Superconductivity in Heavy Alkaline-Earths Intercalated Graphites

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We report the discovery of superconductivity below 1.65(6) K in Sr-intercalated graphite SrC$_6$, by susceptibility and specific heat ($C_p$) measurements. In comparison with CaC$_6$, we found that the anisotropy of the upper critical fields for SrC$_6$ is much reduced. The $C_p$ anomaly at $T_c$ is smaller than the BCS prediction indicating an anisotropic superconducting gap for SrC$_6$ similar to CaC$_6$. The significantly lower $T_c$ of SrC$_6$ as compared to CaC$_6$ can be understood in terms of ”negative” pressure effects, which decreases the electron-phonon coupling for both in-plane intercalant and the out-of-plane C phonon modes. We observed no superconductivity for BaC$_6$ down to 0.3 K.

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The discovery of superconductivity in YbC$_6$ and CaC$_6$ [1, 2] initiated intensive theoretical and experimental investigations [3, 4, 5, 6, 7, 8, 9, 10, 11, 12] on the alkali-earth graphite intercalation compounds (GICs). The results of a recent experimental studies, specially the observation of a Ca isotope effect [12], strongly favor electron-phonon($e$-$ph$) coupling rather than exotic electronic mechanisms [3]. Recent ab-initio electronic structure calculations prove that, in contrast to MgB$_2$, $e$-$ph$ coupling involving electronic interlayer (IL) states becomes relevant [3] and is sufficiently strong to generate the relatively high $T_c$’s [4, 5, 10]. These findings stimulates discussions on the variability of the $e$-$ph$ coupling strength in different branches of the electronic and vibrational states for honeycomb layered compounds like MgB$_2$, CaSi$_6$ [13], (Ca,Sr)AlSi [14] and also the hypothetical Li$_2$B$_2$ [12].

Many issues still remain open, especially about the nature of the relevant phonons. In order to modify the phonon spectrum, Ca isotope substitution [12] and hydrostatic pressure experiments [8, 10] have been performed. The isotopic experiments reported a surprisingly high isotope exponent for Ca, $\alpha$(Ca) $\approx 0.5$, close to the BCS limit, suggesting a dominant role of the Ca phonons in the $e$-$ph$ coupling [12]. However, ab-initio calculations predicted similar isotope exponents $\sim 0.25$ for Ca and C, pointing to comparable contributions to the $e$-$ph$ coupling from the Ca and C phonons [2]. The positive pressure dependence of $T_c$ found for CaC$_6$ has been discussed in terms of phonon softening for the in-plane Ca vibrations [4, 10]. Although the experimentally determined $T_c$’s grow almost linearly with pressure, the ab-initio calculations predicted a non-linear increase with a reduced magnitude [2]. To resolve these discrepancies, possible anharmonic effects of the ultrasoft intercalant phonon modes, or a continuous superconducting gap distribution due to anisotropic $e$-$ph$ coupling have been suggested [17, 18], asking for further investigations.

Another way to modify the relevant phonon modes is to vary the intercalant species and replace Ca with other alkaline-earths such as Sr or Ba. Mazin pointed out that for CaC$_6$ and YbC$_6$ the square root of the mass ratio of the intercalants is only 15% larger than the ratio of their $T_c$’s [4]. Thus, according to this ”isotope” effect argument other alkaline-earths GICs may as well be superconducting. In fact, subsequent ab-initio calculations predicted superconductivity for SrC$_6$ at 3.1 K and BaC$_6$ at 0.2 K [10]. In this Letter, we report the discovery of superconductivity in SrC$_6$ at $T_c = 1.65(6)$ K by susceptibility and specific heat measurements and the absence of superconductivity in BaC$_6$ down to $\sim 0.3$ K. The superconducting properties of SrC$_6$ as well as the ab-initio calculations clearly demonstrate that SrC$_6$ can serve to bridge the two seemingly different classes of the superconducting GICs: the low-$T_c$ alkali GICs and the newly-discovered ”high-$T_c$” systems, CaC$_6$ or YbC$_6$. Furthermore, the comparison of SrC$_6$ with CaC$_6$ provides a better insight into the unconventional nature of superconductivity in alkaline-earth GICs.

Samples of SrC$_6$ and BaC$_6$ were synthesized from pieces of highly oriented pyrolytic graphite (Advanced Ceramics, size $\approx 3 \times 1 \times 1$ mm$^3$) and Sr (99.95%) or Ba (99.95%) metal by a vapor phase reaction performed for more than a month at 470°C and 500°C, respectively. X-ray diffraction patterns show no reflections due to pristine graphite or other higher stage intercalated phases, indicating good sample homogeneity. The graphite layer distance increases from CaC$_6$ (4.50 Å) to SrC$_6$ (4.95 Å) and to BaC$_6$ (5.25 Å) as expected from the size of the intercalant atoms. The stacking sequence of SrC$_6$ and BaC$_6$ is found to be of the $\alpha\beta$-type (space group P6$_3$mmc) [19] which differs from the $\alpha\beta\gamma$-type stacking in CaC$_6$. Superconductivity for SrC$_6$ was first observed by ac magnetic susceptibility (119 Hz) measurements to 0.3 K, and subsequently confirmed by specific heat measurements using a PPMS $^3$He calorimeter (Quantum Design). The pressure dependence of $T_c$ was measured up to $\sim 1$ GPa as described in detail elsewhere[9]. In order to understand the
superconducting properties of SrC₆ and compare with those of CaC₆, we also performed ab-initio calculations of the electron-phonon properties for SrC₆ using the experimental αβ stacking [20, 21].

Figure 1 shows a sharp superconducting transition in the magnetic susceptibility \( \chi(T) \) at \( T_c = 1.65 \) (6) K in SrC₆. The transition width \( \Delta T_c \approx 0.06 \) K was determined as the temperature difference between 10% and 90% of the diamagnetic shielding. In a magnetic field, \( T_c \) shifts to lower temperatures and the superconducting transition broadens. In BaC₆, we cannot find any signature of superconductivity down to 0.3 K.

The upper critical fields, \( H_{c2} \), for \( H \) parallel and perpendicular to the \( c \) axis follow the Werthamer-Helfand-Hohenberg (WHH) prediction rather well (Fig. 1(b)). A slight deviation from the WHH curve is found at low temperatures, which has been observed in other GICs such as CaC₆ and KC₈ [24]. Within the scope of the WHH approximation, we obtained \( H_{c2}^{ab}(0) \approx 138 \) Oe and \( H_{c2}^c(0) \approx 276 \) Oe as well as the corresponding coherence lengths, \( \xi_{ab}(0) \approx 1510 \) Å and \( \xi_c(0) \approx 700 \) Å. Similar to CaC₆, \( \xi_c(0) \) is larger than the graphite layer distance, indicating 3-dimensional (3D) superconductivity.

Bulk superconductivity in SrC₆ is confirmed by specific heat \( (C_p) \) measurements. The characteristic \( C_p \) anomaly at \( T_c = 1.65 \) K is clearly observed at \( H = 0 \), and completely disappears with \( H = 500 \) Oe \( (H > H_{c2}(0)) \). There is no offset of \( C_p/T \) at \( H = 0 \) as \( T \to 0 \) K, indicating a complete superconducting phase. Similar to CaC₆, the normal state \( C_p \) deviates slightly from a \( T^3 \) dependence (the inset of Fig. 2), due to low-lying Einstein phonon modes. The normal state \( C_p \) can well be described by \( C_p(T) = \gamma_N T + C_{ph}(T) \) where \( \gamma_N \) is the Sommerfeld constant, and \( C_{ph}(T) = \beta T^3 + \delta T^5 \) is the lattice contribution. The best fit to the \( H = 500 \) Oe data yields \( \gamma_N = 5.92(1) \) mJ/mol K², \( \beta = 0.191(1) \) mJ/mol K⁴, and \( \delta = 0.801(4) \) µJ/mol K⁶. The estimated Debye temperature \( \Theta_D(0) = 414(1) \) K is lower than that of CaC₆ \( (\Theta_D(0) = 598 \) K) as expected from the atomic mass difference. From a comparison of \( \gamma_N \) with the calculated density of states at the Fermi level \( E_F \), \( N(0) \), we estimate the e-ph coupling strength \( \lambda \) using the relation \( \gamma_N = (2\pi^2k_B^2/3)N(0)(1+\lambda) \). With \( N(0) = 1.63 \) states/eV-cell, we arrive at \( \lambda = 0.54(1) \), somewhat lower than in CaC₆, but still in the intermediate coupling regime.

The difference \( \Delta C_p \) between the normal and the superconducting state is shown in Fig. 2. At low temperatures, \( \Delta C_p(T) \) exceeds the BCS prediction while it is slightly lower than the BCS value near \( T_c \). Using the ‘α-model’ which assumes an isotropic s-wave BCS gap \( \Delta(T) \) scaled by the factor \( \alpha = \Delta(0)/k_B T_c \), we were able to fit the detailed temperature dependence of \( \Delta C_p(T)/T \) by adjusting the gap ratio to \( \alpha = 1.67 \). Accordingly, the corresponding \( 2\Delta(0)/k_BT_c = 3.34 \) is somewhat reduced below the weak coupling BCS limit of 3.52.

First, we discuss the anisotropy of the superconducting properties of SrC₆. The anisotropy of the upper critical fields, \( \Gamma_H = H_{c2}^c/H_{c2}^{ab} \) amounts to \( \approx 2 \) at \( T \approx T_c/2 \), close to that of YbC₆ [11], but significantly smaller than found in CaC₆ (\( \Gamma_H \approx 4 \)) [2]. Assuming an isotropic superconducting gap, the anisotropy \( \Gamma_H \) reflects the anisotropy of the Fermi velocities. Our ab-initio calculations for the Fermi surface (FS) of CaC₆ and SrC₆ clearly reveal an elliptical sheet, associated mainly to interlayer states, and a tubular structure, of \( \pi^* \) character (cf. Ref. [16]).

![FIG. 1: (Color online) (a) Temperature dependence of the ac susceptibility of SrC₆ for various fields (as indicated) perpendicular to the c-axis. \( T_c \) is determined from the intersection between the extrapolated lines of the steepest slope of \( \chi(T) \) and of the normal state \( \chi(T) \) as shown by the solid (black) lines. (b) The \( H_{c2}(T) \) for \( H \parallel ab \) plane and \( H \parallel c \) axis. The WHH curve for both \( H \) directions are shown with (red) lines.](image)

![FIG. 2: (Color online) Temperature dependence of \( \Delta C_p(T)/T = C_p(H = 0)/T - C_p(H = 500 \) Oe)/T. The (blue) dashed and (red) solid lines represent the BCS curve and the best fit according to the α-model (see text), respectively. The inset shows the temperature dependence of \( C_p \) at \( H = 0 \) and 500 Oe. The solid (black) line through the data points for \( H = 500 \) Oe is a fit to a polynomial as described in the text.](image)
SrC₆ the FS for the IL bands has a more pronounced 2D character and is open, which results from the 10% increase of the c axis lattice parameter as compared to CaC₆. The anisotropy of the average Fermi velocities \( \Gamma_{\text{av}} \) is very close in the two compounds: \( \Gamma_{\text{av}} \approx 1.9 \) in CaC₆ and \( \approx 1.7 \) in SrC₆. If we, however, consider only the IL sheets where the superconducting gap is larger \[18\], we find a much larger difference: \( \Gamma_{\text{av}} = 1.1 \) for CaC₆ and \( \Gamma_{\text{av}} = 2.1 \) for SrC₆. Therefore, \( \Gamma_{\text{av}} \) of SrC₆ is expected to be larger or at least similar to that of CaC₆. The significantly enlarged anisotropy of \( H_{c2} \) in CaC₆ with respect to SrC₆ therefore cannot be understood in terms of the anisotropy of the Fermi velocity but must be attributed to an anisotropy of the superconducting gap as well.

This conclusion is supported by the reduced \( C_p \) jump observed in SrC₆. Assuming an isotropic gap, the normalized jump, \( \Delta C_p(T_c)/\gamma_N T_c \), grows with the \( e \)-ph coupling strength over the BCS weak coupling limit of 1.432. With \( \lambda \approx 0.54 \) estimated from \( C_p \), \( \Delta C_p(T_c)/\gamma_N T_c \) is expected to be enhanced over the BCS value. The experimental \( \Delta C_p(T_c)/\gamma_N T_c = 1.426 \), however, is smaller than the BCS value. As a characteristic feature of the anisotropic superconducting gap, the entropy "lost" near \( T_c \) is transferred to lower temperatures (Fig. 2) \[18\]. These findings indicate that the superconducting gap in CaC₆ as well as in SrC₆ has a marked anisotropy, which is also supported by recent calculations \[18\], showing that CaC₆ indeed exhibits a strongly \( k \)-dependent superconducting gap due to anisotropic \( e \)-ph interaction. Considering that the deviation of \( \Delta C_p(T) \) from the predicted curve for the isotropic gap model is less pronounced for SrC₆ than for CaC₆ \[17\], the superconducting gap anisotropy is weaker for SrC₆. This is also consistent with the reduced anisotropy in \( H_{c2} \). Therefore, replacing Ca with Sr decreases not only the strength of the \( e \)-ph coupling, but also its anisotropy.

We can now discuss the reduced \( T_c \) of SrC₆, which is about an order of magnitude smaller than \( T_c \) of CaC₆. When Ca is replaced with Sr, \( T_c \) decreases much more than it would be expected in the view of the alkaline-earth "isotopic" substitution \[4\]. With \( \sqrt{M_{Sr}/M_{Ca}} \approx 1.48 \), one would expect a \( T_c \) of 7.8 K for SrC₆, hence much smaller than the experimental value. We thus conclude that the mass of the intercalant is not the main factor which determines \( T_c \). Instead, we found that the \( T_c \)'s of the superconducting GICs strongly depend on the graphite interlayer distance, \( d \). Figure 4 illustrates that \( T_c \) decreases rapidly, almost exponentially with increasing \( d \) for both alkali- and alkaline earth-GICs \[25, 26\]. The increase of \( T_c \) with pressure found for CaC₆ \[8, 9, 10\] and SrC₆ (\( dT_c/dP \sim 0.35 \) K/GPa, the inset of Fig. 4) clearly manifests a similar trend. Obviously, the main factor that governs the significant decrease of \( T_c \) in SrC₆ as well as the absence of superconductivity in BaC₆ down to 0.3 K, is the increased distance between the graphite layers.

Figure 4 clearly demonstrates why. In the calculated phonon density of states (PhDOS) (Fig. 4(c)) and the corresponding Eliashberg functions \( \alpha^2 F(\omega) \) (Fig. 4(d)) for CaC₆ and SrC₆, we observe three groups of phonons: intercalant-related vibrations (\( I_{xy} \) and \( I_z \)) at \( \omega \leq 20 \) meV, C out-of-plane vibrations (\( C_z \)) around

![FIG. 3: \( T_c \) as a function of the graphite layer distance, \( d \) for the alkali-GICs, \( XC_6 \) (\( X = K, Rb \) and Cs) and the alkaline earth-GICs \( XC_6 \) (\( X = Ca, Yb, Sr \) and Ba). For CaC₆, \( T_c \) at high pressure (\( P = 8 \) GPa) \[11\] is also plotted (the half-shaded square) and the graphite layer distance for the compressed CaC₆ is estimated from the theoretically calculated bulk modulus \[4\]. The upper limit of \( T_c \) for BaC₆ is indicated by the arrow. The inset shows \( T_c \) vs. pressure for SrC₆.](attachment:image.png)

![FIG. 4: (Color online) (a) \( T_c \) vs. the position of the bottom of the interlayer bands (\( E_b \)) with respect to \( E_F \) (b) \( T_c \) vs. the band width of the interlayer bands along the \( c \) axis (\( W_c \)). The grey line is meant as guide to the eye. (c) Phonon density of states and (d) Eliashberg function \( \alpha^2 F(\Omega) \) and frequency-dependent electron-phonon coupling \( \lambda(\omega) = 2 \int_0^\infty \alpha^2 F(\Omega)/\Omega d\Omega \) for CaC₆ (orange) and SrC₆ (black).](attachment:image.png)
50 meV, and C bond-stretching vibrations (C\textsubscript{xy}) at ω > 150 meV. The qualitative shape of α^2 F(ω) is the same in the two compounds, indicating a similar spectral distribution of the e-ph interaction. But the total λ decreases from 0.83 in CaC\textsubscript{6} to 0.56 in SrC\textsubscript{6}, while the logarithmic-averaged phonon frequency (ω\textsubscript{ln}) remains unchanged at ∼ 305 K. The results are in very good agreement with the previous calculations for SrC\textsubscript{6} with the αβγ stacking\cite{4}. Within computational accuracy, the difference between the αβ and αβγ stackings seems negligible in contrast to a previous conjecture\cite{4}. Using the Allen-Dynes formula, with μ\textsuperscript{*} = 0.145, we obtain T\textsubscript{c} = 11.4 K for CaC\textsubscript{6} and T\textsubscript{c} = 3.1 K for SrC\textsubscript{6}, in reasonable agreement with the experimental results and previous calculations\cite{16}.

The reduction of T\textsubscript{c} in SrC\textsubscript{6} is due to the simultaneous decrease of the I\textsubscript{xy} and C\textsubscript{z} contribution to the e-ph coupling. The reduced coupling for the low-lying I\textsubscript{xy} vibrations has a negative effect on T\textsubscript{c}, but it is also very effective in increasing ω\textsubscript{ln}, thus, the effect is partly compensated. On the other hand, the large reduction of coupling associated to C\textsubscript{z} vibrations, which happens at energy scales comparable to ω\textsubscript{ln}, reduces λ leaving ω\textsubscript{ln} unchanged, and thus has a large effect on the T\textsubscript{c}. The reduction of e-ph coupling for C\textsubscript{z} vibrations in the intermediate energy range is essential to explain the significantly lower T\textsubscript{c} for SrC\textsubscript{6} than CaC\textsubscript{6}.

The e-ph interaction for the C\textsubscript{z} modes, and to a lesser extent for the I\textsubscript{xy} ones, is associated to the interband coupling between the IL and π\textsuperscript{*} states\cite{27}. Going from CaC\textsubscript{6} to SrC\textsubscript{6}, this interband coupling is essentially reduced by the increase of the c axis lattice constant, which decreases the real-space overlap between IL and π\textsuperscript{*} wavefunctions. The characteristic parameter monitoring the IL-π\textsuperscript{*} overlap is the bandwidth of the IL band along the c axis (W\textsubscript{IL}). Figure 4(b) demonstrates that T\textsubscript{c} for both alkalii- and alkaline-earth-GICs is directly correlated to W\textsubscript{IL}, clearly explaining the T\textsubscript{c} dependence on the graphite layer distance. This observation is in strong contrast to the dependence of T\textsubscript{c} on the degree of filling for the IL band (Fig. 4(a)). Even though this band has to be occupied for superconductivity to occur\cite{3}, there is no clear correlation of T\textsubscript{c} with the number of IL electrons.

Our findings indicate that C phonon modes play a nontrivial role in the superconductivity of the GICs, in contrast with the conjecture from the Ca isotope experiments\cite{12}. Since C would give a sizable contribution to the isotope effect, the total isotope exponent would exceed the BCS limit α\textsubscript{BCS} = 0.5, which requires further studies on the effects of C isotope substitution.

In conclusion, we reported that SrC\textsubscript{6} becomes superconducting at T\textsubscript{c} = 1.65(6) K, but BaC\textsubscript{6} stays normal conducting down to 0.3 K. The reduced C\textsubscript{p} jump at T\textsubscript{c} in SrC\textsubscript{6} and the reduced anisotropy H\textsubscript{c2} in comparison with the corresponding data for CaC\textsubscript{6} strongly supports the idea of an anisotropic superconducting gap\cite{17, 18}.

We give clear evidence that T\textsubscript{c} of the GICs essentially depends on the graphite layer distance due to sensitive change of e-ph coupling for both in-plane intercalant and the out-of-plane C phonon modes. Our results suggest that a possible route to increase T\textsubscript{c} is to replace Ca by smaller atoms, such as Mg. Several attempts to prepare pure MgC\textsubscript{6} have failed so far, but partial substitution of Mg or Li, as long as the filling of the IL bands is kept, could be possible to reduce d, stabilize the structure, and as a result, increase T\textsubscript{c}.

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Here we do not consider the metal-rich GICs synthesized under high pressures such as LiC$_2$ which are known to be metastable.

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