Pressure dependence of the superconducting transition temperature in C$_6$Yb and C$_6$Ca

Robert P. Smith,* Anna Kusmartseva, Yuen T. C. Ko, and Siddharth S. Saxena
Cavendish Laboratory, University of Cambridge, J. J. Thompson Avenue, Cambridge CB3 0HE, United Kingdom

Ana Akrap and László Forró
IPMC/SB, EPFL, CH-1015 Lausanne-EPFL, Switzerland

Mukul Laad
Department of Physics, Loughborough University, Leicestershire, LE11 3TU, United Kingdom

Thomas E. Weller, Mark Ellerby, and Neal T. Skipper
Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

We have studied the evolution, with hydrostatic pressure, of the recently-discovered superconductivity in the graphite intercalation compounds C$_6$Yb and C$_6$Ca. We present pressure-temperature phase diagrams, for both superconductors, established by electrical transport and magnetization measurements. In the range $0-1.2$ GPa the superconducting transition temperature increases linearly with pressure in both materials with dT_c/dP = $+0.37 \pm 0.01$ and $+0.50 \pm 0.05$ K/GPa for C$_6$Yb and C$_6$Ca, respectively. The transition temperature in C$_6$Yb, which has been measured up to 2.3 GPa, reaches a peak at around 1.8 GPa and then starts to drop. We also discuss how this pressure dependence may be explained within a plasmon pairing mechanism.

PACS number(s): 74.25.Dw, 74.62.Fj, 74.70.$-$b

I. INTRODUCTION

Our recent discovery of superconductivity in C$_6$Yb and C$_6$Ca at temperatures of 6.5 and 11.5 K, respectively,[1] has generated renewed interest in the study of superconductivity in graphite intercalation compounds. Pure graphite is not superconducting down to the lowest temperatures measured, but it has long been known that the introduction of metal atoms in-between the graphite sheets, in a process known as intercalation, can produce superconductivity. The first of these graphite intercalate materials to be reported as superconducting was C$_8$K which has a transition temperature (T_c) of 0.15 K.[2,3] Subsequently, several more examples of superconducting graphite intercalation compounds were found,[4] but their transition temperatures are generally low. The superconductivity in these compounds was generally accepted to be due to a conventional phonon mechanism. However, the elevated transition temperatures discovered in C$_6$Yb and C$_6$Ca has caused this question to be reexamined.[5–8] Studying how the superconductivity evolves with pressure will contribute to a fuller understanding of the superconductivity in graphite intercalate compounds (GICs), and help shed light on the question of the pairing mechanism.

The pressure dependence of T_c in GICs was first studied in the potassium-mercury systems C$_8$KHg and C$_4$KHg, with two and one carbon layers between intercalant layers, respectively.[9,10] The superconducting transitions of these materials were found to decrease linearly with pressure as dT_c/dP=-0.65 and -0.5 K/GPa, respectively. These dT_c/dP gradients are similar to typical values for three-dimensional elemental superconductors such as tin. This suggested that the observed pressure dependence in these compounds is due to known mechanisms such as the pressure dependence of the density of states at the Fermi level and the stiffening of the phonon frequencies under pressure.[10] The

pressure dependence of T_c in C$_8$K has also been measured;[9] in this case there is a nonmonotonic, nonreversible increase in T_c which is probably due to structural transitions.

In this paper, we present studies of magnetization and resistivity measurements showing how the superconducting transition temperature of C$_6$Yb and C$_6$Ca evolves at pressures up to 2.3 GPa. This extends some previous work carried out under pressure on C$_6$Yb by some of the authors.[11]

II. METHODS

Magnetization measurements were made using a miniature CuBe piston clamp cell in a Quantum Design superconducting quantum interference device magnetometer (MPMS7); the superconducting transition of tin served as a pressure gauge. Resistivity measurements were carried out with silver paint contacts on samples of typical dimensions $3 \times 1 \times 0.1$ mm^3 from two different batches in two different laboratories. Measurements in Cambridge used samples with residual resistivity ratios (RRRs) of around 10 in a piston cylinder clamp cell and a low-frequency ac four-probe technique with an adiabatic demagnetization refrigerator, an n-pentane–isopentane pressure medium, and a tin pressure gauge. Measurements in Lausanne used better-quality samples with RRRs of 25 mounted into a Cu-Be clamped pressure cell. The pressure medium was kerosene and a calibrated InSb pressure gauge was used.

III. RESULTS

A. C$_6$Yb

The data used to deduce the pressure dependence of T_c in C$_6$Yb were obtained by magnetization and resistivity measurements. The values of T_c from all these measurements
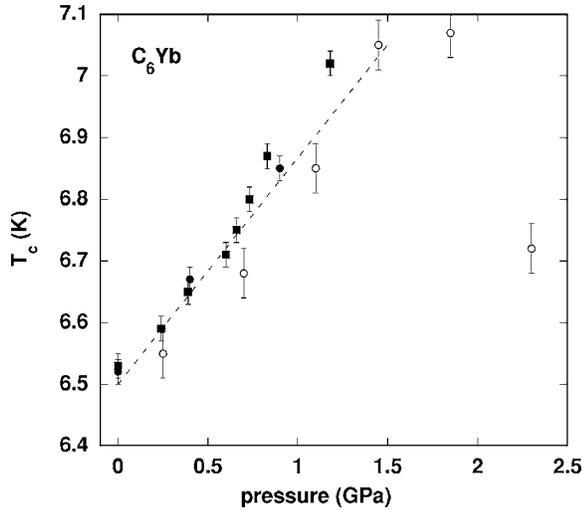
FIG. 1. The superconducting transition temperature T_c of C_6Yb as a function of pressure inferred from magnetization data (■) and resistivity data from Cambridge (●) and Lausanne (○); see Sec. II. T_c is determined by the maximum of the temperature derivative of the data. The dotted line has a gradient of 0.37 ± 0.01 K/GPa. The magnetization data were taken during the application, removal, and reapplication of pressure.

show reasonable agreement and are shown in Fig. 1.

Examples of the data used to determine T_c are shown in Fig. 2. In each case the transition temperature is determined by the maximum in the temperature derivative of the data. The two sample orientations appropriate to GICs (measuring ρ and M parallel and perpendicular to the c axis) were measured. There is no significant difference in T_c between the two orientations. There is no evident broadening of the transition with pressure. These results were found to be reproducible after the removal and reapplication of pressure, and demonstrate that the shift in T_c is reversible.

We can see from Fig. 1 that the superconducting transition temperature of C_6Yb initially increases linearly with pressure with a gradient of $dT_c/dP = +0.37\pm0.01$ K/GPa over the range $0-1.2$ GPa. There is then a peak in the transition temperature of just under 7.1 K at around 1.8 GPa before the transition temperature drops at higher pressures. This drop needs to be studied further with higher-pressure measurements.

An interesting feature of the resistivity data is that the normal-state resistivity increases with increasing pressure. This is unusual as the application of pressure would normally be expected to make the material more metallic. In addition, limited measurements of the c-axis resistivity [Fig. 2(b) inset] seem to show a reduction of the normal-state c-axis resistivity with increasing pressure.

We were also able to estimate the pressure dependence of the upper and lower critical fields using magnetization measurements. However, due to the field dependence of the susceptibility of the pressure cell we can only state that the superconducting critical fields also appear to increase with pressure up to 1.1 GPa.

B. C_6Ca

Plots of magnetization versus temperature, at several pressures, for C_6Ca are shown in Fig. 3. The transition tempera-
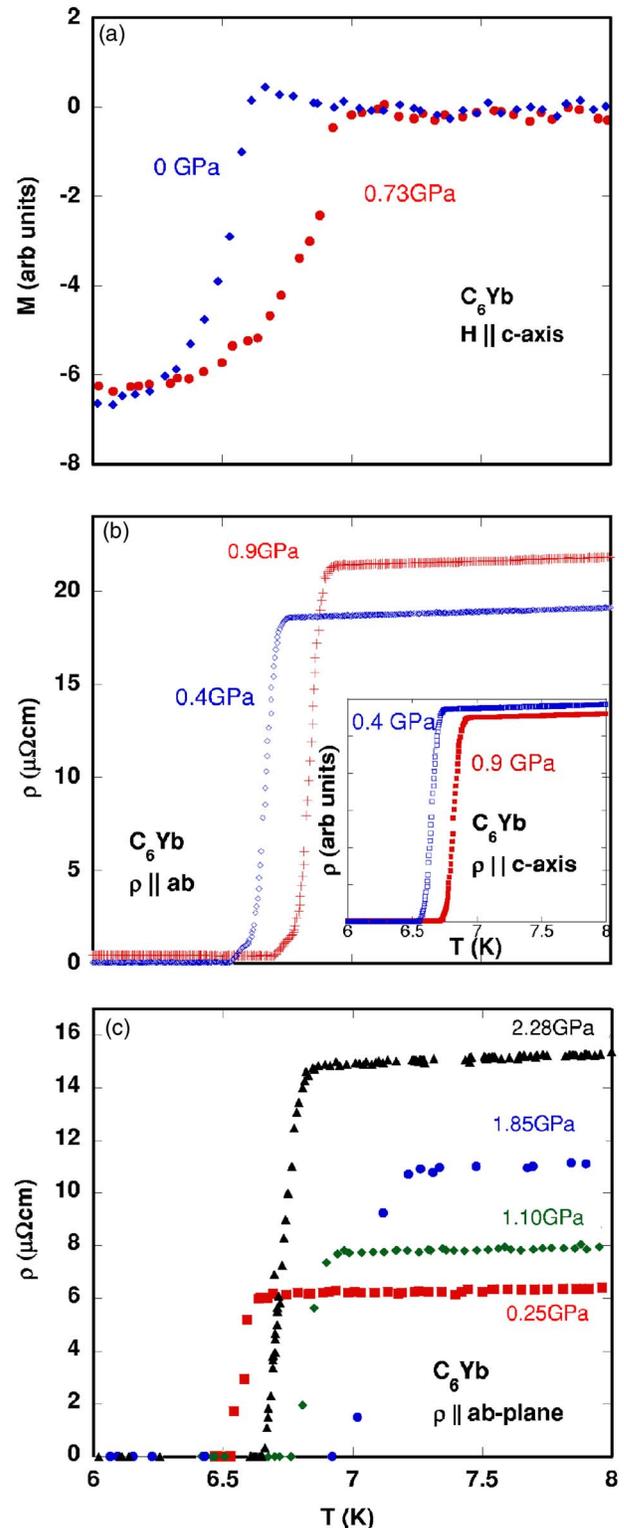

FIG. 2. (Color online) Sample plots of the data used to determine the phase diagram in Fig. 1. (a) Magnetization as a function of temperature at pressures of 0 and 0.73 GPa in the $H\|c$ axis field orientation; the background due to the pressure cell has been subtracted. (b) Resistivity as a function of temperature (Cambridge) at pressures of 0.4 and 0.9 GPa in the $\rho\|ab$ plane and $\rho\|c$ axis orientations (inset). (c) Resistivity as a function of pressure (Lausanne) at pressures of 0.25, 1.1, 1.85, and 2.28 GPa in the $\rho\|ab$ plane orientation.
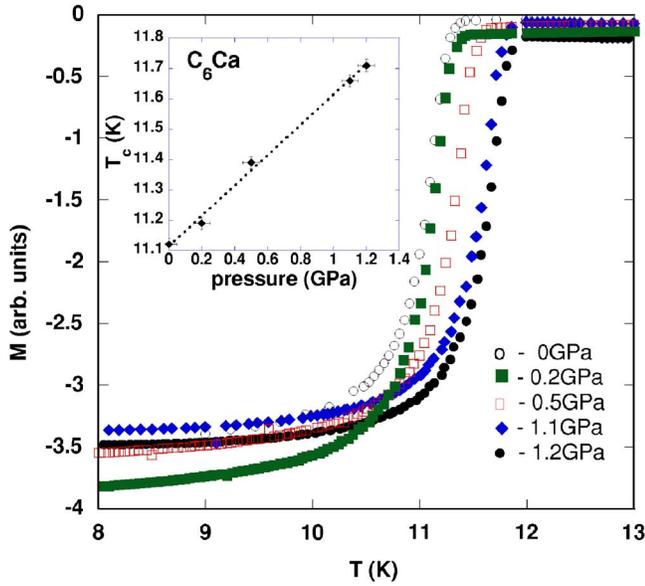
FIG. 3. (Color online) Plots of magnetization versus temperature for C_6Ca at several pressures. The data were taken in a field of 50 Oe and a temperature-independent background of the pressure cell has been subtracted. Inset shows how T_c (as defined by the maximum of dM/dT) varies with pressure; the dotted line is a guide to the eye and has a gradient of 0.5 K/GPa.

tures can be obtained from these using the maximum of dM/dT. The variation of T_c with pressure is shown in the inset of Fig. 3. We see that in the range 0 to 1.2 GPa the transition temperature varies linearly with pressure with a gradient of 0.5 K/GPa.

IV. DISCUSSION

The transition temperature of a superconductor would generally be expected to depend on a number of factors. If we consider the case of superconductivity being mediated by some bosonic mode then in the weak coupling limit we may expect

$$T_c \approx \theta_B e^{-1/\lambda}, \tag{1}$$

where θ_B is the typical energy of the bosonic modes and λ is given by

$$\lambda = 2 \int_0^\infty \frac{\alpha^2 F(\Omega)}{\Omega} d\Omega. \tag{2}$$

For modes that have typical energies much smaller than the Fermi energy, $\alpha^2 F(\Omega) \sim N(E_F) M^2 F(\Omega)$, where $N(E_F)$ is the electron density of states, M is the electron-boson matrix element, and $F(\Omega)$ is the boson density of states.

In simple elemental superconductors the effect of pressure is generally to reduce T_c due to two main factors: (i) the stiffening of the phonon modes, which decreases the phonon density of states at low energies, and (ii) the reduction of $N(E_F)$ due to band broadening. In more complicated systems the effect of pressure on the phonon spectrum and the density of states is more complex and harder to predict. In addition

there may be some pressure dependence of the matrix element M.

In the cases of C_6Yb and C_6Ca the initial positive pressure dependence of T_c is opposite to the simple expectation but may still be explained within a phonon pairing model by an increase of $N(E_F)$ or a softening of the phonon modes, particularly if pressure induces charge transfer between the intercalant and the graphite electron states. Two very recent studies[12,13] have reported the pressure dependence of T_c in C_6Ca and confirm an initial linear increase of T_c. Some theoretical analysis in one of these papers[13] suggests that the increasing T_c in C_6Ca is due to the softening of the relevant phonon mode. A similar mechanism may explain the increasing T_c in C_6Yb, but this needs to be checked theoretically. In C_6Ca the transition temperature is reported[12] to increase linearly up to 8 GPa before dropping at higher pressures, probably due to a structural phase transition. It could be that we are seeing a similar effect in C_6Yb although our results above 1.5 GPa are tentative and require confirmation. Comparing how the predicted[14] [using the density functional theory within the local density approximation (LDA)] cell volumes for C_6Yb and C_6Ca vary with pressure shows that the cell volume of C_6Ca is reduced from 69.5 $Å^3$ at ambient pressure to 66 $Å^3$ at 8 GPa whereas the cell volume of C_6Yb is reduced from 68.9 $Å^3$ at ambient pressure to 67.5 $Å^3$ at 2.3 GPa. This suggests that 2.3 GPa may not be a high enough pressure to induce a phase transition in C_6Yb similar to that seen in C_6Ca. Thus the drop in T_c we observe at 2.3 GPa is probably not related to a structural phase transition. There are many similarities between C_6Ca and C_6Yb; one significant difference is the Yb f-orbitals which at ambient pressure are predicted[5] to be well below the Fermi surface. At high pressures, in analogy with many Yb compounds which become more magnetic under pressure,[15] we may expect the Yb f-orbitals to move close to the Fermi surface, leading to the possibility of magnetism in C_6Yb, which would be expected to have a significant effect on the superconductivity.

We should also point out that the above results do not rule out the suggested acoustic plasmon mechanism[5] as it would be possible for the relevant bosonic acoustic plasmon mode also to be softening with pressure. With reference to Csanyi *et al.*,[5] the part of the interlayer (Ca-derived) band hybridizing with the graphite π^* band is quasi-two-dimensional in nature (Fig. 2 of Ref. 5 for C_6Ca). It is this hybridized band that would supply the plasmons necessary for plasmon-mediated superconductivity.

With increasing pressure, LDA work shows charge transfer from this interlayer band to the π^* bands of graphite. While Kim *et al.*[13] argue that this decrease in the filling of the interlayer band is evidence against plasmon-mediated superconductivity, we argue that this is not necessarily true.

To show this we idealize the actual band structure, replacing the Ca interlayer band by a narrower two-dimensional (2D) band and the graphite π^* bands by a wider band. In this idealized picture we can follow the argument of, for example, Refs. 16 and 17. In the interlayer band the plasmon spectrum is computed in the random-phase approximation (RPA) from the poles of the denominator of

$$\Gamma_{q\omega} = \frac{V_q}{1 - V_q \Pi_{q\omega}} = \frac{V_q}{\epsilon_{q\omega}} \tag{3}$$

where $\epsilon_{q\omega}$ is the dynamical dielectric function, $\Pi_{q\omega}$ is the RPA polarizability of the 2D layer, and V_q is the electron-electron interaction function. Using the RPA polarizability for a two-dimensional electron layer, given by

$$\mathrm{Re}\,\Pi_{q\omega} = -2N(E_F)\left(1 - \frac{\omega}{\sqrt{\omega^2 - (qv_F)^2}}\right), \tag{4}$$

results in a plasmon spectrum of the form

$$\omega_q = v_f q \sqrt{1 + \frac{(N(E_F)V_q)^2}{1/4 + N(E_F)V_q}}. \tag{5}$$

For weakly-coupled 2D layers this leads to a spectrum that has an acoustic branch. Reducing the number of electrons in a 2D layer reduces v_F, making the plasmons slower, thus enhancing the plasmon density of states $\alpha_{pl}^2 F_{pl}(\omega)$ and therefore T_c.

We now consider how the real systems may compare to this model. In C_6Ca the interlayer band that is hybridized with the π^* bands has 2D character. In the case of C_6Yb, the interlayer band of hybridized Yb-graphite character has a finite dispersion along c; this leads to the formation of a small gap and hence an optical plasmon. Again, this is not necessarily an argument against the plasmon-mediated superconductivity, as coupling to optical phonons is required

within the phonon-mediated picture.[13] In summary, the reduction of the number of electrons in the interlayer band with increasing pressure reduces v_F for the interlayer band, making the plasmons slower and enhancing the plasmon density of states and hence T_c. This qualitative conclusion would hold until the interlayer band becomes empty, at higher pressure, when the plasmon mechanism would switch off.

V. CONCLUSIONS

In conclusion, we have shown that the pressure dependence of the superconducting transition temperature in both C_6Yb and C_6Ca is initially positive, up to 1.2 GPa, with $dT_c/dP = +0.37 \pm 0.01$ and 0.50 ± 0.05 K/GPa, respectively. This initial increase is followed by a maximum and subsequent decrease in C_6Yb. This behavior is claimed to provide evidence for a phonon-mediation mechanism but we show that it may also be consistent with a plasmon-mediated superconductivity.

ACKNOWLEDGMENTS

*Electronic address: rps24@phy.cam.ac.uk

[1] T. E. Weller, M. Ellerby, S. S. Saxena, R. P. Smith, and N. T. Skipper, Nat. Phys. **1**, 39 (2005).

[2] N. B. Hannay, T. H. Geballe, B. T. Matthias, K. Andres, P. Schmidt, and D. MacNair, Phys. Rev. Lett. **14**, 225 (1965).

[3] Y. Koike, H. Suematsu, K. Higuchi, and S. Tanuma, Physica B & C **99**, 503 (1980).

[4] Y. Iye and S. Tanuma, Phys. Rev. B **25**, 4583 (1982).

[5] G. Csanyi, P. B. Littlewood, A. H. Nevidomskyy, C. J. Pickard, and B. D. Simons, Nat. Phys. **1**, 42 (2005).

[6] I. I. Mazin and S. L. Molodtsov, Phys. Rev. B **72**, 172504 (2005).

[7] I. I. Mazin, Phys. Rev. Lett. **95**, 227001 (2005).

[8] M. Calandra and F. Mauri, Phys. Rev. Lett. **95**, 237002 (2005).

[9] Y. Iye and S. Tanuma, Synth. Met. **5**, 291 (1983).

[10] Y. Iye and S. Tanuma, Synth. Met. **5**, 257 (1983).

[11] R. P. Smith, T. E. Weller, A. F. Kusmartseva, N. T. Skipper, M. Ellerby, and S. S. Saxena, Physica B **378-380**, 892 (2006).

[12] A. Gauzzi, S. Takashima, N. Takeshita, C. Terakura, H. Takagi, N. Emery, C. Herold, P. Lagrange, and G. Louupias, cond-mat/0603443 (unpublished).

[13] J. S. Kim, L. Boeri, R. K. Kremer, and F. S. Razavi, cond-mat/0603530 (unpublished).

[14] G. Csanyi (private communication).

[15] H. Winkelmann, M. M. Abd-Elmeguid, H. Micklitz, J. P. Sanchez, P. Vulliet, K. Alami-Yadri, and D. Jaccard, Phys. Rev. B **60**, 3324 (1999).

[16] A. Bill, H. Morawitz, and V. Z. Kresin, Phys. Rev. B **68**, 144519 (2003).

[17] G. F. Giuliani and G. Vignale, *Quantum theory of the electron liquid* (Cambridge University Press, Cambridge, U.K., 2005).