Predicted Superconductive Properties of Lithium under Pressure

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A superconducting state of lithium has not been found at ambient pressure, but the present theoretical work shows that high values of the critical temperature, T_c, may be expected for some high-pressure phases. *Ab initio* electronic structure calculations are used to calculate the electron-phonon coupling in a "rigid-muffin-tin approximation," and estimates using McMillan's formula suggest that under increasing pressure T_c in fcc-Li may reach 50–70 K before transitions occur to the rhombohedral ($hR1$-Li) and subsequently to the $cI16$-Li phase near 40 GPa. In $cI16$-Li T_c may reach a maximum in the range 60–80 K.

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Lithium is often considered to be a "simple" metal in the sense that it assumes a high-symmetry structure (bcc), and its electronic properties are well described within a nearly free electron model. However, the complexity of the various structures of high-pressure Li phases [1–4] and the martensitic transformation to the $9R$ structure observed [5–8] in the vicinity of 75 K indicate strong electron-lattice coupling. In view of this it seemed natural to expect that Li might exhibit superconductivity, and *ab initio* calculations of the electron-phonon coupling, Ref. [9] and references therein, did predict the coupling constant λ to be so large that Li (bcc as well as $9R$) should be superconducting below $\approx$1 K at ambient pressure. Experiments [7], however, had determined the upper limit on T_c in Li to be 6 mK, and Lang *et al.* [10] found no evidence of a Meissner effect in Li down to 4 mK. Jarlborg [11] suggested that the calculated λ values are correct, but that spin fluctuations [12] suppress superconductivity in Li at zero pressure. Whereas λ itself was found to increase with pressure (P), the spin fluctuation contribution is essentially volume independent [11], and therefore the calculations (bcc-Li and hcp-Li) showed [11] that T_c increases with P. At $P \approx 22$ GPa, Jarlborg found $T_c = 2.4$ K. Measurements performed by Lin and Dunn [13] showed that the electrical resistivity of Li at this pressure exhibits a sharp drop around 7 K. The authors associated [13] this with a phase transition, "possibly a superconducting transition."

Recent experiments have shown [2] that Li near 39 GPa transforms from the high-pressure face-centered cubic phase, via a primitive rhombohedral modification, to a cubic polymorph with 16 atoms in the cubic cell. This cubic structure ($cI16$), so far observed only for Li, can be viewed as a $2 \times 2 \times 2$ bcc supercell with displaced atoms (space group 220) occupying the Wyckoff $16c$ positions. The experimental study did not include pressures above $\approx$50 GPa, and therefore the stability range of $cI16$-Li is so far unknown. According to the calculations [2], $cI16$-Li becomes identical to a BC8 structure relaxed to space group 230 at 165 GPa before it transforms to a "paired" *cmca* structure ($oC8$) (see also Ref. [1], which mentions possible superconductivity in $oC8$-Li). The structural transformations are associated with a softening of the lattice caused by the pressure-induced electronic $s \rightarrow p$ transition. This effect is similar to the softening [14] in the heavy alkali metals, where it is caused by an $s \rightarrow d$ transition [15,16]. For that reason it was suggested [2] that the superconductive properties of Li around $P = 40$ GPa should be examined. No experimental data are available, but theoretical estimates of T_c within the framework of strong-coupling theory are presented here.

The calculations use a modified McMillan equation [17],

$$T_c = \frac{\langle\omega\rangle}{1.2} \exp\left\{\frac{-1.04(1 + \lambda + \lambda_{\rm sp})}{\lambda - \mu^*(1 + 0.62\lambda) - \lambda_{\rm sp}}\right\}, \quad (1)$$

where $\lambda_{\rm sp}$ represents contributions from the paramagnons (spin fluctuations) [11,12]. It is assumed to be volume independent, and its order of magnitude is 0.1. The Coulomb coupling constant μ^* is here taken to be a constant (0.13). The prefactor in Eq. (1) contains $\langle\omega\rangle$, the average phonon energy, and it is sometimes replaced by a constant times the Debye energy. The electron-phonon coupling parameter, λ, is related [17] to the Hopfield parameter, η, through

$$\lambda = \frac{\eta}{M\langle\omega^2\rangle}, \quad (2)$$

where M is the atomic mass. The Hopfield parameter contains the electron-phonon matrix elements. We calculate here a spherically averaged value using the *rigid-muffin-tin* approximation (RMTA) [18,19].

Before discussing some details of the calculations, we show in Fig. 1 the estimated T_c values for fcc-Li. The curves are labeled by the values of $\lambda_{\rm sp}$. As found earlier [9,11] for bcc-Li, $h9R$-Li, and hcp-Li we also find fcc-Li to have T_c much higher (0.76 K) than the experimental upper limit (4 mK) at $P = 0$ if the spin-fluctuation term is omitted. With the value $\lambda_{\rm sp} = 0.1$ preferred in Refs. [9,11] we

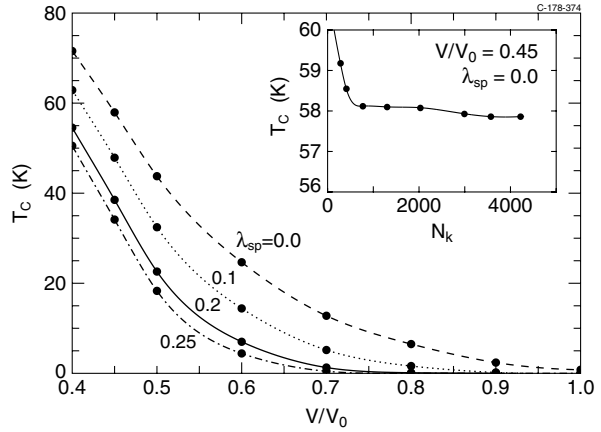

FIG. 1. T_c calculated for fcc-Li vs volume for various choices of λ_{sp}. V_0 is the equilibrium volume of bcc-Li, 21.273 Å^3/atom. An example of a convergence test is shown as an inset. N_k is the number of k points in the irreducible (1/48) Brillouin zone.

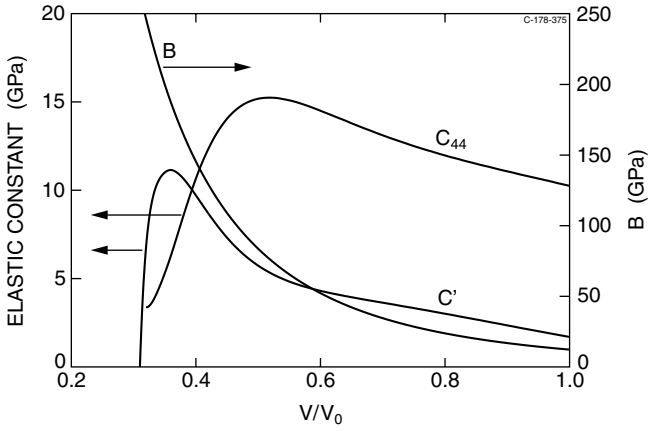

FIG. 2. Calculated bulk modulus, B, and elastic constants, $C' = (C_{11} - C_{12})/2$, and C_{44}, versus V/V_0, for fcc-Li.

find that T_c can increase with P from a few mK to ≈60 K before the lattice distorts into the rhombohedral structure and then to $cI16$.

The volume (V) dependence predicted for T_c depends critically on the scaling of $\langle\omega\rangle$ and $\langle\omega^2\rangle$ with V. Often experiments or calculations at a reference volume, usually the $P = 0$ value, is scaled with V and the bulk modulus, B. Skriver and Mertig [19] used

$$\omega^2 \sim B(P)V^{1/2}, \tag{3}$$

and a similar scaling was used by Jarlborg [with the more usual exponent 1/3 instead of 1/2 in Eq. (3), though] [11]. This method cannot be applied to compressed lithium, where it leads to overestimates of $\langle\omega\rangle$ and $\langle\omega^2\rangle$, in particular in the regime near the phase transitions ($P \approx 40$ GPa, $V/V_0 \approx 0.4$, V_0 being the volume of bcc-Li at $P = 0$). The prefactor [Eq. (1)] is overestimated by this B scaling, but since λ [Eq. (2)] simultaneously is underestimated for small volumes, the resulting T_c will be too small. More accurate calculations of the phonon characteristics are needed, and we applied *ab initio* electronic total-energy calculations to derive the elastic and vibrational properties. The electronic structure properties used in the calculations of η were calculated [2] within the density functional theory using the generalized gradient approach [20], and we used the full-potential [21] linear muffin-tin-orbital (LMTO) method [22]. The Li-1s states were treated as "local orbitals" [23]. Three sets ("triple-κ basis" [21]) of LMTO envelopes were used, and in each channel s-, p-, d-, and f-partial waves were included. The calculations of the electron-phonon matrix elements require a careful mapping of the Fermi surface, and also reliable calculations of structural energy differences, elastic constants, and phonon frequencies require accurate k-space sampling. The inset of Fig. 1 shows an example of how the calculated T_c varies with the number of k points. All calculations reported here used a density in k space corresponding to $N_k = 2992$ in the irreducible 1/48 zone (16 416 points in the full fcc Brillouin zone). This was simultaneously sufficient to ensure convergence of the total energies and the derived properties. Total energies were used to derive structural energy differences, P-V relations, elastic shear constants, etc. Figure 2 shows the volume variation of the bulk modulus, B, and the elastic constants, C' and C_{44}, for fcc-Li. The bulk modulus increases rapidly with P, whereas C' and C_{44} behave quite differently. Their increase under compression is much more modest, and for volumes below $0.37V_0$ they go negative. At these volumes, though, the transitions to $hR1$-Li and $cI16$ have taken place [2].

First we tried to take the softening into account in the phonon calculations by application of the method used for cesium in Ref. [14]. The model uses the elastic constants [14,24]. The spectrum calculated in this way for $V = V_0$ is shown in Fig. 3. Figure 4 compares the results obtained for the LA and TA modes at the X point of the Brillouin zone for fcc-Li to direct frozen-phonon calculations using supercells. The model works well at moderate pressures, but at high pressures, $V/V_0 < 0.7$, the frequencies, X-TA in particular, are overestimated. Therefore we chose to calculate the volume variation of $\langle\omega\rangle$ and $\sqrt{\langle\omega^2\rangle}$ for fcc-Li by applying the scaling found for $[\omega(X - \mathrm{LA}) + 2\omega(X - \mathrm{TA})]/3$ from the supercell calculations. At $V = V_0$ we have, from the full fcc-Li phonon spectrum, $\langle\omega\rangle = 289$ K and $\sqrt{\langle\omega^2\rangle} = 303$ K.

In order to examine the accuracy of the phonon calculations we also calculated the full spectrum for bcc-Li at zero pressure. The frequencies, in THz, obtained at three symmetry points P, H, and N are $P(6.8)$, $H(8.6)$, and $N(9.1, 6.1, 2.1)$ (the modes are degenerate at P and H). The corresponding experimental values are [25] $P(7.02)$, $H(8.86)$, and $N(9.04, 5.78, 1.97)$. The averages, $\langle\omega\rangle$ and $\sqrt{\langle\omega^2\rangle}$, are 291 and 307 K, and for η and λ we found the values 0.474 eV/Å^2 and 0.401, respectively. Consequently, T_c for bcc-Li (zero pressure) is estimated to be 0.54 K with $\lambda_{sp} = 0$, and 0.003 K with $\lambda_{sp} = 0.1$. The

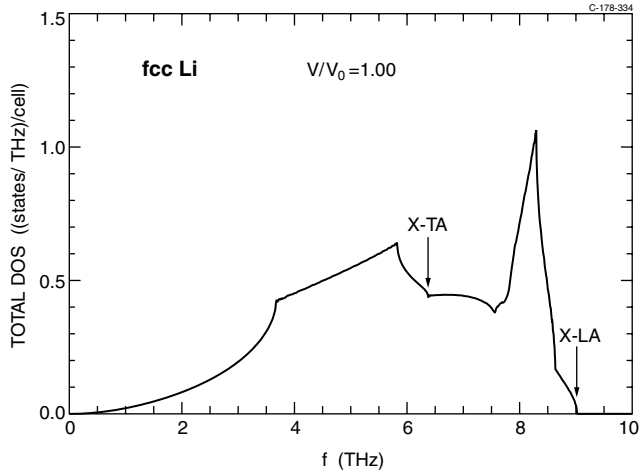

FIG. 3. Calculated phonon spectrum for fcc-Li at $V/V_0 = 1.0$. The averages, $\langle f \rangle$ and $\sqrt{\langle f^2 \rangle}$, are 6.02 and 6.31 THz, respectively, corresponding to 289 and 303 K.

T_c values found here are somewhat lower than the 1.73 and 0.18 K found for bcc-Li in Ref. [9], where a smaller $\langle \omega \rangle$ value was used.

The volume variations of λ and η are shown in Fig. 5. It is seen that a B scaling of the phonon frequencies produces too small λ values for compressed lattices. The increase in the value of η, Fig. 5b, with pressure is caused by the increase in electron-phonon matrix elements. At $V/V_0 = 1$ the s-p and d-f matrix elements are both around 1/3 of the p-d matrix element. At $V/V_0 = 0.45$ s-p scattering dominates, the s-p element being twice that of p-d which again is $\approx$2 times the d-f elements. The η values, on the other hand, are over the entire volume range dominated by the s-p contribution. The p-d and d-f contributions are strongly reduced because the partial d and f densities of states at E_F are much smaller than the s and p components. The density of electronic states at the Fermi level decreases

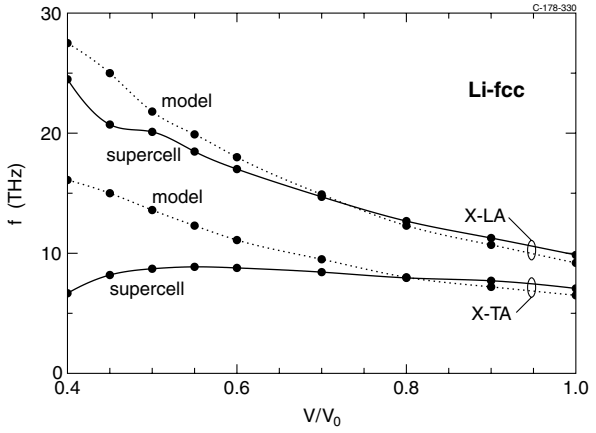

FIG. 4. Frequency of X-LA and X-TA (doubly degenerate) phonons in fcc-Li vs volume. The "model" results were obtained in the same way as in the case of Cs [14]. The "supercell" calculation is a direct frozen-phonon calculation using the total energy calculated for various distortion amplitudes in the relevant displacement mode.

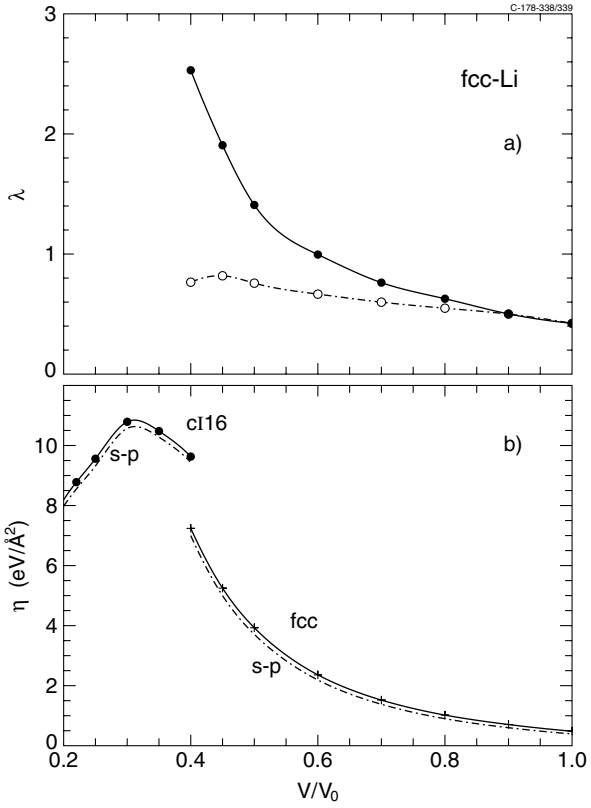

FIG. 5. The calculated electron-phonon coupling parameter, λ, for fcc-Li (a). The results shown as filled circles used the scaling of the phonon frequencies as obtained by the supercell calculations, whereas the open circles were derived by the use of Eq. (3). The lower part (b) shows the Hopfield parameters for fcc-Li (crosses) and $cI16$-Li (filled circles) vs volume. Symbols and full lines represent the total η values, whereas the dash-dotted lines are for s-p contributions only.

(see Fig. 6) as fcc-Li is compressed, but the increase in the matrix elements is strong enough to ensure an overall increase in η. In $cI16$-Li we find that the matrix elements continue to increase as the volume is reduced, and,

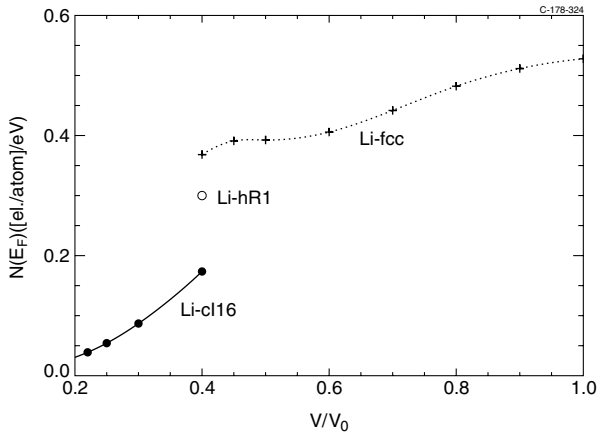

FIG. 6. Density of states at the Fermi level for fcc-Li and $cI16$-Li. A single point (open circle) for $hR1$-Li which exists only in a small pressure range.

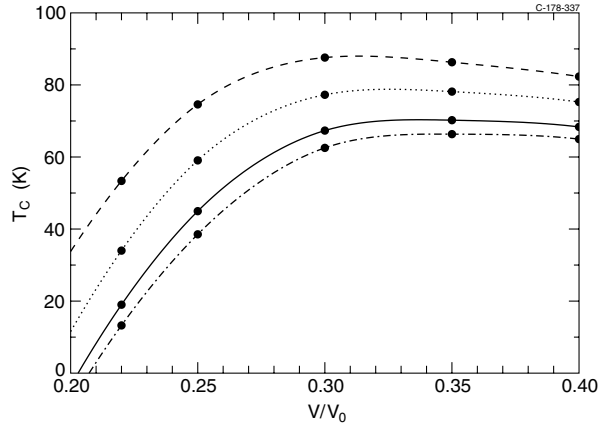

FIG. 7. T_c calculated for $cI16$-Li vs volume for the same choices of λ_{sp} as in Fig. 1.

in particular, the s-p matrix element increases rapidly with pressure. The fact that η nevertheless decreases as the volume is reduced below $V/V_0 = 0.30$ is due to the decrease in $N(E_F)$ in $cI16$-Li.

We did not calculate T_c for $hR1$-Li, but Fig. 7 shows results obtained for $cI16$-Li. However, in this case we did not calculate the phonon spectra. The values of $\langle\omega\rangle$ and $\sqrt{\langle\omega^2\rangle}$ were simply assumed to be the same in $cI16$-Li and fcc-Li at $V/V_0 = 0.40$, and the "standard" scaling, Eq. (3), was assumed to be valid in the relatively small volume range where this Li phase exists. Further, the new phases are stabilized by the opening of a (pseudo)gap as P increases, and this acts to decrease T_c, and therefore we consider the regime near the upper end of the pressure range where fcc-Li is stable to be the most interesting as far as superconductivity with high T_c is concerned. As is expected from the results shown in Fig. 5, T_c has a maximum for V/V_0 close to 0.3, and then it decreases as the volume is further reduced.

The McMillan formula, Eq. (1), contains numerical constants which are obtained from computer fits [17] for coupling parameters in the range $0 < \lambda < 1.5$. The highest λ values found here are above this range, Fig. 5a. It is, however, known [26,27] that the McMillan formula *underestimates* T_c for $\lambda > 1.4$, and therefore this does not invalidate the claims of a high T_c. It has been pointed out that spin fluctuations may not [28] be the cause of T_c suppression at ambient pressure, and that a nonzero value of λ_{sp} seems to be [9] inconsistent with specific-heat data. With $\lambda_{sp} = 0$, but by increasing μ^* to 0.25, Eq. (1) gives $T_c = 0.2$ mK at $P = 0$, but still a high value (55 K) at $P = 40$ GPa. The present work mainly discusses calculations for the close-packed fcc structure. Investigation of possible superconductivity in the low-coordinated phases may require [1] a different approach [28,29].

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