Intercalant-Driven Superconductivity in YbC₆ and CaC₆

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Recently discovered superconductivity in YbC₆ and CaC₆ at temperatures substantially higher than previously known for intercalated graphites, raised several new questions: (1) Is the mechanism considerably different from the previously known intercalated graphites? (2) If superconductivity is conventional, what are the relevant phonons? (3) Given extreme similarity between YbC₆ and CaC₆, why their critical temperatures are so different? We address these questions on the basis of first-principles calculations and conclude that coupling with intercalant phonons is likely to be the main force for superconductivity in YbC₆ and CaC₆, but not in alkaline-intercalated compounds, and explain the difference in $T_c$ by the “isotope effect” due to the difference in Yb and Ca atomic masses.

Recent discovery of relatively high temperature superconductivity in graphite intercalated compounds (GIC) YbC₆ and CaC₆ [1] of 6.5 and 11.5 K, respectively, the highest among GIC, has renewed theoretical interest in superconductivity in GIC [2,3]. In particular, it inspired Csanyi et al [2] to analyze four superconducting and three non-superconducting GIC in order to elucidate common trends and get more insight into the mechanism of superconductivity. They discovered an interesting empirical correlation between the occupation of the only 3D band in the system, and the appearance of superconductivity, and, using this observation, they argued that superconductivity in all GIC is electronic by origin, intermediate bosons being probably excitons or acoustic plasmons. This calls for revising the conventional wisdom that superconductivity in GIC is conventional by nature and mostly due to carbon phonons.

In this Letter we shall argue, using first principle calculations and experimental data [1,4], that while the standard picture of electron-phonon coupling mainly with the C modes is probably in doubt, at least in these two compounds, superconductivity is likely to arise from the intercalant vibrations, and not from electronic excitations. In this sense, YbC₆ and CaC₆ are somewhat close to another high-$T_c$ (18K) transition metal - carbon superconductor, Y₂C₃, where superconductivity seems to be related to Y phonons [5].

Our analysis is based on highly accurate all electron fully relativistic LAPW calculations [6]. LDA+U correction was applied to the f-electrons in Yb, to account for Hubbard correlations. Details of the calculations for YbC₆ are described elsewhere [3]. Calculations for CaC₆ and for other materials discussed below were performed in the same setup as for YbC₆, but without LDA+U and spin-orbit corrections. For the purpose of comparison, we also performed similar calculations for Li GIC: LiC₆ and LiC₃.

Let us first discuss the viability of the electronic mechanism scenario [2]. This conjecture is based on four assumptions: (1) the 3D free electron like band crosses the Fermi level in all superconducting GIC and is fully empty in all nonsuperconducting ones; (2) this band is not related to intercalant $s$ or $p$ states, but is formed by free electrons propagating in the interstitial space; (3) this band is much weaker coupled with the phonons than the other bands, and (4) such band structure is advantageous for the excitonic ”sandwich” mechanism [7] or for the acoustic plasmons mechanism [8].

The first assumption is correct for many, but, apparently, not all GIC. For instance, in LiC₃, in pseudopotential calculations of Ref. [2], the band in question touches the Fermi level. In our fully converged all-electron calculations with a fine k-mesh (13x13x10) this band was 0.2 eV above the Fermi level (Fig. 1). Yet, according to the experiment, superconductivity was observed in this compound [4], although because of low temperature and broad transition the authors failed to give the exact number for $T_c$. On the other hand, Eu in EuC₆ is known to be divalent [9], just as Yb or Ca, and forms exactly the same crystal structure, yet the material is not superconducting [10]. Eu in EuC₆ is magnetic, but, if Eu electrons are not involved in superconductivity, the long coherence length in GIC would have prevented magnetic pair-breaking, as long the material remains well ordered antiferromagnetically (cf., for instance, superconducting antiferromagnetic Chevrel phases).
FIG. 1. LAPW band structure of LiC₃. The left panel shows the partial Li character, and the right panel interstitial character. Note uniform participation of the interstitial states in all bands, and selective participation of the Li states in the free electron like band. (color online)

The second assumption is somewhat philosophical, because it is hard to tag an itinerant free-electron like band as an interstitial or as an sp band of an alkali metal. However, decomposition of the wave function of this band shows (for instance, in case of LiC₃, displayed in Fig. 1), that while interstitial plane wave states have the same weight in this band as in the other, 2D states, Li s and p (mostly pₓ) orbitals participate nearly exclusively in this band, and provide much more share of the total weight than the volume occupied by the Li MT spheres. By the standard band theory parlance, this identify them as at least substantially Li-derived. As an independent test, we performed calculations for a hypothetical compound in which the Li atom were replaced by a free electron, and found that the 3D band dispersion changed enormously (Fig.2).

FIG. 2. Band structure of LiC₃ (thick blue lines) and C₃ (thin red lines). Note that the most affected band is the free electron like one, specifically, its in-plane dispersion. (color online)

The validity of the third assumption can be tested by direct calculations: one can evaluate the electron-phonon matrix elements at a particular high-symmetry point in the Brillouin zone with a specific phonon by applying a frozen displacement and looking at the induced band splittings. We employed this technique to compute the coupling at the point half-way between Γ and A with the “breathing” Li phonon, that is, the one corresponding to a breathing displacement of Li along c. The results for LiC₆ are shown in Fig. 3. One can see that within ± 5 eV of the Fermi level the free-electron like band in the one with the strongest electron-phonon coupling. In view of the noticed in Ref. [2] high sensitivity of this band to interplane distance, one should also expect a strong coupling with the buckling C modes, but we did not test this numerically.

Turning to the "sandwich" mechanism [7], we observe that the original papers were strongly based on the idea that the electronic excitations reside in a dielectric layer (otherwise metallic screening prevents exciton formation), while the interlayer band is metallic in the well superconducting GIC, as observed in Ref. [2]. Finally, acoustic plasmons would form in this band either if its effective mass were much heavier than in the other bands, or if it were 2D. Neither condition holds.

FIG. 3. LAPW band structure of LiC₃. The radii of the filled circles half-way between Γ and A are proportional to the electron-phonon interaction matrix elements of the corresponding band with the Li breathing mode. Note that the most affected band is the free electron like one.

Since electronic superconductivity appears to be rather unlikely, we need to find another mechanism. It was conjectured in Ref. [3] that superconductivity in YbC₆ is largely due to Yb phonons, in analogy with Y₂C₃ [5]. Comparison between YbC₆ and CaC₆ lends additional support to this scenario. Indeed, a detailed examination of the two band structures (Fig. 4) finds practically no difference for all but one band in the vicinity of the Fermi level, including the 3D interlayer band. There is some effect of additional hybridization with the f-states on the lowest unoccupied state at the M point, which, however, affects one band out of six, and does not change the den-
sity of states near the Fermi level (Fig.5). If superconductivity were not related to the intercalant atom, one would expect the critical temperature to change only slightly, a situation analogous to YBa$_2$Cu$_3$O$_7$, where Y can be substituted by any trivalent rare-earth with $T_c$ changing within a few per cent only. On the contrary, critical temperature of CaC$_6$ is 1.77 of that of YbC$_6$.

At this point we observe that $\sqrt{M_{Yb}/M_{Ca}}$, where $M_{Ca(Yb)}$ is the atomic mass of Ca(Yb), is 2.08. This means that “isotope effect” on $T_c$, due to substitution of Yb by Ca, is $1.77/2.08=0.85$ of the “full” isotope effect if superconductivity were entirely due to Yb/Ca modes, and no other differences between the two materials was relevant for superconductivity. Recalling that partial isotope effects in binaries are scaled with partial coupling constants, we find that $\lambda_R/(\lambda_R + \lambda_C) \approx 0.85$, (here $R$ stands for either Ca or Yb), that is, 15% of the electron-phonon coupling comes from C, and the rest from Ca/Yb. It is more curious than important that the rough estimate given in Ref. [5] for Y$_2$C$_3$ was 10% of total coupling coming from C-C phonons, and the rest from pure Y or mixed Y-C modes, in an interesting agreement with the above estimate for YbC$_6$.

To summarize, we propose that unusually high for intercalated graphites critical temperatures in CaC$_6$ and YbC$_6$ are mainly due to substantial participation of the intercalant electronic states at the Fermi level, and, as a consequence, sizeable coupling with soft intercalant modes. It remains unclear to what extent the same mechanism is present in other, low $T_c$ GIC, such as KC$_x$, LiC$_x$ and NaC$_x$. Although their electronic structure shares some similarities with YbC$_6$/CaC$_6$, it is substantially different, especially regarding intercalant states. It seems unlikely that intercalants in the former are involved in superconductivity nearly as strong as in the latter.

Finally, let us discuss what experiments can test the proposed scenario. Measuring isotope effect on Ca is predicted to yield an exponent of the order 0.4, and that on C of 0.1 or less. Another prediction is that mixed intercalation of Ca and Yb should produce samples whose $T_c$ scales with concentration as the average logarithmic phonon frequency, that is, as $T_c^x T_{Yb}^{(1-x)}$, where $x$ is the Ca concentration. An interesting question is, what would be a result of partial substitution of Ca with Mg or Sr? Their ionic radii are substantially different from those of Ca or Yb (which are practically the same in hexagonal coordination). A moderate substitution with, say, Mg will reduce the interplanar distance, thus making Ca-C force constants larger and the coupling constant with electrons for Ca modes smaller. On the other hand, Mg ions themselves will sit a pore relatively large for their ionic radius, and thus will have smaller force constant, leading to some increase of $\lambda$. The third effect is that the corresponding Mg modes will have higher frequency for the same force constants because of smaller mass. If the first two effect approximately cancel each other, co-doping with Mg may be a route to even higher $T_c$. Obviously, more experimental and computational work is required to clarify this issue.

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