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Large energy gaps in CaC_6 from tunneling spectroscopy: Possible evidence of strong-coupling superconductivity

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Tunneling in CaC_6 crystals reproducibly reveals superconducting gaps Δ of 2.3 ± 0.2 meV that are $\sim$40% larger than reported earlier. In an isotropic *s*-wave scenario, that puts CaC_6 into the class of very strongly coupled superconductors, since $2\Delta/kT_c \sim 4.6$, implying that soft Ca phonons are primarily involved in the superconductivity. This conclusion explains the relatively large Ca isotope effect found recently for CaC_6, but it could also signal a strong anisotropy in the electron-phonon interaction.

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The discovery of superconductivity at 11.6 K in CaC_6 at ambient pressures,[1] and up to 15.1 K at 8 GPa,[2] has reinvigorated interest in graphite intercalation compounds. While the possibility of unconventional superconductivity has been suggested,[3] the collective experimental data on CaC_6 are consistent with weakly coupled electron-phonon-driven superconductivity with a nearly isotropic energy gap. The recent scanning tunneling spectroscopy,[4] specific heat,[5] and penetration depth measurements[6] all indicate BCS weak-coupling superconductivity that is consistent with linear response theory.[7] However, Mazin *et al.*[8] have pointed out several outstanding problems with the above picture, including its inconsistency with recent data[9] showing a large isotope effect for Ca and the less than perfect agreement with theory for the temperature dependence of the specific heat and the upper critical field $H_{c2}(T)$ data. The specific heat data are better fitted with an anisotropic energy gap.[10] Furthermore, the isotope effect and $H_{c2}(T)$ problems would disappear if CaC_6 were a strongly coupled superconductor. These results suggest that further studies of electron-phonon coupling in CaC_6 are warranted.

Here we report large energy gaps and possible evidence for strong coupling in CaC_6 based on tunneling in both superconductor–insulator–normal metal (SIN) and SIS junctions. Both junction types reveal a gap parameter significantly larger than previously reported, yielding a strong-coupling ratio $2\Delta/kT_c \sim 4.6$. Andreev reflection spectroscopy (SN junctions) on the same crystals support this large gap. We show that within a conventional isotropic *s*-wave picture such a large strong-coupling ratio indicates that soft phonon modes must dominate the pairing of electrons. Low-frequency modes in CaC_6 involve only Ca and, therefore, our results would lead to a natural explanation of the large Ca isotope effect. However, puzzles still remain, and this result may have broader implications by constraining the band structure and/or the calculation of gap anisotropy.[10]

Preparation of CaC_6 used the alloy method as described by Emery *et al.*[11] A stainless steel (SS) tube is cleaned, baked at 900 °C in vacuum, and loaded with lithium and calcium in a 3:1 atomic ratio. Natural, single-crystal graphite flakes are added and then the SS ampoule is mechanically sealed and placed inside a one-zone furnace, evacuated to 2×10^{-7} Torr, and then filled with argon gas. The reaction takes place in an argon atmosphere for 10 days at 350 °C. The ampoule is then transferred to an argon glove bag, where the alloy is remelted and the Ca intercalated graphite crystals are extracted.

Figure 1 displays the x-ray diffraction pattern of a typical CaC_6 crystal showing the (00ℓ) diffraction peaks obtained using Cu $K\alpha$ radiation taken in the Bragg-Brentano geometry. No lines corresponding to hexagonal graphite are present within our detection limits, confirming the bulk nature of the samples. Magnetization data, shown in the inset of Fig. 1, were taken in a μ-metal-shielded, noncommercial superconducting quantum interference device magnetometer on warming in a field of 0.1 G parallel to the *c* axis of the sample after zero-field cooling. They reveal a sharp ultralow-field superconducting transition onset at 11.6 K.

Tunnel junctions were obtained at $T=1.65$ K by contacting a Au tip to CaC_6 crystals (see Ozyuzer *et al.*[12]), while

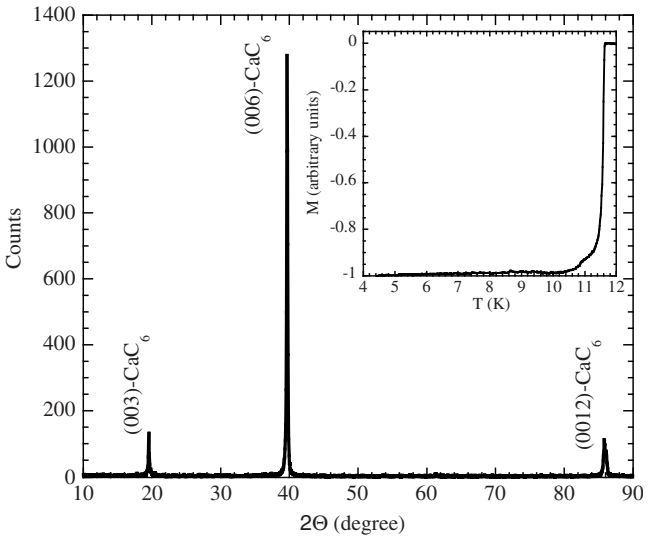

FIG. 1. (00ℓ) diffraction peaks using Cu $K\alpha$ radiation. Inset: Normalized magnetization in a field of 0.1 G.

SIS junctions use a CaC_6 tip. The CaC_6 samples were mounted on the cryostat insert in a N_2 atmosphere and immediately cooled down to 4.2 K. For SIN junctions, CaC_6 crystal flakes were oriented such that the vertical motion of the gold tip was nominally along the *c* axis. For SIS junctions, a tip was fabricated from another CaC_6 crystal and aligned such that the tip and substrate crystals had similar *c*-axis orientations. Initial contacts of the tips in both configurations led to junctions of varying quality but with typical gap parameters $\Delta < 1.7$ meV. The relative ease of forming SIN and SIS tunnel junctions indicates that there is an insulating surface layer on CaC_6, which is presumably the high-band-gap CaO. After repeated contacts of tip and sample, likely resulting in some mechanical cleaning of the CaC_6 surface, the junction characteristics improved and the gap parameters were greater than 2–2.5 meV. The proof that this procedure enabled low-temperature, effective, ultrahigh-vacuum cleaning of the surface was the fairly common appearance of Andreev reflection spectra which indicate a clean superconductor-Au junction.

Figure 2 shows *I*-*V* and dI/dV vs *V* for some of the high-quality tunnel junctions (two SIN and one SIS) and one SN Andreev contact. The well-defined conductance peaks for the SIS junctions are seen at exactly twice the voltage of the SIN peaks, as expected. The large ratio of peak height to high voltage background as well as the relatively low zero-bias conductance (near zero for the SIS junction) attest to the high quality of the junctions. Thus far we have not observed the flat subgap conductance expected for an isotropic *s*-wave energy gap, which may itself be an indication of gap anisotropy,[10] in which case the values reported here would be the maximum gaps. For convenience, fits of the raw conductance data to a modified BCS density of states (as in Ref. 4) with an empirical scattering rate[13] Γ are shown as dashed lines in Figs. 2(a) and 2(b). The gaps for these SIN and SIS junctions are 2.3 and 2.4 meV, respectively. The Andreev reflection data [Fig. 2(a), left inset] show the expected factor of 2 enhancement of the conductance below the energy-gap voltage for a clean metal-to-metal contact. The SN energy gap can only be estimated to be 2.1–2.6 meV as there is no rigorous fitting procedure available for the entire spectrum.

Figure 3 displays a set of SIN tunneling data obtained on three different CaC_6 crystals. As in previous reports,[4] the tunneling conductance shows no evidence of multiband superconductivity like the distinct energy gaps observed in MgB_2 (for a review, see Ref. 14). While the numerous junctions analyzed after initial surface cleaning exhibit a varying degree of quality, they all exhibit a single gaplike feature, and fits to all such SIN and SIS data lead to a range of gaps from 2.1 to 2.5 meV, with an average value of 2.3 meV.

We can easily rule out the possibility of extrinsic factors emulating the large gap we observe in this work. For example, the SIN data could be from an inadvertent SIS break junction caused by a piece of the CaC_6 crystal sticking to the Au tip. In such a case, the peak at 2.3 mV would be the result of two pieces with an average $\Delta = 1.15$ meV, a value much smaller than the published range of 1.6–1.8 meV. This is unlikely. Furthermore, the temperature dependencies of SIN and SIS junctions are very different. For example, as *T* increases, SIS junctions reveal a closing of the 2Δ conductance peak in the raw data, as well as the development of a conductance peak at zero bias due to thermally created quasiparticles. The temperature dependence of one SIN junction with $\Delta = 2.3$ meV is shown in Fig. 4. Although not as high a quality junction, the data show typical SIN behavior without any evidence for a zero-bias peak or any other subgap peak developing at higher *T*.

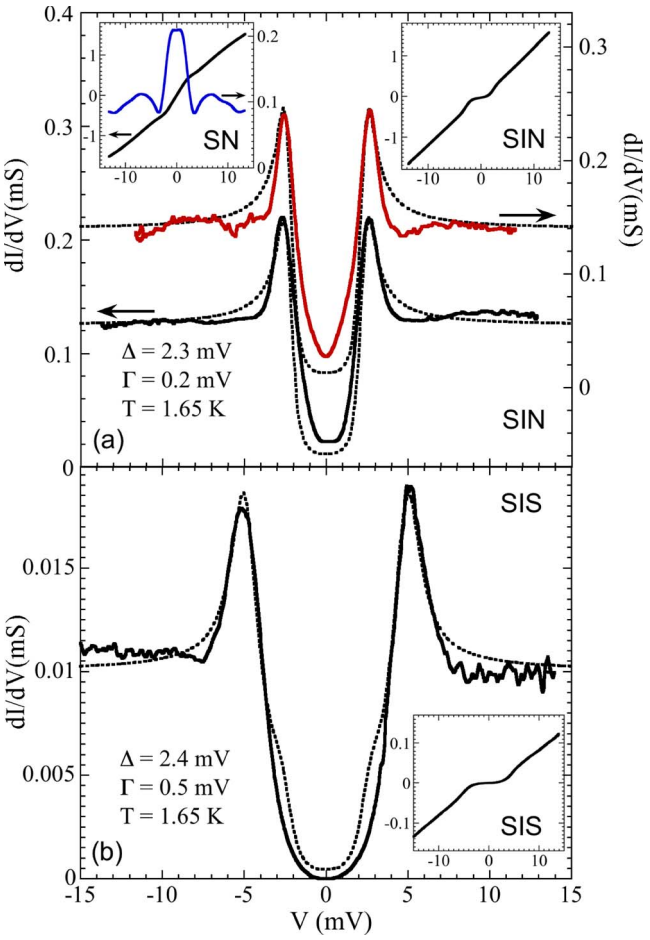

FIG. 2. (Color online) (a) Two SIN $(dI/dV)(V)$ are shown for different junctions at 1.65 K, each fitted with an identical BCS curve. (b) One $(dI/dV)(V)$ of a SIS junction at 1.65 K, along with the BCS fit. Fits use the parameters shown in the respective plots. Right-hand insets: Corresponding $I(V)$ data; the $I(V)$ curve in (a) corresponds to the lower dI/dV. Left-hand inset in (a): An example of measured Andreev reflection characteristics, $I(V)$ and corresponding $(dI/dV)(V)$. All insets: Horizontal axes are voltages in mV, left vertical axes currents in μA, right vertical axes, when present, conductance in mS.

Multijunction effects are also easily ruled out as they lead to additional structures not seen in the data. For example, consider the SIS junction in Fig. 2(b) as a multiple junction, e.g., two independent SIS junctions in series. In this case the observation of a single conductance peak would require that the two independent junctions have identical resistances, a highly unlikely scenario. No such multiple-junction structure can be conceived for the Andreev reflection data.

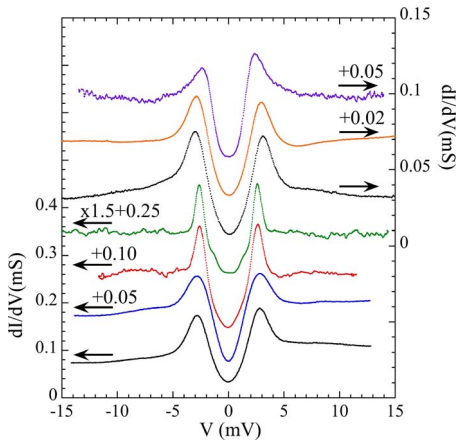

FIG. 3. (Color online) A variety of SIN junctions made on three different crystals of CaC_6 showing consistent gap values of 2.1–2.5 meV.

The increase in T_c from 11.5 to $\sim$15.1 K at a pressure[2] of 8 GPa in CaC_6 forces us to consider the possibility that the larger Δ results from a larger T_c brought about by local tip pressure. Noting that the yield stress of high-purity Au at 4.2 K is less than 100 MPa readily dispels this possibility.[15] In addition, we find similar large gaps for SIS junctions without the soft Au tip. Therefore we conclude that the common observation of $\Delta \sim 2.3$ meV for SIN, SIS, and SN junctions is not a consequence of extrinsic factors.

Turning now to the interpretation of these results, we first consider an isotropic *s*-wave scenario. Our measured gaps would put CaC_6 in the class of very strongly coupled superconductors ($2\Delta/kT_c \sim 4.6$), which would imply that the electron-phonon coupling strength λ is significantly larger than the theoretical result[7] of 0.83. Here, λ is an integral over $\alpha^2F(\omega)/\omega$, where α is the electron-phonon matrix element and $F(\omega)$ is the density of phonon states of frequency ω. Clearly, the integrand of λ is heavily weighted by the low-frequency contributions, so the combination of large λ and

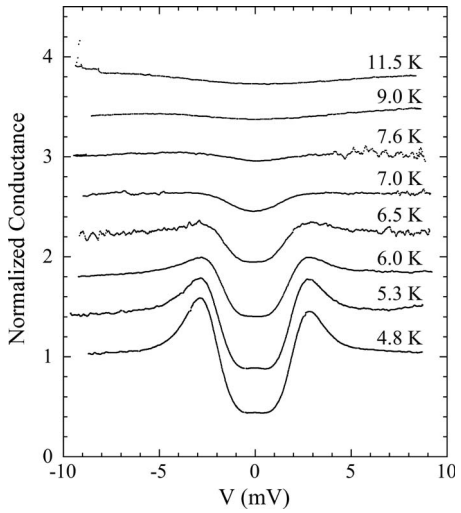

FIG. 4. Temperature dependence of dI/dV is shown for one SIN junction.

modest T_c can occur within the standard strong-coupling theory of Allen and Dynes[16] only if their T_c equation prefactor $\omega_{\log}$, defined therein, is very small. It is useful to remember another strongly coupled superconductor, Pb, where the origins of the large strong-coupling ratio and similar T_c of 7.2 K are its low-energy (4–8 meV) phonons.[17] Using the empirical results for conventional superconductors,[18] a strong-coupling ratio of 4.6 and T_c of 11.6 K leads to a characteristic phonon energy $\omega_{\log} \sim 5-7$ meV. In the case of CaC_6, such soft modes are a characteristic of the Ca intercalant only.[7,8] This then suggests that Ca phonons are primarily involved in the pairing of electrons, a result which is quite different from the weak-coupling picture, but which would readily explain the large isotope coefficient found with Ca isotopic substitution.[9]

The phonon density of states in CaC_6 determined from band structure and linear response theory[7,8] shows in-plane zone boundary Ca modes near 10 meV. This energy has been confirmed by inelastic x-ray scattering,[19] indicating that there is no strong renormalization of the Ca modes due to electron-phonon coupling. The characteristic frequency of 5–7 meV found in the above analysis is therefore difficult to reconcile with measured Ca mode frequencies. Furthermore a low-frequency peak in $\alpha^2F(\omega)$ should be observable in the tunneling conductance, as for the classic case of Pb.[16] We see a noticeable and reproducible negative deviation of the raw SIN data [Fig. 2(a)] in high-quality junctions from the smeared BCS fit for $|eV| > \Delta$; however, the quality of the present tunneling data and our understanding of the normal-state background are insufficient to confirm that this feature is due to such a low-frequency excitation.

The above analysis shows that puzzles remain in an isotropic *s*-wave scenario. Our large energy gaps may therefore be an indication of anisotropy in the electron-phonon interaction. It is intriguing that the maximum gap predicted by Sanna *et al.*[10] using density functional calculations is near our measured value of 2.3 meV. This large gap originates from the intercalant band that would be most sensitive to the Ca phonons. The large Ca isotope effect may therefore be linked to an anisotropic electron-phonon coupling. In that case, our data average the gap over a (tunneling) cone of momenta angles centered along the *c* axis. The measured value of 2.3 meV represents the maximum value within that cone.

In summary, the superconducting gap, or its maximum value in an anisotropic scenario, is found to be 2.3 meV in CaC_6. This value exceeds the previously reported one by approximately 40%. Noting the consistency of SIN, SIS, and SN junction configurations, and ruling out possible extrinsic causes, we conclude that this value of the energy gap is intrinsic to CaC_6. The resulting strong-coupling ratio of $\sim$4.6 changes the current understanding of superconducting pairing in CaC_6 considerably. Although this result departs from the present consensus of isotropic weak coupling,[4–7] it provides a direct explanation for the large isotope effect found with Ca substitution[9] and may help resolve the linear temperature dependence of $H_{c2}(T)$. This result may have a broader impact on band structure and electron-phonon

calculations,[8] arguing in favor of an anisotropic gap. In any scenario our result points toward the importance of the intercalant in the superconductivity, an idea that was proposed earlier.[20]

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