

Intercalant-Driven Superconductivity in YbC_6 and CaC_6

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(Received 6 April 2005; published 21 November 2005)

Recently discovered superconductivity in YbC_6 and CaC_6 , at temperatures substantially higher than previously known for intercalated graphites, raises several new questions. (1) Is the mechanism considerably different from that of previously known intercalated graphites? (2) If superconductivity is conventional, what are the relevant phonons? (3) Given the extreme similarity between YbC_6 and CaC_6 , why are their critical temperatures 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 YbC_6 and CaC_6 , 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.

DOI: 10.1103/PhysRevLett.95.227001

PACS numbers: 74.25.Jb, 74.70.Ad

Recent discovery of relatively high temperature superconductivity in graphite intercalated compounds (GIC) YbC_6 and CaC_6 [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 Csányi *et al.* [2] to analyze four superconducting and three nonsuperconducting 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 most likely being excitons or acoustic plasmons. This calls for revising the conventional wisdom that superconductivity in GIC is conventional by nature and due mostly to carbon phonons.

In this Letter, we shall argue, using first-principles 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, YbC_6 and CaC_6 are somewhat close to another high- T_c (18 K) transition metal-carbon superconductor, Y_2C_3 , where superconductivity seems to be related to Y phonons [5].

Our analysis is based on highly accurate all-electron fully relativistic linearized augmented plane wave method (LAPW) calculations [6]. The LDA + U correction was applied to the f electrons in Yb, to account for Hubbard correlations. Details of the calculations for YbC_6 are described elsewhere [3]. Calculations for CaC_6 and for other materials discussed below were performed with the same setup as for YbC_6 but without LDA + U and spin-orbit corrections. For the purpose of comparison, we also performed similar calculations for Li GIC: LiC_6 and LiC_3 .

Let us first discuss the viability of the electronic mechanism scenario [2]. This conjecture is based on four assump-

tions: (1) the 3D free-electronlike 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 more weakly 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 LiC_3 , 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 ($13 \times 13 \times 10$), 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 a broad transition, the authors failed to give the exact number

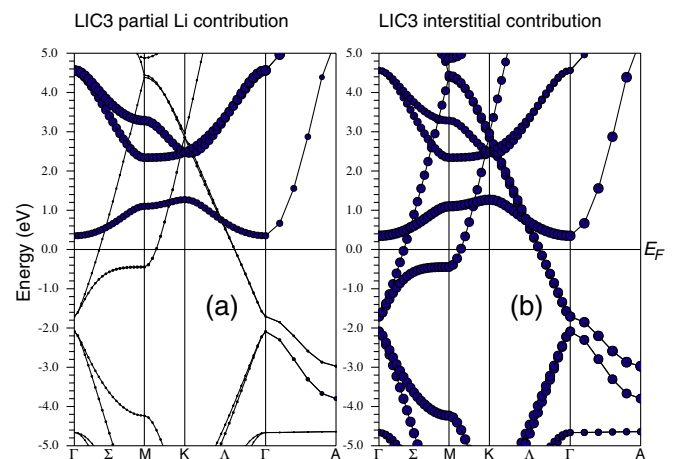


FIG. 1 (color online). LAPW band structure of LiC_3 . The left panel shows the partial Li character, and the right panel the interstitial character. Note the uniform participation of the interstitial states in all bands, and the selective participation of the Li states in the free-electronlike band.

for T_c . On the other hand, Eu in EuC_6 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 EuC_6 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 as the material remains well ordered antiferromagnetically (cf., for instance, superconducting antiferromagnetic Chevrel phases).

The second assumption is somewhat philosophical, because it is hard to tag an itinerant free-electronlike 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 the case of LiC_3 , 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 p_z) orbitals participate nearly exclusively in this band and provides a much greater share of the total weight than the volume occupied by the Li muffin tin spheres. In the standard band theory parlance, this identifies them as at least substantially Li-derived. As an independent test, we performed calculations for a hypothetical compound in which the Li atom was replaced by a free electron and found that the 3D band dispersion changed enormously (Fig. 2).

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 halfway 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 LiC_3 are shown in Fig. 3 (for the AC_6 structure, the corresponding deformation potentials vanish by symmetry, as discussed in Ref. [3]). One can see that, within ± 5 eV of the Fermi level, the free-electronlike band is the one with the *strongest* electron-phonon coupling. In view of the noticed (in

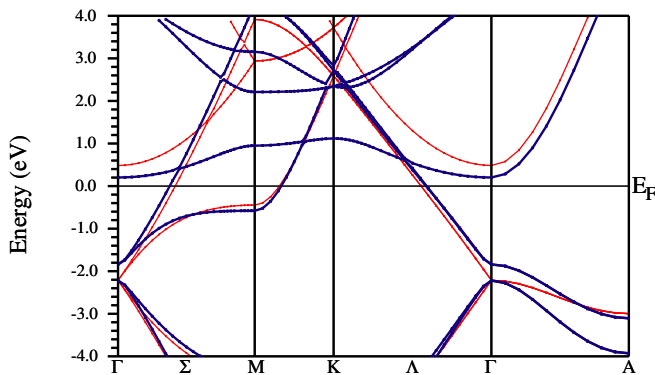


FIG. 2 (color online). Band structure of LiC_3 (thick blue lines) and $e\text{C}_3$ (thin red lines). Note that the most affected band is the free-electronlike one, specifically, its in-plane dispersion.

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 based strongly 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 of the conditions holds.

Since electronic superconductivity appears to be rather unlikely, we need to find another mechanism. It was conjectured in Ref. [3] that superconductivity in YbC_6 is due largely to Yb phonons, in analogy with Y_2C_3 [5]. Comparison between YbC_6 and CaC_6 lends additional support to this scenario. Indeed, a detailed examination of the two band structures (Fig. 4) finds practically no difference for any but one band in the vicinity of the Fermi level, including the 3D interlayer band. This is due to the fact that Yb in this compound is strictly two-valent [3], and two-valent Yb is electronically very close to the alkali earth metals such as Ca or Sr (Li and other alkali metals are quite different). 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 density 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 $\text{YBa}_2\text{Cu}_3\text{O}_7$, where Y can be substituted by any trivalent rare-earth with T_c changing within a few percent only [11]. On the contrary, critical temperature of CaC_6 is 1.77 of that of YbC_6 .

At this point, we observe that $\sqrt{M_{\text{Yb}}/M_{\text{Ca}}}$, where $M_{\text{Ca}(\text{Yb})}$ is the atomic mass of $\text{Ca}(\text{Yb})$, is 2.08. This means

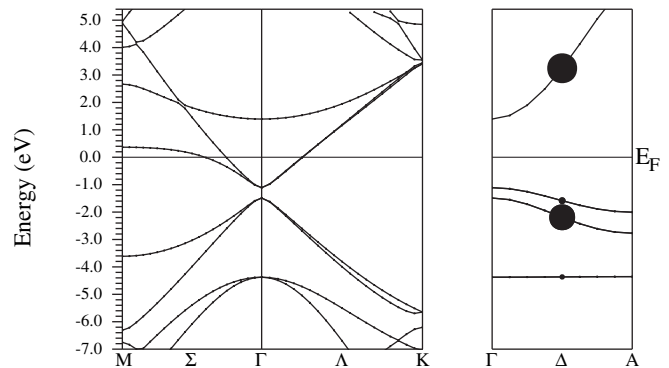


FIG. 3. LAPW band structure of LiC_3 . The radii of the solid circles halfway between Γ and A are proportional to the electron-phonon interaction matrix elements of the corresponding band with the Li breathing mode. Note that the most affected band is the free-electronlike one.

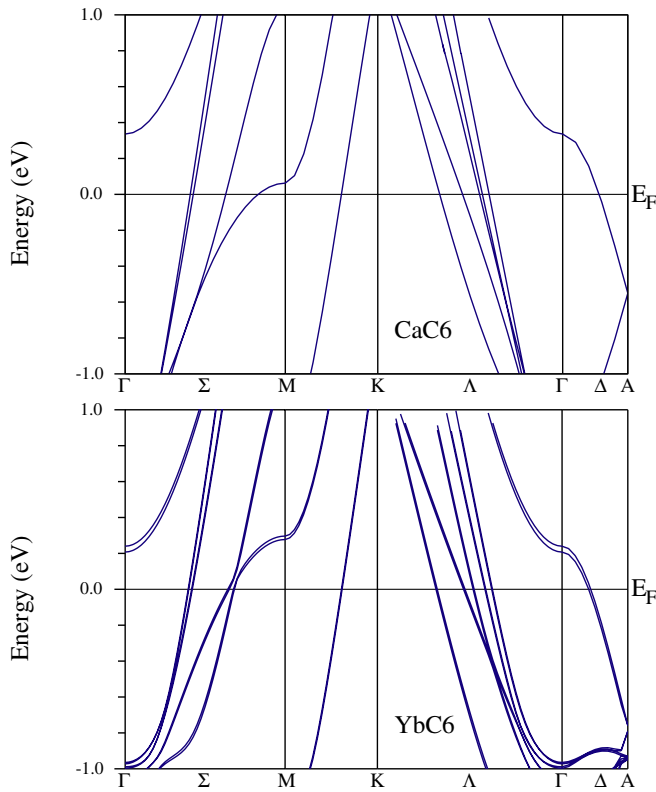


FIG. 4 (color online). Band structure of CaC_6 near the Fermi level, compared with that of YbC_6 .

that the “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 due entirely to Yb/Ca modes and no other differences between the two materials were 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

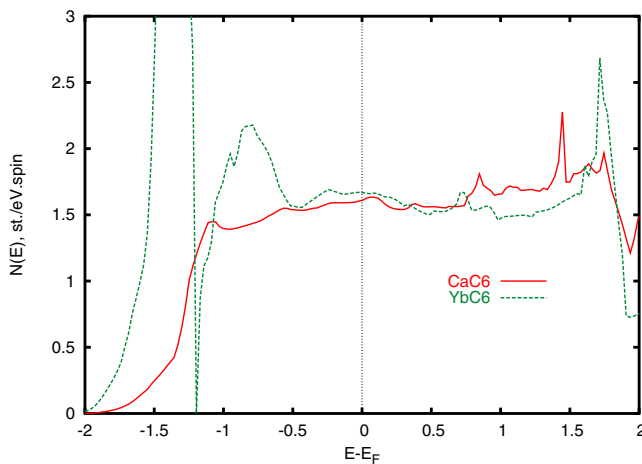


FIG. 5 (color online). Density of states of CaC_6 near the Fermi level, compared with that of YbC_6 .

more curious than important that the rough estimate given in Ref. [5] for Y_2C_3 was 10% of total coupling coming from C-C phonons, and the rest from pure Y or mixed Y-C modes, in interesting agreement with the above estimate for YbC_6 . In reality, of course, there are small but not negligible differences in the two band structures (due mostly to hybridization with the f bands, as discussed above), so the number 0.85 should be understood as a semiquantitative guideline, not an exact prediction for the actual isotope effect.

To summarize, we propose that unusually high for intercalated graphites critical temperatures in CaC_6 and YbC_6 are due mainly to substantial participation of the intercalant electronic states at the Fermi level and, as a consequence, sizable 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 structures share some similarities with $\text{YbC}_6/\text{CaC}_6$, 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. It is worth noting that the free-electronlike three-dimensional band is quite important for superconductivity in GIC in general, as observed in Ref. [2]. The matter of debate is about the mechanism of an enhancement of T_c in YbC_6 and CaC_6 compounds.

Finally, let us discuss which experiments can test the proposed scenario. Measuring isotope effect on Ca is predicted to yield an exponent of the order of 0.4 (again, we cannot make more precise predictions because we completely neglect the possible effect of small differences in the electronic structures of CaC_6 and YbC_6) and that on C of the order of 0.1. 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 $T_{\text{Ca}}^x T_{\text{Yb}}^{(1-x)}$, where x is the Ca concentration. An interesting question is: What would be the 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 in an environment relatively large for their ionic radius and, thus, will have a smaller force constant, leading to some increase of λ . The third effect is that the corresponding Mg modes will have higher frequencies for the same force constants because of smaller mass. If the first two effects appear to cancel each other, codoping with Mg may be a route to even higher T_c . Obviously, more experimental and computational work is required to clarify this issue.

This work was supported by the Office of Naval Research.

Note added in proof.—After this work had been submitted for publication, a preprint [12] appeared that claims that the crystal structure of CaC_6 differs from that of YbC_6 by stacking sequence. While this does not change our conclusions qualitatively, it leaves more room for small differences in the electronic structure and opens a possibility for more contribution of the C modes than anticipated in our work. Indeed, an accompanying linear-response calculation [13] found that superconductivity in CaC_6 is of electron-phonon origin, confirming our prediction, and due to C and Ca phonons in about equal proportion.

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