Calculations of the superconducting properties of scandium under high pressure

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In recent years the number of elements in the periodic table that become superconductors under pressure has increased to the point that this is no longer considered a rare phenomenon. Recent experiments suggest that scandium reaches a superconducting temperature of 9 K at a pressure of 74 GPa. Using the results of self-consistent band theory calculations, the McMillan theory, and the rigid-muffin-tin approximation, we have calculated the electron-phonon coupling and T_c for scandium, in good agreement with experiment.

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Recent experimental and theoretical works have established that several metals that are not superconducting under normal conditions become superconducting under high pressures.[1,2] This phenomenon has been observed in the alkali metals Li and Cs and proposed in K and Rb.[3–5] The effect has also been found in Y, Sc, Ca, Se and others.

Recently, Hamlin and Schilling[6] extended the experimental measurement of the pressure dependence of the superconducting transition temperature T_c in scandium, finding that at 74 GPa the transition temperature rises to 9 K. As in our recent papers[3,4,7] we combine the McMillan theory,[8] the rigid-muffin-tin approximation (RMTA) of Gaspari and Gyorffy,[9] and the results of electronic structure calculations to obtain a quantitative evaluation of T_c within the electron-phonon interaction mechanism.

In our model we make the approximation of performing our calculations as a function of pressure in the fcc lattice. All of the elements in the IIIA column of the periodic table undergo a sequence of structural phase transitions under pressure. The heavier elements follow the sequence[10] hcp$\rightarrow\alpha$-Sm$\rightarrow$dhcp$\rightarrow$fcc or trigonal. Scandium, however, follows a different sequence, transforming from Sc-I (hcp) through Sc-V at pressures of 23, 104, 140, and 240 GPa.[11] Most of these structures are poorly characterized.

The highest-pressure Sc-V structure[11] is described as a helical chain structure. Of the mid-pressure structures, only the Sc-II structure has been extensively studied, with a variety of results: the structure has variously been described as β-Np,[12] tetragonal,[13] distorted body-centered cubic,[14] and, most recently, a body-centered host structure interlinked with an incommensurate "guest" structure consisting of Sc chains.[15,16] Even here there is disagreement, with one analysis of the x-ray diffraction profile indicating that the atoms in the chain are much closer to each other than are the atoms in the host,[15] and another[16] showing comparable in-chain and host-host interatomic distances. Recent first-principles calculations,[17] approximating the incommensurate structure by a large supercell, favor the latter structure.[16]

Computation of a superconducting transition temperature in this Sc-II structure would be extremely difficult. However, first-principles calculations show that the electronic density of states (DOS) of the proposed Sc-II structure[16] is very similar to the DOS of a fcc scandium crystal (Fig. 4 of Ref. 17.) Accordingly, in this work we will approximate the Sc-II structure by an fcc scandium crystal. An indication that this is a reasonable approximation is given in Fig. 1, which compares the DOS of fcc scandium to that of hcp scandium volume $V=90$ (a.u.)^3/atom. The differences are minimal, especially near the Fermi level.

We have used the augmented plane wave (APW) method to generate the band structure and total energy of Sc for lattice constants ranging from $a=7$ to 8.6 a.u. with a calculated equilibrium value of 8.45 a.u., determined from a Birch fit[18] of energy versus volume. The pressure versus volume graph taken from this fit, shown in Fig. 2, covers the range of the experiments. Figure 3 shows the density of states $N(E_F)$ at the Fermi level as a function of pressure. We note a steady decrease of $N(E_F)$ as the pressure increases. Following McMillan, we have calculated the electron-phonon coupling with the formula

$$\lambda = \frac{\eta}{M\langle\omega^2\rangle}. \tag{1}$$

The quantity

$$\eta = N(E_F)\langle I^2\rangle, \tag{2}$$

which is often referred to as the Hopfield parameter, was calculated using the RMTA. This quantity, as shown in Fig. 3, increases with increasing pressure, in contrast with $N(E_F)$, indicating a rapid increase of the electron-ion matrix element

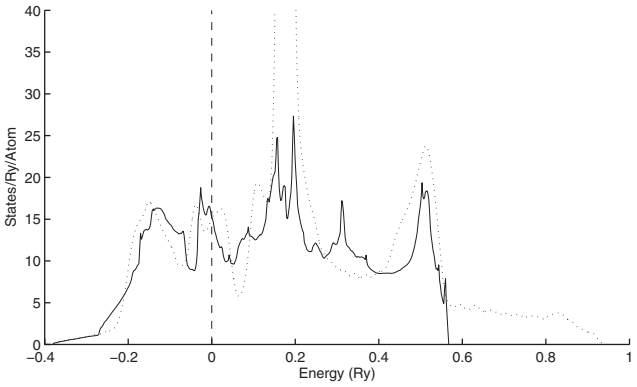

FIG. 1. Total density of states for fcc (solid line) and hcp (dotted line) scandium at an equivalent volume of 90 $(a.u.)^3$ per atom. The Fermi level is at 0 Ry.

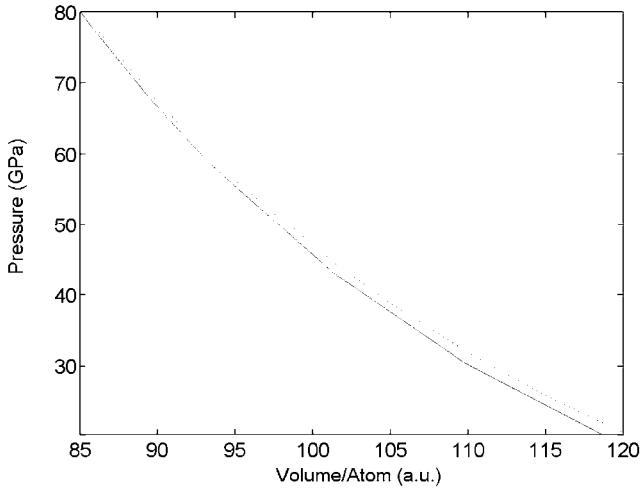

FIG. 2. Pressure versus volume for fcc (solid line) and hcp (dotted line) scandium from first-principles APW calculations.

$\langle I^2 \rangle$. The matrix element $\langle I^2 \rangle$ is calculated from the angular momentum components of the DOS, the scattering phase shifts, and the free-scatterer DOS, all evaluated at E_F. The detailed procedure followed is given in Ref. 7.

For the determination of the average phonon frequency $\langle \omega^2 \rangle$ we use the Debye-like approximation

$$\langle \omega^2 \rangle = \frac{1}{2}\theta_D^2, \tag{3}$$

where the volume variation of $\langle \omega^2 \rangle$ is found by taking[19]

$$\langle \omega^2 \rangle = cB(V)V^{1/2}. \tag{4}$$

We determine the constant of proportionality c using the measured values of the Debye temperature θ_D and the bulk modulus B. We find this approach to be more reliable than the formula for θ_D proposed by Moruzzi *et al.*,[20] which gives

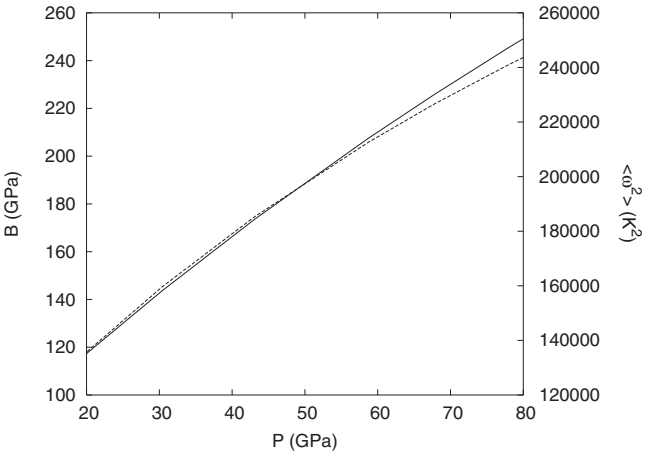

FIG. 4. Bulk modulus (solid line, left axis) and average phonon frequency $\langle \omega^2 \rangle$ (dashed line, right axis) for fcc scandium.

θ_D=254 K, seriously underestimating the measured value of 360 K.

In Fig. 4 we display the pressure variation of our calculated B and $\langle \omega^2 \rangle$. It is noted that $\langle \omega^2 \rangle$ increases monotonically with P. Therefore, the simultaneous increase of η and $\langle \omega^2 \rangle$ with P makes the prediction of the pressure dependence of λ nonobvious. However, it appears that the increase of the numerator of η dominates, so λ increases with P as shown in Fig. 5. This increase of λ from 0.4 to about 0.6 signals the probability of the increase of the superconducting transition temperature T_c.

To complete our calculation we used the McMillan equation for T_c. Our calculated results and the experimental values[6] are shown in Fig. 6, plotted as functions of pressure. The agreement is very good. In using the McMillan equation for T_c, we employed the following formula suggested by Bennemann and Garland[21] to determine the Coulomb pseudopotential:

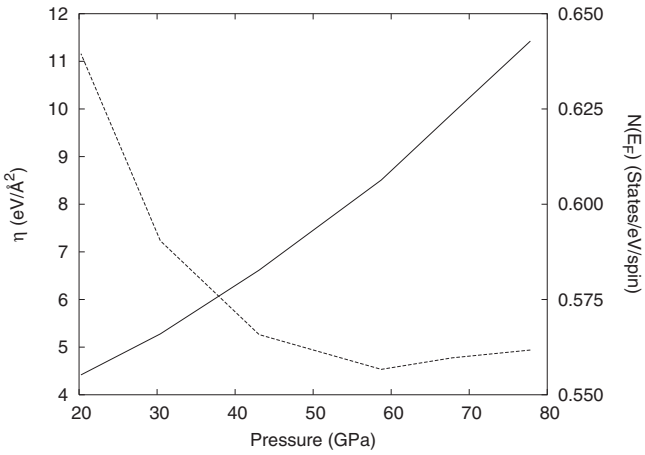

FIG. 3. Hopfield parameter η (2) (left axis, solid line) and electronic density of states at the Fermi level (right axis, dashed line) versus pressure for fcc scandium.

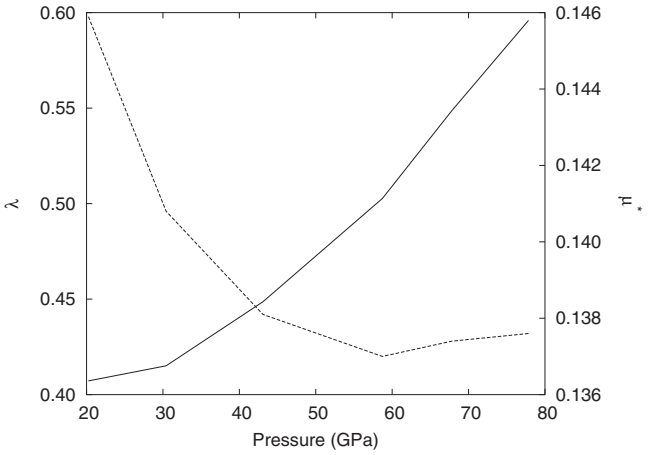

FIG. 5. Electron-phonon coupling parameter λ (1) (left axis, solid line) and Bennemann-Garland Coulomb pseudopotential μ^* (5) (right axis, dashed line) for fcc scandium.

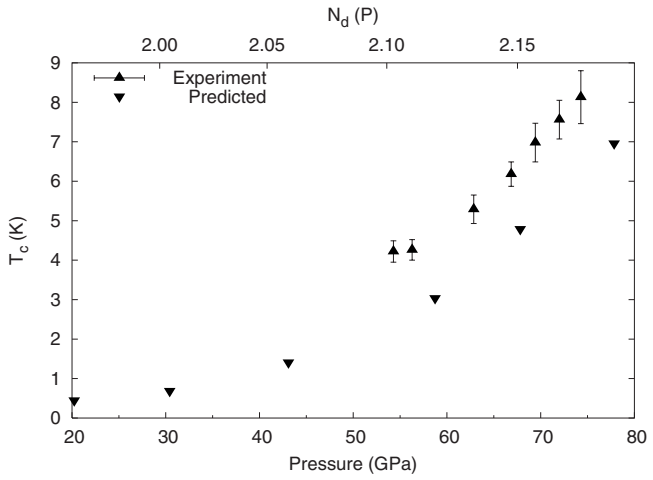

FIG. 6. T_c versus pressure and the number of d electrons for fcc scandium. The experimental values and error bars are from Ref. 6.

$$\mu^* = \frac{0.26N(E_F)}{1+N(E_F)}, \tag{5}$$

where $N(E_F)$ is now the total DOS at E_F for both spins (i.e., twice the value shown in Fig. 3), expressed in units of states/eV. This gives a variation of μ^* from 0.146 at 20 GPa to about 0.1376 at 80 GPa, as shown in Fig. 5. It should be stated that if we had chosen a constant $\mu^*=0.13$ our results for T_c would differ by less than 0.5 K over the pressure range, and the overall trend would still be consistent with that of experiment.

In Fig. 6 we also show the variation of T_c with the number of d electrons in the valence band. This gives a quantitative account of the increase of the number of d electrons as the material is compressed. This compression has often been stated as the cause of superconductivity in such systems.[6] Reading from the graph, we find that the number of d electrons has a value of 1.95 at $P=20$ GPa and approaches the value of 2.2 at $P=80$ GPa, while at equilibrium ($P=0$) there are 1.8 d electrons.

In conclusion, the McMillan theory, coupled with the RMTA and the proportionality of $\langle\omega^2\rangle$ to the bulk modulus as evaluated in our total energy calculations, provides an accurate account of the measured T_c as a function of pressure. It should be stressed that this approach is very efficient and computationally much faster than calculating a complete phonon spectrum. We believe that it is suitable for predicting new superconductors by quickly surveying different classes of materials.

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