = 14$ were included for the GGA.

III. RESULTS AND DISCUSSION

The Brillouin zone integration was provided by a interpolation method in the modified version of the linear tetrahedron method, which is free of adjustable parameters and it should converge to the correct results in the limit of infinitely dense k mesh. In the mesh for the integration procedure 4500 k-points were used, and about 168 inequivalent k-points in the irreducible part of the Brillouin zone were taken. A energy criterion of 0.1 mRy was taken to achieve convergence. A minimization of the binding energy was carried out with variations in the cubic unit cell volume, where the Murnaghan[11]

TABLE I: Experimental[1–3] and calculated lattice constants, bulk moduli, calculated DOS at the Fermi level ($N(E_F)$) and Fermi energy(E_F), experimental T_c [19, 20] and λ [14, 21], calculated and experimental γ .

	lattice calc. (Å)	constant expt. (Å)	B (GPa)	$N(E_F)$ ($\frac{\text{states}}{\text{eV.cell}}$)	E_F (eV)	T_c (K)	λ	γ calc. ($\frac{\text{mJ}}{\text{K}^2.\text{g-at}}$)	expt.
Nb ₃ Al	5.210	5.187	156.33	16.60	9.87	18.8	1.59	12.67	8.72
Nb ₃ Ga	5.200	5.171	156.93	18.23	10.12	20.2	1.74	14.72	
Nb ₃ Ge	5.185	5.166	168.04	14.40	10.40	23.6	1.80	11.88	
Nb ₃ In	5.323	5.303	152.71	18.10	10.04	9.2		13.39	
Nb ₃ Sn	5.336	5.289	160.51	21.34	10.50	18.9	1.78	17.48	14.3

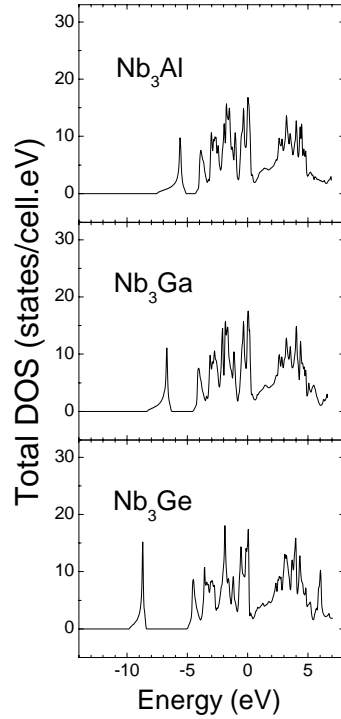


FIG. 1: Total densities of states. The Fermi level is shifted to the origin.

equation of state was used to plot the energy vs volume. The determined theoretical equilibrium lattice spacing are listed in Table I together with the experimental values. It can be seen that the calculated values for the lattice constants of the studied compounds are larger than the experimental values, as is usually obtained with GGA. The best agreement between calculated and experimental lattice constant was observed for Nb₃Ge. In Table I is also listed the bulk moduli for all studied compounds. The largest value belongs to Nb₃Ge, and the smallest one to Nb₃In.

In Figs. 1-2 are shown the total DOS for these A_3B -type compounds. Similar topological features are observed in these diagrams. The separate peak which appears at lower energies (-5.6 eV for Nb₃Al, -6.6 eV for Nb₃Ga, -8.9 eV for Nb₃Ge,

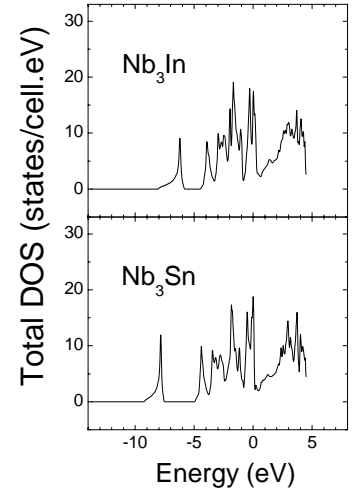


FIG. 2: Total densities of states. The Fermi level is shifted to the origin.

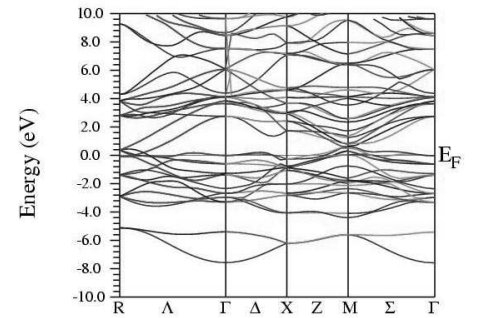
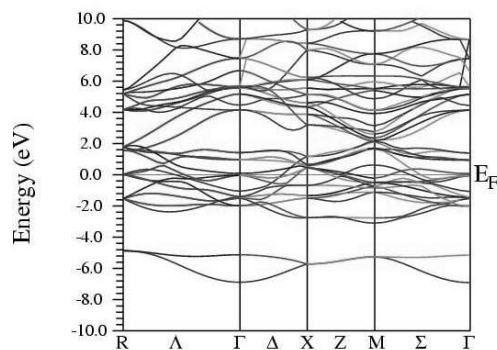
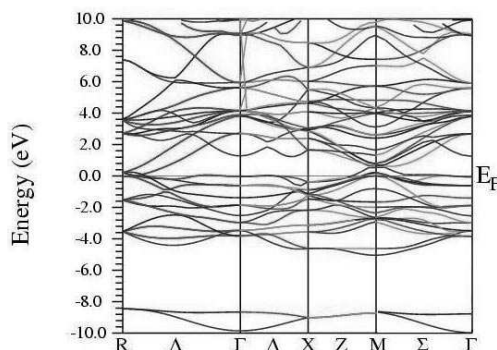


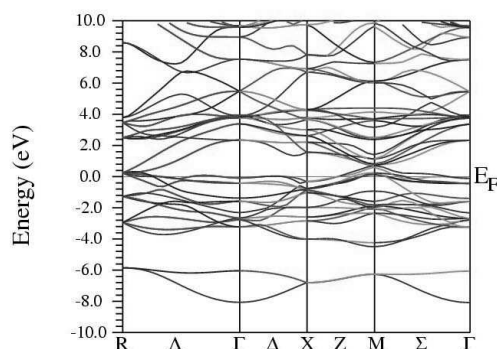
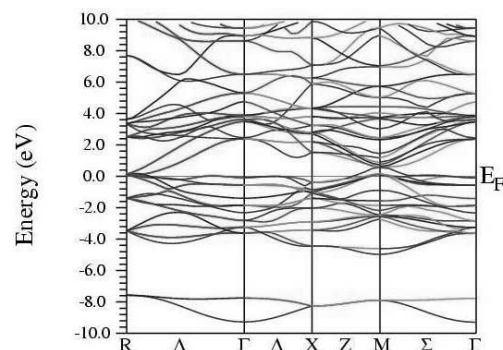
FIG. 3: Band structure of Nb₃Al along symmetry directions. The Fermi level has been placed at the zero of energy.

-6.2 eV for Nb₃In and -7.9 eV for Nb₃Sn), corresponds to the s-electrons of the B atoms. The separation increases with increasing Z, as a result of the electronic filling up of the bands. A tendency for the formation of a small gap can be seen just above the Fermi level, which separates the d states into bonding and antibonding bands. This terminology derives from

FIG. 4: Band structure of Nb₃Ga along symmetry directions.FIG. 5: Band structure of Nb₃Ge along symmetry directions.

the effect of the reinforcement or cancellation on the total energy of the molecular orbital, which leads to a corresponding increase or decrease in electron density in regions of space equidistant from each nucleus. The result is that the energy of the molecular orbital is lowered or raised, relative to the combined energy of the two atomic orbitals depending on whether the molecular orbital is bonding or antibonding. From Nb₃Al to Nb₃Ge in Fig. 1 one can observe how the weight of the DOS is being shifted towards lower energies.

The Brillouin zone for the cubic A-15 structure is a cube

FIG. 6: Band structure of Nb₃In along symmetry directions.FIG. 7: Band structure of Nb₃Sn along symmetry directions.

with symmetry points (in units of π/a) $\Gamma = (0,0,0)$, $X = (1,0,0)$, $M = (1,1,0)$ and $R = (1,1,1)$; the symmetry lines are $\Delta = (\xi, 0, 0)$, $\Sigma = (\xi, \xi, 0)$, $\Lambda = (\xi, \xi, \xi)$, $Z = (1, \xi, 0)$, $S = (1, \xi, \xi)$, and $T = (1, 11, \xi)$, with $0 < \xi < 1$. The band structures of the studied compounds are presented in Figs. 3-7. The lowest band observed at the zone center (Γ) corresponds to the s,p electrons of the nontransition elements. Just above the Fermi level the bands arise mostly from the p-states of Al \rightarrow In. At higher energies there is a hybridization of these states with the Nb d states. From Figs. 3-7 a feature observed from Nb₃Al to Nb₃Sn is that, around the Fermi level, there is a tendency of the bands to become more flatter, for both bonding and antibonding orbitals. Moreover, the extreme flatness of the bonding subbands near the Fermi level at the zone center can be seen in Fig. 7 for the Nb₃Sn compound. The features pointed out by the present calculations are in good agreement with results of earlier calculations on the Nb₃Al, Ga, Ge and Sn compounds[12–17]. The results for Nb₃In are original.

The total DOS at the Fermi level $N(E_F)$ and the Fermi energy for these compounds are listed in Table I. The highest $N(E_F)$ in this series was observed for Nb₃Sn, whereas the smallest value was obtained for Nb₃Ge, which has the highest T_c value. As mentioned above, one has argued that the high T_c superconductivity of Nb₃Ge does not appear to stem only from a high $N(E_F)$ but rather from another property such as a resonant enhancement of the electron-phonon coupling parameter λ resulting from cation-anion hybridization at the Fermi level[9]. The present calculations corroborates this description. It is noteworthy that the Fermi level was observed to be located at about the same energy for these compounds, as is seen in Table I. Despite this, quite different values are observed for the critical temperatures of Nb₃In and Nb₃Sn, although the difference between the $N(E_F)$ values are $\approx 15\%$ for them. The experimental values calorimetrically determined[18] of the electron-phonon coupling parameter λ are also shown in Table I. Apart from the result for Nb₃Al, no large differences are observed this quantity for all studied compounds. No report has been found in the literature for λ of Nb₃In.

Junod *et al.*[18] have pointed out that the microscopic parameters describing superconductivity of the Nb-based A15 compounds follow a rather simple tendency which can be ap-

proximately expressed by $\lambda \simeq 0.175\eta$ (eV/Å²), where η is a electronic parameter which is proportional to $N(E_F)$ for the Nb-based compounds. This result has been interpreted as reflecting the picture of superconductivity determined by the Nb atoms placed on the chain sites. From Table I it can be observed that, for the Nb₃Al and Nb₃Ga compounds, a similar value (0.096 eV.cell/states) is obtained for the ratio $\lambda/N(E_F)$; for Nb₃Sn, this ratio yields a numerical result 0.083 eV.cell/states. Therefore, if one considers that a similar result should be expected for Nb₃In, a rough estimate for the electron-phonon coupling parameter gives $\lambda \approx 1.51$. This result put Nb₃In within the same range of the so-called strong electron-phonon coupling materials ($\lambda \gtrsim 1.5$), as the other compounds in Table I. Nevertheless, the somewhat lower T_c value of Nb₃In indicates that the Debye Θ for the characteristic phonon frequency might be in the source of this result.

The electronic heat-capacity coefficient γ is proportional to the electronic density of states at the Fermi energy $N(E_F)$ times the enhancement factor $(1+\lambda)$ from the electron-phonon interaction as $\gamma = 2\pi^2 k_B^2 (1+\lambda)N(E_F)/3$. Hence, a rough estimate of this quantity can be obtained from the calculated values of $N(E_F)$ and with the available experimental results for λ . The corresponding values are shown in Table I. As seen the Nb₃In compound possess $N(E_F)$, γ and E_F values which are comparable to those of Nb₃Ga, and despite its estimated λ value put him within the strong-coupling limit, its T_c value is only modest, an effect which might be arising from a low phonon frequency, or equivalently, a small Debye temperature. Although the calculated γ values are larger than the experimental ones, they seemingly are describing the correct trends. In spite of the fact that the influence of spin fluctuations has not been taken into account in the calculations its

effect are not expect to be overwhelming for Nb-based A₃B compounds.

Finally, in the current work the reliability of the results is based on the implicit assumption of validity of the adiabatic Born-Oppenheimer principle, as it is a large part of the common wisdom about electron-phonon effects in solids. Although the validity of the adiabatic hypothesis is challenged in several families of recently discovered small-Fermi-energy compounds, including high- T_c superconductors, organic materials and others, in conventional metals where the Fermi energy is the highest energy scale of the system, the effects of the breakdown of the adiabatic Born-Oppenheimer assumption are minimized. In this case the nuclei are so much more massive than the electrons that the characteristic energy scale of the phonon spectrum of these compounds is much lower than the electronic Fermi energy, which rules the electron dynamics. In these compounds the phonon frequency is small enough to be comparable with the Fermi energy, and in such a situation the dynamics of the electronic and lattice degrees of freedom are by no means comparable.

IV. SUMMARY

The electronic structure of Nb₃Al, Nb₃Ga, Nb₃Ge, Nb₃Sn and Nb₃In was studied with density functional full-potential first-principles calculations. Theoretical values for the equilibrium lattice constants of these compounds were obtained. An attempt to extract quantities related to superconductivity from it was undertaken. The results obtained generally agree well with experimental values. An estimation of the electron-phonon coupling parameter λ and of the electronic heat-capacity coefficient γ were deduced for the Nb₃In compound.

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