Ab initio prediction of pressure-induced superconductivity in potassium

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(Received 30 September 2005; published 17 April 2006)

We report first principles calculations of the superconducting properties of fcc potassium under high pressure. Using a completely *ab initio* method we predict a superconducting phase transition at 18 GPa. A maximum critical temperature of about 2 K is observed around 23 GPa, the pressure at which the crossover between the fcc phase and the KIII structure experimentally occurs. At higher pressure, when the fcc phase is experimentally unstable, we find, in the phononically stable range, values of T_c up to 11 K. In order to understand the underlying mechanisms inducing superconductivity in potassium, we study the effect of pressure on the electronic and vibrational properties, showing a progressive phonon softening near the *K* point of the Brillouin zone and a concomitant enhancement of the electron-phonon coupling constant λ. Interestingly, we find that the pressure induced *s-d* charge transfer causes an increasing anisotropy of the superconducting gap Δ. Although similar to dense Li in many respects, K displays interesting peculiar features.

DOI: 10.1103/PhysRevB.73.144512 PACS number(s): 74.62.Fj, 74.25.Jb, 74.25.Kc

I. INTRODUCTION

In solid-state physics textbooks alkali are reported to be nearly free-electron-like systems, with almost spherical, *s*-like, Fermi surfaces. This is based on the assumption that their valence *s* electrons are not strongly affected by the underlying lattice. This picture is certainly true at ambient conditions (atmospheric) where the *low density* approximation is verified and the nearly free-electron picture is valid. However, with the advent of high pressure experimental techniques and first principles electronic structure methods, it was demonstrated by Neaton and Ashcroft[1–3] that alkali metals are more complex than one can believe. In fact, several theoretical reports[4–9] point to the same direction. Pressure increases the electronic density and the overlap of valence wave functions, causing a progressive modification of the orbital character. This leads to an *s* to *d* charge transfer in Cs, Rb, and K,[4–6] where delocalized *s*-valence electrons become more localized *d*-valence electrons, and to an *s* to *p* transfer in Li.[9] These electronic changes are responsible for several structural phase transitions.[1,10–16] Potassium, in particular, has the bcc structure up to 11.6 GPa then it transforms into fcc up to 23 GPa where it undergoes a further transition to an experimentally still undetermined KIII phase. As recently demonstrated,[17–19] electronic structure changes are associated in alkali with unstable phonon frequencies and very strong electron-phonon (*e-ph*) couplings. These strong couplings lead to the appearance of superconductivity.

These findings boosted the search of superconductivity in high pressure phases of alkali metals.[20–22] Up to now only Li (Refs. 23–26) and Cs (Ref. 27) have been experimentally found to exhibit a superconducting phase. Li, in particular, shows the highest critical temperature, $T_c \approx 20$ K, so far occurring in an elemental material. The peculiar superconducting properties of compressed Li have been the subject of several studies, which were able to uncover the physical origin of the phonon-mediated superconducting transition in terms of phonon softening and Fermi surface nesting.[17,18] On the other hand, very sparse and preliminary investigations on Na, Cs, K, and Rb (Refs. 28–30) exist. The aim of this work is a deep investigation of the possibility of superconducting phase on dense fcc K. The present paper completes the description of SC in alkali given in Ref. 17 through a detailed comparison of K and Li.

Our work is based on the density functional theory for the superconducting state (SCDFT),[31,32] which has been able to describe successfully, without adjustable parameters, the superconducting properties of several materials,[31–33] including the high transition temperature of compressed lithium.[17] Due to its predictive nature, the method is well suited to search for new superconducting materials. Furthermore, as we demonstrated in the case of lithium, this approach is particularly useful for low density materials, where a first principles treatment of the *e-ph* and electron-electron (*e-e*) interaction is needed.[34] The physics of K is discussed through a comparison with dense lithium, in order to highlight differences and similarities between these two metals. Our results show that fcc K is a superconductor with T_c up to ≈ 2 K in the experimental stability range of the fcc phase. A further increase of pressure still gives a stable phononic structure and an ever increasing critical temperature.

The paper is organized as follows: In Sec. II we describe the method and provide the computational details. In Sec. III, we present and discuss the results. Finally, in Sec. IV, we draw our conclusions.

II. METHOD

Calculations of equation of state (EOS), band structure, vibrational properties, and electron-phonon matrix elements are performed using the plane-wave pseudopotential approach [PWSCF (Ref. 35) code] within the local density approximation to the density functional theory (DFT), in the Perdew-Zunger parametrization scheme. We used an ultrasoft pseudopotential for potassium with valence electron configuration $3s^2 3p^6 4s^1$. The reliability of this pseudopotential under extreme pressure has been tested by a careful comparison with all-electron FLAPW (Ref. 36) results. Well converged structural and electronic properties have been computed using an energy cutoff of 25 Ry and a $16\times16\times16$ Monkhorst-Pack **k**-point grid. Phonon calculations have been performed for a $8\times8\times8$ **q**-mesh. The calculation of the EOS was refined using a denser $20\times20\times20$ **k**-mesh.

To calculate the superconducting (SC) properties of K, we used the density functional theory for superconductors (SCDFT), described in full length in Refs. 31 and 32. Here we briefly recall the basis of the method. The central equation of the SCDFT is a generalized gap equation of the form

$$\Delta_{n\mathbf{k}} = -\mathcal{Z}_{n\mathbf{k}}\Delta_{n\mathbf{k}} - \frac{1}{2}\sum_{n'\mathbf{k}'} \mathcal{K}_{n\mathbf{k},n'\mathbf{k}'} \frac{\tanh\left(\frac{\beta}{2}E_{n'\mathbf{k}'}\right)}{E_{n'\mathbf{k}'}}\Delta_{n'\mathbf{k}'}, \quad (1)$$

where n and $\mathbf{k}$ are, respectively, the electronic band index and the wave vector inside the Brillouin zone. β is the inverse temperature and $E_{n\mathbf{k}}=\sqrt{(\varepsilon_{n\mathbf{k}}-\mu)^2+|\Delta_{n\mathbf{k}}|^2}$ are the excitation energies of the quasiparticles, defined in terms of the gap function $\Delta_{n\mathbf{k}}$, the Kohn-Sham eigenenergies of the normal state $\varepsilon_{n\mathbf{k}}$, and the chemical potential μ. The kernel $\mathcal{K}$ appearing in Eq. (1) is made of two contributions $\mathcal{K}=\mathcal{K}^{e\text{-}ph}+\mathcal{K}^{e\text{-}e}$, representing the effects of the *e-ph* and the *e-e* interactions, respectively. $\mathcal{K}^{e\text{-}ph}$ involves the *e-ph* coupling matrix, while $\mathcal{K}^{e\text{-}e}$ contains the matrix elements of the screened Coulomb interaction. Equation (1) has the same structure as the BCS gap equation, with the kernel $\mathcal{K}$ replacing the model interaction of BCS theory. This similarity allows us to interpret $\mathcal{K}$ as an effective interaction, responsible for the binding of the Cooper pairs. On the other hand, $\mathcal{Z}$ plays a similar role as the renormalization term in the Eliashberg equations. We emphasize that Eq. (1) is not a mean-field equation (as in BCS theory), since it contains correlation effects. Furthermore, it has the form of a static equation, i.e., it does not depend explicitly on the frequency, and therefore has a simpler structure than the Eliashberg equations. However, this certainly does not imply that retardation effects are absent from the theory: as a matter of fact, an Eliashberg-type spectral function $\alpha^2F(\Omega)$ enters the calculation of $\mathcal{Z}$ and $\mathcal{K}^{e\text{-}ph}$.

The gap equation has been solved using 2×10^4 independent **k** points in the Brillouin zone, forming a highly nonuniform mesh, denser on the Fermi surface. In the present paper we used two different procedures to calculate the superconducting gap. In one case we assume that the gap is constant on isoenergy surfaces, i.e., it depends on the energies only. In this approximation, the matrix elements entering the gap equation will also be averaged over isoenergy surfaces; in the case of electron-phonon coupling, this means that they will depend on $\alpha^2F(\Omega)$ but not on the $\mathbf{k},\mathbf{k}'$-resolved *e-ph* coupling matrix elements. In the second method, we keep the full **k**-space resolution, and we obtain a gap varying over isoenergy surfaces. The *e-ph* coupling matrix elements have been computed on a regular grid of $(8\times8\times8)^2$ **k** and **q** points. The Coulomb repulsion has been included using the Thomas-Fermi screening within the approximated Sham-Kohn approach described in Refs. 31 and 32, which gave good results for elemental materials, including Li under pressure. Further details can be found in Refs. 31 and 32.

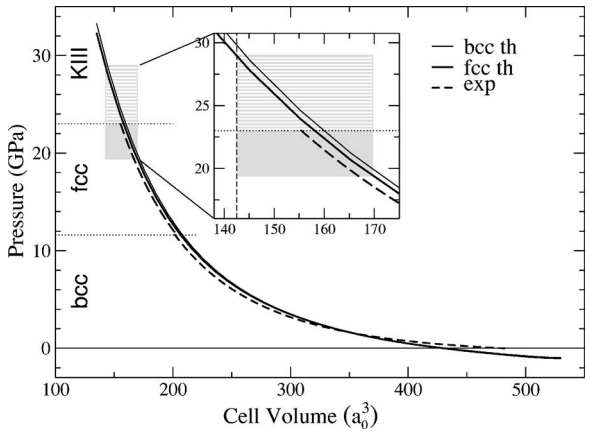

FIG. 1. Calculated equation of state for the fcc and bcc phases (full lines); 0 K extrapolation (see text) of the experimental equations of state from Ref. 12 (dashed lines). The gray area indicates the interval where we predict a superconducting ground state for the fcc structure. Dotted lines at 11.6 GPa and 23 GPa indicates, respectively, the experimental bcc→fcc and the fcc→KIII phase transitions.

III. RESULTS AND DISCUSSION

We start our study by investigating the structural properties of K. At ambient pressure potassium, as the other alkali metals crystallizes in the bcc phase; room temperature x-ray diffraction data[13] show a bcc to fcc phase transition at 11.6 GPa and a second transition, at 23 GPa, to a tetragonal body centered phase, having at least eight atoms in the primitive cell, whose structure is still under debate.[13,14,37,38] No other phase transition has been reported up to 50 GPa.[13,14] In Fig. 1 we show the calculated equation of state (EOS). As the experimental data of Winzenick *et al.*[13] were taken at room temperature, we had to extrapolate them at low temperature to make a comparison. This was done by shifting the experimental EOS by −24.8 a.u.[3] Such a shift was chosen as to match the bcc volume measured at low temperature;[39] the same shift has been applied to the fcc phase. The experimental EOS, so extrapolated at low T, turns out to be in pretty good agreement with our unshifted theoretical ($T=0$) calculations over the whole range of pressures. This makes us confident on the procedure used and on the accuracy of the calculations. Clearly, some uncertainty in the assignment of pressure remains (basically related to the temperature dependence of the equation of state), but we can assume it to be within at most 2–3 GPa.

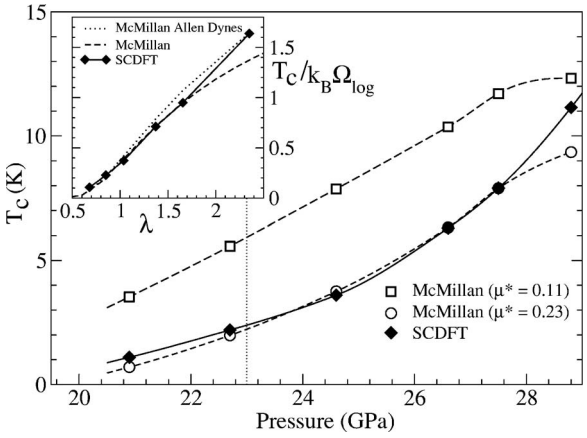

FIG. 2. T_c versus pressure as calculated within SCDFT (full line), and using McMillan's equation with $\mu^*=0.11$ (squares) and $\mu^*=0.23$ (circles). The vertical dotted line marks the experimental fcc to KIII transition. In the inset the comparison, in a $T_c/\Omega_{\log}$ versus λ plot, between SCDFT results and values obtained using the Allen and Dynes correction to McMillan formula ($\mu^*=0.23$).

At each pressure P, the solution of the gap equation as a function of temperature gives $T_c(P)$. As the calculated bcc structure, in its range of stability, does not reach an appreciable critical temperature ($T_c \leqslant 0.2$ K), we focus our attention on the fcc phase. In Fig. 2 we plot T_c as a function of pressure, using both our SCDFT approach and the McMillan's equation[40]

$$T_c = \frac{\Omega_{\log}}{1.20}\exp\left(-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right), \tag{2}$$

where the Coulomb pseudopotential μ^* measures the strength of the *e-e* interaction. This parameter, quite difficult to calculate, is often adjusted to fit experimental data. $\Omega_{\log}$ is a weighted average of the phonon frequencies

$$\Omega_{\log} = \exp\left(\frac{2}{\lambda}\int d\Omega \ln(\Omega)\frac{\alpha^2F(\Omega)}{\Omega}\right) \tag{3}$$

and the Eliashberg function $\alpha^2F(\Omega)$ is the *e-ph* coupling averaged over the Fermi surface:

$$\alpha^2F(\Omega) = \frac{1}{N(0)}\sum_{ij}\sum_{\nu,\mathbf{q}}|g^{ij}_{\nu,\mathbf{q}}|^2\delta(\xi_i)\delta(\xi_j)\delta(\Omega-\Omega_{\nu,\mathbf{q}}) \tag{4}$$

(i,j stand for band and $\mathbf{k}$ point indices, $\mathbf{q}$ and ν are the phonon wave vector and mode, respectively). $\alpha^2F(\Omega)$ also defines the *e-ph* coupling constant λ as

$$\lambda = 2\int \frac{\alpha^2F(\Omega)}{\Omega}d\Omega. \tag{5}$$

The McMillan formula is known to reproduce the solution of Eliashberg equations for $\lambda<1.5$; for larger λ values it tends to saturate, underestimating T_c. Furthermore, this equation has a poor dependence on the shape of the $\alpha^2F(\Omega)$, as shown by the solutions of Eliashberg equations at high coupling. For this reason, Allen and Dynes[41] proposed the introduction of the prefactor f_1f_2 in front of Eq. (2), where

$$f_1 = \left[1+\left(\frac{\lambda}{2.46(1+3.8\mu^*)}\right)^{3/2}\right]^{1/3}, \tag{6}$$

$$f_2 = 1+\frac{(\bar{\Omega}_2/\Omega_{\log}-1)\lambda^2}{\lambda^2+3.31(1+6.3\mu^*)(\bar{\Omega}_2/\Omega_{\log})}. \tag{7}$$

This correction has the right asymptotic limit $\sqrt{\lambda}$ of the Eliashberg equations, and better accounts for the shape of $\alpha^2F(\Omega)$ using the parameter

$$\bar{\Omega}_2 = \left\{\frac{2}{\lambda}\int \Omega\alpha^2F(\Omega)d\Omega\right\}^{1/2}. \tag{8}$$

Figure 2 shows that T_c increases with P and that, in the range of pressure where the fcc phase is experimentally stable, K is a superconductor with a modest but non-negligible T_c going up to ≈2 K. A further increase of T_c up to ≈11 K occurs above the experimental instability pressure, $P=23$ GPa (see discussion below).

We notice that, similarly to what was observed in Li, McMillan's equation reproduces the SCDFT (and, in that case, also the experimental) results only by using $\mu^*\approx 0.22$, much higher than the "standard" ≈0.13–0.15 values. This problem, discussed in detail by Richardson and Ashcroft in the case of Li,[34] seems therefore to be common to low density systems. As there are no available experiments on SC properties of K under pressure, our predictive results, in view of their peculiar differences relative to "standard" McMillan results, can be challenged by experiments. The good agreement with measured T_c obtained for Li gives us confidence in these predictions.

The McMillan equation deviates from SCDFT results only above 28 GPa ($\lambda\approx 2$). To understand better this behavior, we show in the inset our calculated $T_c/\Omega_{\log}$, compared to McMillan results with and without the Allen and Dynes correction, as a function of λ. The saturation of McMillan T_c occurs out of the range of validity of this equation. In this range, as the phonon instability approaches (see below), $\Omega_{\log}$ drops very rapidly without a corresponding decrease of the full frequency width of the phonon spectrum. The standard McMillan approach does not describe properly these changes of $\alpha^2F(\Omega)$. The results obtained with the introduction of the Allen and Dynes correction, on the other hand, follow very closely the SCDFT results. In turn, as the corrected McMillan equation is known to reproduce the full solution of Eliashberg equations, our findings indicate the capability of SCDFT approach to follow the trends of Eliashberg equations, over a very large range of λ, when the Coulomb repulsion can be modeled by a constant value of the single parameter μ^*.

From the theoretical point of view, a comparison can be made with McMillan calculations by Shi *et al.*[30] Using electron-phonon parameters obtained within the rigid muffin-tin approximation (RMTA), they find rather high critical temperatures, with values up to 10 K at 13.5 GPa, in both the fcc and bcc phases. A similar large overestimate of $\lambda(P)$ within the RMTA was found in Li,[7] mainly due to the effects of phonon softening on $\Omega_{\log}$.

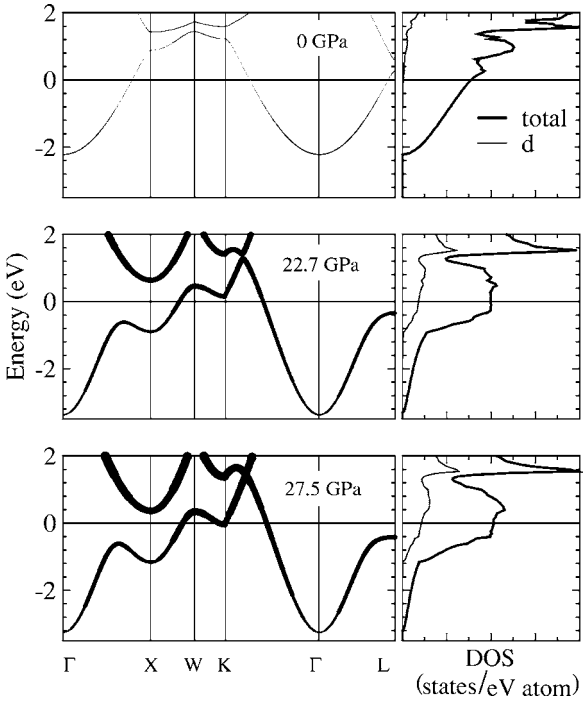

FIG. 3. Band structure and density of states for K around the Fermi energy, at the equilibrium lattice parameter (upper panel) and under high pressure (below). The thickness is proportional to the average of the squared modulus of the electron phonon matrix elements.

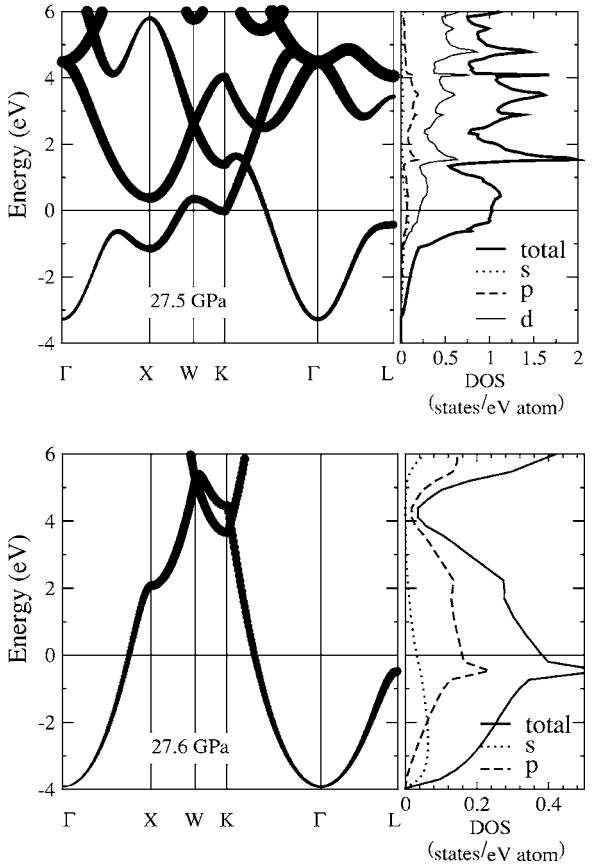

FIG. 4. Band structure and projected density of states for K (upper panel) and Li (lower panel) at high pressure. The thickness of bands is proportional to the amount of charge projected over *d* (K) and *p* (Li) orbitals.

In order to understand and explain the origin of the superconducting phase transition in K, we carry out a detailed analysis of the electronic and dynamical properties, in close comparison with Li. The electronic energy bands of fcc K as a function of P are reported in Fig. 3, where the line thickness is proportional to the squared modulus of the *e-ph* matrix elements, averaged over the electronic states and summed on the phonon spectrum. Starting from the free-electron-like behavior expected in an alkali metal at zero pressure, we end up with energy bands showing a complex behavior at high pressure. This is not surprising, since volume compression acts differently on extended 4*s* and on localized 3*d* states, producing an *s* to *d* promotion. This can be clearly seen in the high pressure energy bands shown in Fig. 4(a): K tends to have a transition metal character, with localized 3*d* states at the Fermi level. Remarkably, the comparison of Figs. 3 and 4 shows a close correlation between *d*-like character and strong electron-phonon coupling.

This scenario shows some similarities with Li, where we find an almost purely *p*-like band, very strongly coupled to phonons, close to E_F around the L point (see Fig. 4). The two metals, however, are only roughly similar: due to the difference between 2*p* and 3*d* states, the Li bands look more free-electron-like than those of K, especially around *X-W-K*.

In order to understand the phonon-mediated superconductivity, the central quantity to study is the Eliashberg spectral function $\alpha^2F(\Omega)$. Figure 5 reports its behavior at selected pressures. As the pressure is raised, we observe that the frequency range spanned by this function increases due to the strengthening of covalent bonding induced by pressure. As in Li, however, we observe the presence of a peak in the low frequency region of the spectrum, which keeps growing with pressure. This peak leads to the increase of the *e-ph* coupling parameter λ, which according to its definition [Eq. (5)], gets a large contribution from low frequencies.

It is interesting, at this point, to make a detailed comparison between K and Li. In Fig. 6 we compare the behavior of T_c and of related relevant quantities as a function of pressure

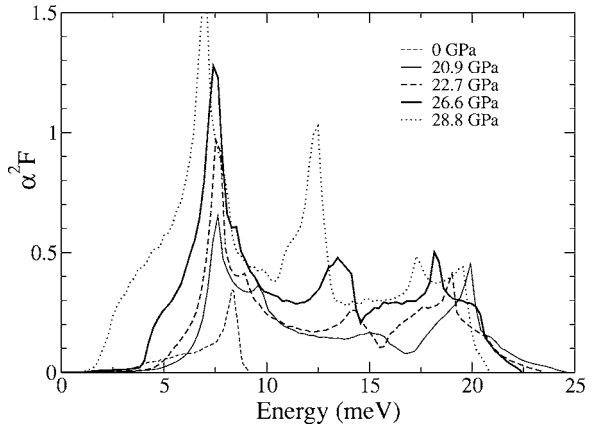

FIG. 5. Calculated $\alpha^2F(\Omega)$ for fcc K for different values of pressure.

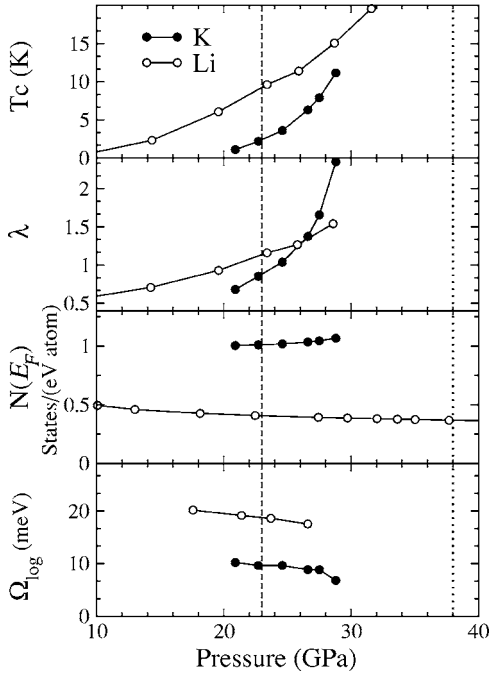

FIG. 6. Pressure behavior of critical temperature, $\omega_{\log}$, $N(E_F)$ and λ in K and Li. Vertical dashed (dotted) line represents the K (Li) critical pressure at which the structural phase transition takes place.

for both systems. T_c is clearly lower for K, despite the rather large values of λ reached. A simple explanation, within McMillan's approach, can be given in terms of the small $\Omega_{\log}$ values for K, related mostly to the larger nuclear mass. In fact, the value of μ^* required to reproduce the SCDFT results is very similar for the two systems, and does not depend significantly on pressure. Figure 6 also shows that the T_c of K is slightly enhanced by the slow increase of the DOS at the Fermi level, $N(E_F)$; from band structure calculations we saw that this effect is due to the increased *d* character of the bands at E_F. In lithium, on the other hand, $N(E_F)$ decreases due to a shift of the Fermi level near a Van Hove peak in the DOS caused by the flat *s*-*p* band at *L*. A similar band exists in K as well, however, in this case, the largest contribution to

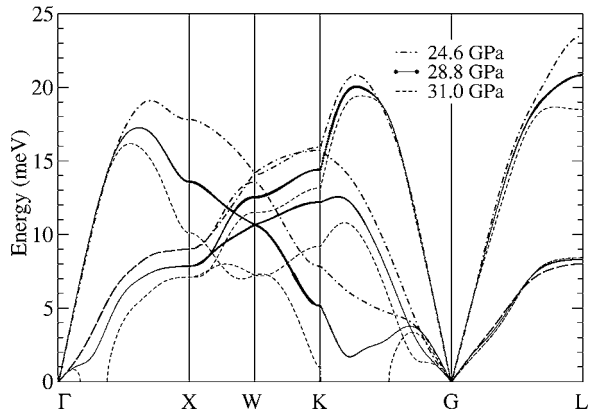

FIG. 7. Phonon dispersion at selected pressures for K. For the energies at 28.8 GPa is also reported the linewidth due to electron phonon coupling.

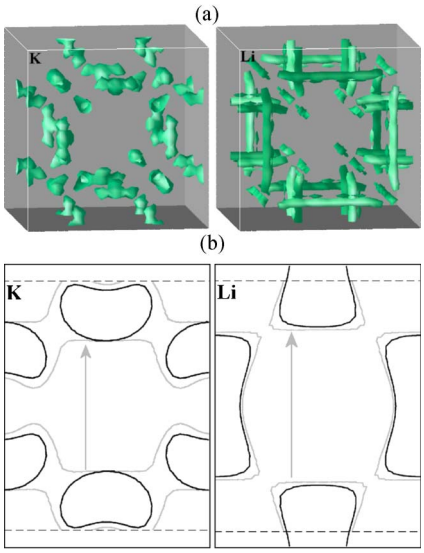

FIG. 8. (Color online) $\lambda_{\mathbf{q}j}$ for K (24.5 GPa) and Li (29.6 GPa) (upper panels), for the lowest phonon mode ($j=1$), in a box centered on the Γ point. The isosurfaces contain the values of maximum λ, of about 1.5 in K and 6 in Li. Below, two cuts of the Fermi surface in the (110) direction for K (left) and Li (right). The gray line corresponds to a plane passing through Γ the full line to a plane slightly shifted.

$N(E_F)$ comes from the *d* states which pin E_F near the *K* point.

In order to understand the $\alpha^2F(\Omega)$ functions in Fig. 5, we plot the phonon dispersion of K in Fig. 7, at selected pressures.

Upon pressure increase, the lowest branch softens and becomes unstable at ≈29 GPa. The softening occurs around the $\vec{\mathbf{k}}$-point *K* as in Li, and at higher pressures around Γ, as well. Notably, the softening occurs above the experimental

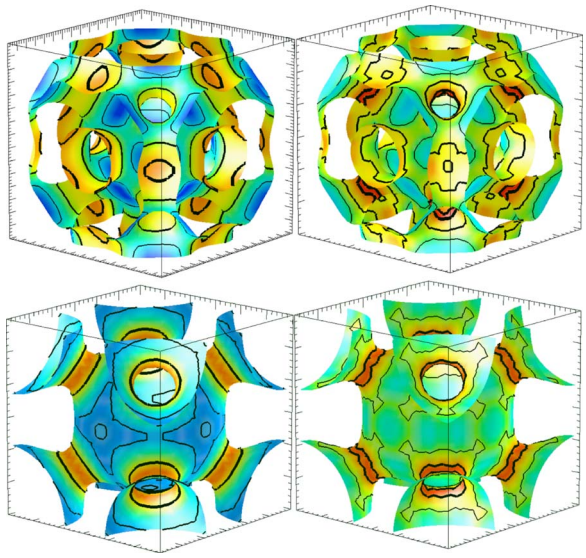

FIG. 9. (Color online) Fermi surface of K (up) and Li (down). On the left-hand side the color map/isosurfaces gives the projection of the charge at the Fermi level over *d* and *p* orbitals for K and Li, respectively, and on the right-hand side the superconducting gap [values increase from thin lines (blue) to thick lines (red)].

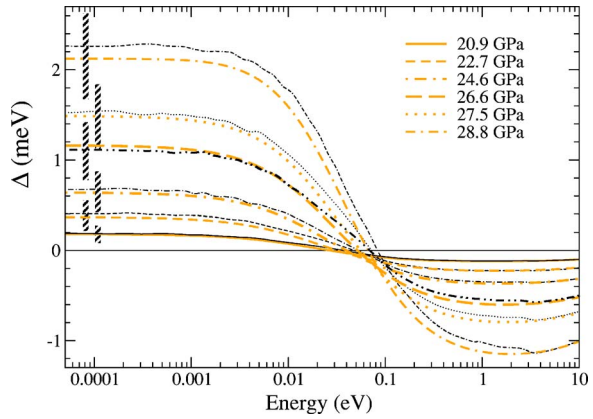

FIG. 10. (Color online) Superconducting gap as a function of the energy distance from E_F at different pressures. The gray (orange) lines in the legend were obtained using energy averaged functionals (Ref. 32), while the black lines show the **k**-resolved calculations, later averaged. Vertical bars represent the anisotropy of Δ on the Fermi surface.

transition pressure. Our results therefore suggest either a first order phase transition (the fcc structure being "dynamically" stable up to 29 GPa) related to this phonon mode, or, alternatively, a different transition mechanism taking place before the complete phonon softening. Due to the experimental indetermination of the high pressure phase, we could not calculate the range of "thermodynamical" stability of the fcc phase (certainly lower than 29 GPa) and consider 23 GPa as the upper pressure limit where our results can be compared with experiment. The *e-ph* coupling λ increases with softening (Fig. 6). A similar behavior has been reported for lithium,[17] with a value of $\lambda=2$ close to the fcc-to-hR1 transition.

Similarly to Li, the *e-ph* coupling is very selective in reciprocal space. This is clearly seen in Fig. 8(a) where we plot a high value isosurface of $\lambda_{\mathbf{q}j}$ for the lowest frequency phonon mode. Although the two surfaces show the same topology K and Li do show important differences, mainly K does not show the same well-defined tubular structure fund in Li,[17] this can be ascribed to the more complex FS of K that does not result in an equally sharp nesting, as shown by Fig. 8(b) where we report for both K and Li two (110) cuts of the FS, the first (full line) passing through the Γ point and the second slightly shifted.

Turning our attention on the SC gap around E_F, we find for both systems an anisotropic distribution, as shown in the right-hand panels of Fig. 9 for the two metals. To understand this behavior, we compare the gap distribution with a FS representation with a color scale representing the d (p) contribution for K (Li) on the left-hand panels, and the gap value on the right-hand panels. We see that the gap has a larger value where the d (p) contribution is larger in K (Li).

A further difference between Li and K is in the gap anisotropy, which is not very large in Li, while it is remarkable in K: Fig. 10 shows the superconducting gap Δ at selected pressures, together with its spread on the Fermi surface. The anisotropy in K increases with increasing P, as a consequence of the electronic structure changes. At ambient pressure (where a SC solution can only be achieved by neglecting the Coulomb repulsion), the anisotropy is smaller, consistently with the free-electron nature of K.

IV. CONCLUSIONS

In conclusion, we used the recently introduced density functional theory for the superconducting state to predict the properties of K under high pressure. A superconducting ground state for potassium has been calculated for pressures higher than 19 GPa, with T_c up to 11 K in the range of stable fcc phononic structure. The detailed analysis of electronic and dynamical properties shows an *s-d* charge transfer close to the Fermi level as the pressure increases. Correspondingly, we find a very anisotropic gap, with higher values in the mostly *d*-derived parts of the Fermi surface, strongly coupled to phonons. Upon increasing pressure, phonon softening around the K point finally leads to a phononic instability, found at a pressure larger than the experimental transition pressure. The comparison with Li illustrates common points but also relevant differences, due to the different nature of electronic states at E_F and the Fermi nesting observed in Li but not in K.

ACKNOWLEDGMENTS

The authors thank M. Affronte for useful discussion. This work was partially supported by the Istituto Nazionale di Fisica della Materia (INFM) through a supercomputing grant at Cineca (Bologna, Italy), by the Italian Ministery of Education, through a 2004 PRIN project, by the Deutsche Forschungsgemeinschaft, by the EXCITING Network, and by the NANOQUANTA Network, of Excellence. We acknowledge financial support by MIUR under project PON-CyberSar.

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