



PERGAMON

# Superconductivity in compressed potassium and rubidium

Lei Shi<sup>a</sup>, Dimitrios A. Papaconstantopoulos<sup>a,b,\*</sup>, Michael J. Mehl<sup>b</sup>

<sup>a</sup>School of Computational Sciences, George Mason University, Fairfax, VA 22032, USA

<sup>b</sup>Naval Research Laboratory, Center for Computational Materials Science, 6393, Washington DC 20375-5000, USA

Received 24 April 2001; accepted 5 May 2003 by S.G. Louie

## Abstract

Calculations of the electron–phonon interaction in the alkali metals, potassium and rubidium, using the results of band theory and BCS theory-based techniques suggest that at high pressures K and Rb would be superconductors with transition temperatures approaching 10 K.

© 2003 Published by Elsevier Science Ltd.

PACS: 74.70.-b; 71.20.Dg; 74.25.Jb

Keywords: A. Superconductors; D. Electronic band structure

In a recent paper, Shimizu et al. [1] reported the discovery of superconductivity in compressed lithium with a transition temperature  $T_c = 20$  K. This report is a confirmation of previous theoretical work of Neaton and Ashcroft [2], who predicted that at high pressures lithium forms a paired ground state, and of Christensen and Novikov [3], who suggested that fcc lithium under increased pressure may reach  $T_c = 50$ –70 K.

In this work, we applied a methodology similar to that of Ref. [3] to the alkali metals K and Rb. The procedure goes as follows: we first performed augmented plane wave (APW) calculations of the band structure and total energy of the above alkali metals in both the bcc and fcc structures over a wide range of volumes reaching high pressures. From these calculations we obtained the Fermi level,  $\epsilon_F$ , values of the density of states,  $N_t$ , and its angular momentum decomposition,  $N_l$ , as a function of volume. We also used the APW results to determine the volume variation of the bulk modulus  $B$ . We then used the self-consistent APW potentials to determine the scattering phase shifts  $\delta_l$  again as a function of volume. The quantities  $N_l$  and  $\delta_l$  were then

used in the ‘rigid muffin-tin’ approximation [4,5] to determine the Hopfield parameter  $\eta$ :

$$\eta = \frac{\epsilon_F}{\pi^2 N_t} \sum_{\ell} 2(\ell + 1) \sin^2(\delta_{\ell+1} - \delta_{\ell}) \frac{N_{\ell} N_{\ell+1}}{N_{\ell}^{(1)} N_{\ell+1}^{(1)}}, \quad (1)$$

where  $N_{\ell}^1$  is the single-scatterer density of states defined in Ref. [4]. The next step was to calculate the electron–phonon interaction parameter,

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

which we accomplished by assuming [6] that

$$\langle \omega^2 \rangle = CBV^{1/3}, \quad (3)$$

where the constant of proportionality  $C$  was determined from the experimental values of  $B$ , the volume  $V$  and the Debye temperature  $\theta_D$ , using the relationship

$$\langle \omega^2 \rangle = \frac{1}{2} \theta_D^2. \quad (4)$$

In our discussion of the transition temperature below, we show that  $T_c$  is not very sensitive to the form of the volume dependence of  $\langle \omega^2 \rangle$  in Eq. (3).

In Fig. 1, we show the ratios  $N_l(\epsilon_F)/N_t(\epsilon_F)$  at the Fermi level  $\epsilon_F$  as a function of volume. These ratios are crucial in the determination of  $\eta$ . It is important to note that the ratio  $N_d(\epsilon_F)/N_t(\epsilon_F)$  increases rapidly as we go to

\* Corresponding author. Tel.: +1-202-767-6886; fax: +1-202-404-7546.

E-mail addresses: mehl@dave.nrl.navy.mil (M.J. Mehl), lshi@scs.gmu.edu (L. Shi), papacon@dave.nrl.navy.mil (D.A. Papaconstantopoulos).

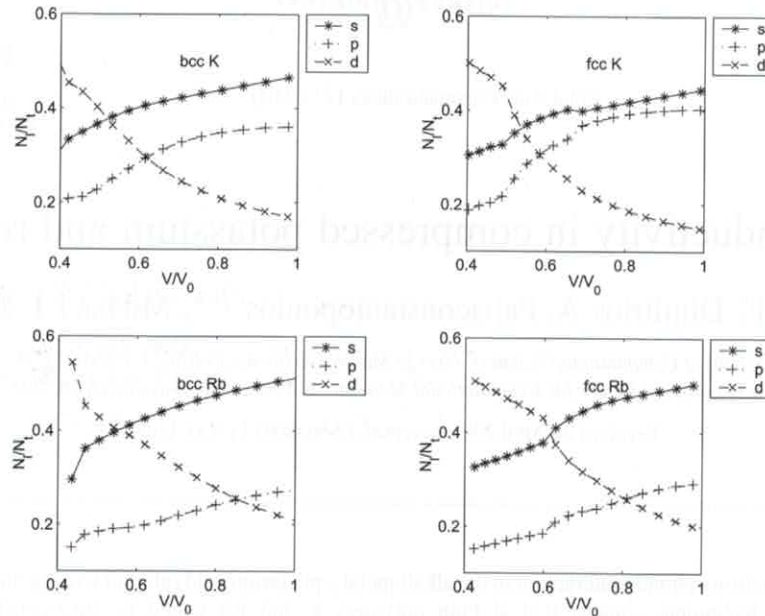


Fig. 1. Angular momentum decomposed DOS divided by total DOS at  $\epsilon_F$ .

smaller volumes. This build up of the d-like DOS under pressure causes the large values of  $\eta$  at small volumes shown in Fig. 2.

In this theory, there are three contributions to  $\eta$  coming from the channels s–p, p–d and d–f. The d–f contribution is negligible but the p–d contribution is comparable to the s–p at large volumes and becomes larger at small volumes where superconductivity occurs. Also in Fig. 2, we show the variation with volume of the

denominator of Eq. (2),  $M\langle\omega^2\rangle$ , which we have extracted from the variation of the bulk modulus.

In Fig. 3, we show the electron–phonon coupling  $\lambda$  as a function of volume determined from Eq. (2). It is evident that at small volumes,  $\lambda$  reaches large values suggesting that these metals can display superconductivity under pressure. To quantify our prediction for superconductivity on the basis of strong electron–phonon coupling, we have calculated  $T_c$  using the

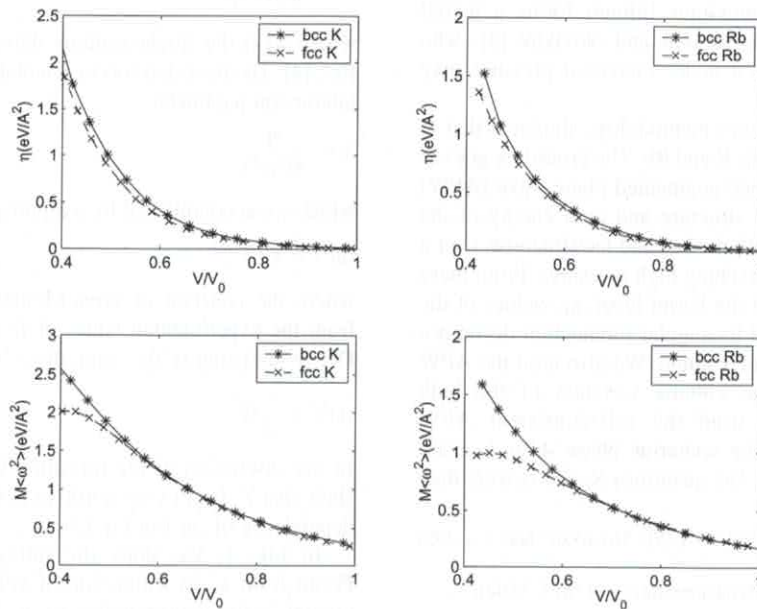
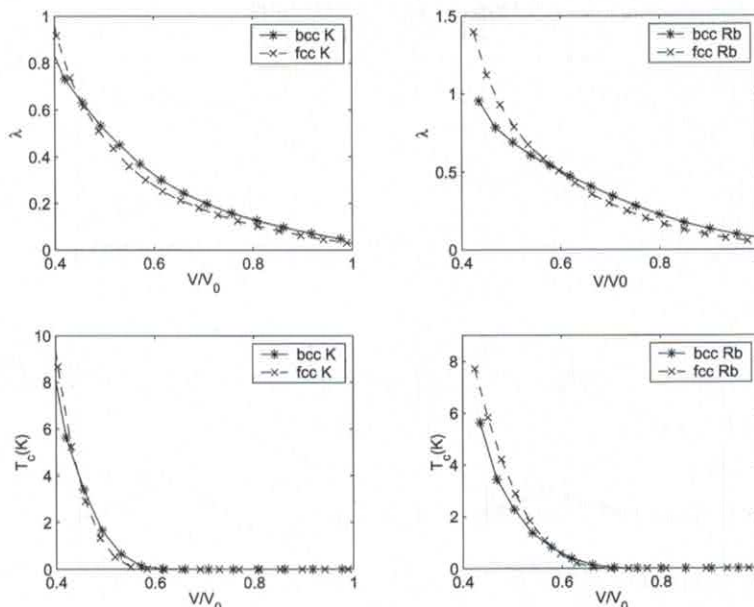


Fig. 2.  $\eta$  and  $M\langle\omega^2\rangle$  as a function of volume.

Fig. 3.  $\lambda$  and  $T_c$  as a function of volume.

McMillan equation [7,8],

$$T_c = \frac{\langle \omega \rangle}{1.20} \exp \left[ - \frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right] \quad (5)$$

with a Coulomb pseudopotential value  $\mu^* = 0.13$ . These results are also shown in Fig. 3. We must stress the McMillan equation for  $T_c$ , because of its exponential form has an accuracy in the range of 10–20%. Therefore our estimate of the phonon frequency using Eq. (3) does not affect our conclusion seriously. To demonstrate the sensitivity of our results with the form of Eq. (3), we have changed the volume exponent from 1/3 to 1/2 and recalculated  $T_c$ . We found that  $T_c$  increases by about 1 K for  $V/V_0 = 0.4$ .

Although it is not reasonable to invoke spin fluctuations in the alkali metals, we checked Eq. (5) using  $\lambda(\text{spin}) = 0.05$  and found that it gives a 1 K reduction of  $T_c$ .

It is clear that transition temperatures in a range of 5–10 K are reachable for both the fcc and bcc lattices at volumes in the neighborhood of  $V/V_0 \approx 0.4$ . We have calculated that such volumes correspond to pressures of 13.5 GPa for K and 8 GPa for Rb, respectively.

The similarity of our fcc and bcc results suggests that our prediction of superconductivity in K and Rb is independent of crystal structure. We believe that our prediction is still valid even if, experimentally, these materials under high pressure transform to other structures such as *hR1* or *cI16* [9]. We propose that the mechanism of superconductivity in these metals is due to the increased d-like character of the wave-functions at  $\varepsilon_F$  at high pressures, as shown in Fig. 1. This validates our use of the ‘rigid muffin-tin’ approximation that is successful in transition metals.

## References

- [1] A. Shimizu, H. Ishikawa, D. Takao, T. Yagi, K. Amaya, Superconductivity in compressed lithium at 20 K, *Nature* 419 (6907) (2002) 597–599. URL: <http://www.nature.com/cgi-taf/DynaPage.taf?file=/nature/journal/v419/n6907/abs/nature>.
- [2] J.B. Neaton, N.W. Ashcroft, Pairing in dense lithium, *Nature* 400 (6740) (1999) 141–144. URL: <http://www.nature.com/cgi-taf/DynaPage.taf?file=/nature/journal/v400/n6740/abs/400141>.
- [3] N.E. Christensen, D.L. Novikov, Predicted superconductive properties of lithium under pressure, *Phys. Rev. Lett.* 86 (9) (2001) 1861–1864. URL: <http://link.aps.org/abstract/PRL/v86/p1861>.
- [4] G.D. Gaspari, B.L. Gyorffy, Electron–phonon interactions, d resonances, and superconductivity in transition metals, *Phys. Rev. Lett.* 28 (13) (1972) 801–805. URL: <http://link.aps.org/abstract/PRL/v28/p801>.
- [5] D.A. Papaconstantopoulos, L.L. Boyer, B.M. Klein, A.R. Williams, V.L. Moruzzi, J.F. Janak, Calculations of the superconducting properties of 32 metals with  $z \leq 49$ , *Phys. Rev. B* 15 (9) (1977) 4221–4226. URL: <http://link.aps.org/abstract/PRB/v15/p4221>.
- [6] T. Jarlborg, Electronic and magnetic structures in bcc and hcp li under pressure, *Phys. Scr.* 37 (1988) 795–799.
- [7] W.L. McMillan, Transition temperature of strong-coupled superconductors, *Phys. Rev.* 167 (2) (1968) 331–344. URL: <http://link.aps.org/abstract/PR/v167/p331>.
- [8] P.B. Allen, R.C. Dynes, Transition temperature of strong-coupled superconductors reanalyzed, *Phys. Rev. B* 12 (3) (1975) 905–922. URL: <http://link.aps.org/abstract/PRB/v12/p905>.
- [9] M. Hanfland, K. Syassen, N.E. Christensen, D.L. Novikov, New high-pressure phases of lithium, *Nature* 408 (6809) (2000) 174–178. URL: <http://www.nature.com/cgi-taf/DynaPage.taf?file=/nature/journal/v408/n6809/abs/408174>.

