Superconductivity in the intercalated graphite compounds C_6Yb and C_6Ca

THOMAS E. WELLER¹, MARK ELLERBY^{1*}, SIDDHARTH S. SAXENA^{2*}, ROBERT P. SMITH²
AND NEAL T. SKIPPER¹

¹Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

²Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK

*e-mail: mark.ellerby@ucl.ac.uk; sss21@cam.ac.uk

Published online: 29 September 2005; doi:10.1038/nphys0010

Low dimensionality is generally considered as a necessary ingredient for high superconducting transition temperatures. Surprisingly, perhaps, systems based on graphite^{1–3} have received little attention in this context. Introducing metal atoms between the carbon layers can tune the interlayer spacing and charging of the graphite host through a variety of electronic ground states. One such ground state is superconductivity³, which is not present in pure graphite. Here we report the discovery of superconductivity in the intercalation compounds C_6Yb and C_6Ca , with transition temperatures of 6.5 and 11.5 K, respectively. These critical temperatures are unprecedented in graphitic systems and have not been explained by a simple phonon mechanism for the superconductivity. This discovery has already stimulated several proposals for the superconducting mechanism^{4–6} that range from coupling by way of the intercalant phonons through to acoustic plasmons. It also points towards the potential of superconductivity in systems such as carbon nanotubes.

The first superconducting graphite intercalation compound to be reported^{7,8} was C_8K , which has a transition temperature of 0.15 K. Interestingly, whereas the metastable high-pressure phase C_2Li has a superconducting transition (T_{SC}) at 1.9 K (ref. 9), the compounds C_6Li and C_3Li are not found³ to superconduct down to the lowest measured temperatures. In all these compounds the transfer of charge from the metal to the graphite is thought to play an important role in the superconductivity. However, we see that there must be additional factors at work. For example, both potassium and lithium would be expected to donate one electron each to the graphite, but C_8K superconducts whereas C_6Li does not. This behaviour encouraged us to think that the fabrication and study of subtly different graphite intercalation compounds would be worthwhile. Therefore, we have fabricated the sister intercalation compounds C_6Yb and C_6Ca . Here we present results demonstrating the existence of superconductivity in these compounds together with a structural determination (see Methods and Fig. 1) showing the formation of ordered structures. C_6Yb forms a hexagonal layered structure ($P6_3/mmc$) in which the

intercalant atoms form a triangular array between every graphite layer (stage 1 intercalation). The alternate carbon and metal layers have an $A\alpha A\beta$ registration¹⁰, where the A represents the carbon layers and the α and β the intercalant layers. The structure for C_6Ca has been refined¹¹ and found to differ from that of C_6Yb , having a rhombohedral structure ($R\bar{3}m$), with a carbon and metal layer repeat of $A\alpha A\beta A\gamma$. The rhombohedral structure can be translated to a hexagonal basis and thus these compounds may be seen in a similar light.

Two of the principle signatures of superconductivity are the absence of electrical resistivity and the development of a diamagnetic moment below the ordering transition. Figure 2 shows the results of resistivity and d.c. magnetization measurements made on samples of C_6Yb and d.c. magnetization measurements on C_6Ca . The results for C_6Yb (Fig. 2a,c) show a clear transition at 6.5 K in the magnetization and the resistivity, both of which support the existence of superconductivity. The transition is well defined, having a width of 0.2 K in the resistivity. These intercalation compounds are very difficult to fabricate (see Methods), nevertheless we have managed to prepare samples in which X-ray studies show that over 13% of the final volume of the sample is C_6Yb . However, field-dependent magnetization measurements made parallel to the c^* axis of C_6Yb imply that the superconducting volume fraction is approximately 90%. This difference was resolved by scanning electron microscopy, which revealed that the intercalation process creates a 'shell' of the intercalant with a core of pristine graphite. It is important to stress that the subsequent cleaving of several layers up to 300 μm from these samples did not remove superconductivity. The magnetization measurement shown in Fig. 2c, with the field of 50 Oe applied parallel to the c^* axis was performed on a disk-shaped sample. The zero-field-cooled (ZFC) data reveal the flux expulsion and subsequent flux threading as the temperature is increased. The FC measurements, when compared with the ZFC results, show only partial flux expulsion. In fields exceeding the superconducting upper critical field (H_{C2}) we find a weak paramagnetic signal. The origins of this paramagnetic moment are difficult to attribute, but we do have X-ray evidence (Fig. 1) showing a contamination of less

Figure 1 X-ray diffraction pattern of highly oriented pyrolytic graphite intercalated with ytterbium. These data were taken using a Bragg–Brentano geometry with Cu K α radiation. As a consequence of this, only the (00 l) peaks may be sampled. Top: The derived structure modelled¹⁰ using a stage-1 graphite intercalation compounds with a c^* axis sandwich depth (C–Yb–C) of 4.57 Å. Measurements for C₆Ca have a sandwich depth (C–Ca–C) of 4.51 ± 0.02 Å, in reasonable agreement with the study in ref. 11, which determines a value of 4.524 Å. In the structure of C₆Yb the graphite sheets have an A–A registration whereas the ytterbium have an α – β registration. Calculations based on peak intensities reveal that 13% of the sample volume fraction is made up of C₆Yb. From our analysis we find that the contamination of Yb₂O₃ is less than 1% after surface abrasion.

than 1% Yb₂O₃, which is known to have an ordered moment below 2.4 K (ref. 12).

The C₆Ca magnetization results are shown in Fig. 2b. In the magnetization we see a clear diamagnetic transition at 11.5 K in a field of 50 Oe, but with no saturation of diamagnetism down to 2 K. In addition, the preliminary resistivity measurements demonstrate that the resistivity goes to zero below the transition temperature. However, extreme air sensitivity and difficulties in preparation of this compound¹³ have prevented detailed transport and magnetization measurements thus far. The fact that the magnitude of the diamagnetic moment is about 100 times smaller than in C₆Yb also points to reduced sample quality. We are able to conclude unambiguously that C₆Ca superconducts below 11.5 K.

Figure 2d presents the magnetic phase diagram for C₆Yb inferred from magnetization measurements made with applied magnetic field in the plane of the layers (a – b plane) and perpendicular to them (c^* axis). The lower critical field H_{C1}

Figure 2 The temperature dependence of the magnetization and electrical resistivity for C₆Yb and C₆Ca. **a, b**, Magnetization measurements for C₆Yb (**a**) and C₆Ca (**b**). These measurements were made with a 50 Oe field applied parallel to the c^* axis. These figures reveal the onset of flux expulsion in both the ZFC measurement and the FC measurement. **c**, The resistivity measurement for C₆Yb. There is a clear drop to zero resistivity indicating the existence of superconductivity. **d**, The superconducting phase diagram for C₆Yb. This diagram is compiled from results of the magnetization study. In both geometries the sample appears to be a type-II superconductor. There is little if any anisotropy in H_{C1} for the two geometries, whereas there is a clear anisotropy in H_{C2} .

is approximately the same for both geometries, whereas the upper critical field H_{C2} is clearly anisotropic. The anisotropy parameter of $\Gamma_{H_{C2}}$ given by $H_{H_{C2}}(\perp c)/H_{H_{C2}}(\parallel c)$ is approximately 2 across the temperature range below T_{SC} . In the Ginzburg–Landau theory, this anisotropy depends solely on the ratio of the electron masses along the two symmetry directions. Calculation of the ratio of the effective masses for pure graphite yields a value for $\Gamma_{H_{C2}}$ of 7. A comparison of these two values implies the Fermi surface is more three-dimensional in C₆Yb compared with pure graphite. This observation is consistent with normal-state resistivity measurements above T_{SC} , with the measurements showing a distinct anisotropy depending on whether the current is applied in the c^* axis or in the basal plane. The anisotropy can be quantified by the ratio of the c^* -axis resistivity to the a – b -plane resistivity; at room temperature this ratio is 100 for C₆Yb. This ratio is smaller than that in pure graphite, which at room temperature has an anisotropy ratio¹⁴ of around 10⁴. Further evidence for this change in Fermi surface comes from the temperature-dependent resistivity parallel to the c^* axis, which reveals a significantly different behaviour from that seen in pure graphite. In pure graphite the resistivity is observed¹⁵ to increase with decreasing temperature, reaching a maximum at ~ 50 K, whereas the resistivity parallel to the c^* axis, $\rho_{\parallel c}(T)$, in C₆Yb is found to decrease from room temperature to the transition temperature. These three observations taken together lead us to

believe that the Fermi surface in C_6Yb is more isotropic than that found in pure graphite.

Our results leave us with a significant question. Is a simple charge-transfer model, used to understand earlier studies^{16,17}, adequate in explaining the results reported here? This question arises from the following observations. If charge transfer from the metal to the carbon atoms was the most important effect leading to superconductivity in these systems, then we would expect C_3Li to become superconducting, because the charge transfer is comparable to that of C_6Yb and C_6Ca , with 1/3 of an electron per carbon atom (e per C) being transferred. In fact³ C_3Li is not superconducting. Also, in the case of C_2Li (ref. 9), where the charge transfer is greater (1/2 e per C), the transition temperature is still a factor of three and six smaller than in C_6Yb and C_6Ca , respectively. In the case of C_2Na , which has a T_{SC} of around 5 K, there are no crystallographic data confirming that an ordered intercalation compound is formed¹⁸. In a conventional phonon mechanism we would not expect an order of magnitude change in T_{SC} on going from a charge transfer of 1/8 e per C to 1/3 e per C. Therefore, our results have highlighted that there is no clear trend between the amount of charge transferred and the superconducting transition temperature. Thus, there is a demand for a renewed theoretical effort to place our findings in context with previous experimental results on the superconducting graphite intercalation compounds. In response to our discovery of superconductivity in C_6Yb and C_6Ca , several theoretical investigations have taken place^{4–6}. The first of these⁴ shows that superconductivity in the graphite intercalation compounds is always coincident with the occupation of a modified interlayer state (found in pure graphite 2 eV above the Fermi surface) and thus suggests that an acoustic plasmon mechanism may be at work. The two subsequent and independent papers^{5,6} attribute the superconductivity to the modified electron–phonon spectrum. Previous work¹⁹ concerning the possibility of a resonant valence bond mechanism in the superconductivity has also been discussed in connection with these intercalation compounds. To what extent these proposals model the observed properties remains to be established.

Our work suggests that intercalation increases the isotropy of the graphite system, which is contrary to the simple picture that the metal atoms increase the spacing between the layers; such a view would be expected to make intercalated graphite more two-dimensional, rather than less. In trying to understand this problem further, we will be able to exploit the weak van der Waals bonding between the graphene sheets to explore the impact of interlayer coupling using ‘tuning’ parameters such as hydrostatic pressure or doping with different metals. In addition, this work may also be of more general importance in understanding and exploring superconductivity in the quasi-one-dimensional system formed in single-walled carbon nanotubes¹⁹.

METHODS

The samples were prepared using the well-established vapour transport process³. Highly oriented pyrolytic graphite, grade ZYA from Advanced Ceramics (Cleveland, Ohio), was used as the host for the reaction. The ytterbium was supplied by Goodfellow with a purity of 99.9% and the calcium was supplied by Aldrich with a purity of 99.5%. Before the vapour transport process the graphite has a hexagonal layered structure ($P6_3/mmc$) with an AB registration of graphene layers. Air-abrasion techniques were used to prepare the edges of the graphite to produce open galleries. The surfaces were then

cleaved to provide clean graphite in a variety of shapes for different probes, having a thickness of between 0.1 and 0.25 mm. The graphite and the intercalant (ytterbium or calcium) were sealed at opposite ends of a quartz tube and then treated using a two-zone technique with an appropriate thermal gradient¹⁰. This allows the ytterbium or calcium to enter the graphite galleries.

Initial X-ray diffraction studies revealed the presence of graphite, Yb_2O_3 , YbO and pure Yb in samples of C_6Yb . Corresponding measurements for C_6Ca did not reveal the presence of any oxides or free Ca, but do show the clear presence of graphite as a secondary phase. Subsequent scanning electron microscopy of the C_6Yb samples established that there was surface contamination that may be removed through abrasion. Figure 1 shows an example of the X-ray patterns for the C_6Yb samples after abrasion of the surface. The geometry used is a standard technique¹ for identification of the staging of graphite intercalation compounds, where the stage represents the number of graphene layers between intercalant layers; this technique only allows the observation of (00 l) reflections as indexed. We have been able to model⁷ the intercalation phases present in the X-ray data by considering a stacking registry $AaA\beta$ with the structure C_6Yb shown in Fig. 1.

Received 18 March 2005; accepted 24 June 2005; published 29 September 2005.

References

- Dresselhaus, M. S. & Dresselhaus, G. Intercalation compounds of graphite. *Adv. Phys.* **51**, 1–186 (2002).
- Zabel, H. & Sölin, S. A. *Graphite Intercalation Compounds I* (Springer, Berlin, 1990). (*Ibid* II, 1992).
- Enoki, T., Masatsugu, S. & Morinobu, E. *Graphite Intercalation Compounds and Applications* (Oxford Univ. Press, Oxford, 2003).
- Csányi, G., Littlewood, P. B., Nevidomskyy, A. H., Pickard, C. J. & Simons, B. D. Electronic structure of the superconducting graphite intercalates. *Nature Phys.* **1**, 42–45 (2005).
- Mazin, I. I. Intercalant-driven superconductivity in YbC_6 and CaC_6 . Preprint at <http://xxx.soton.ac.uk/PS.cache/cond-mat/pdf/0504/0504127.pdf> (April 2005).
- Calandra, M. & Mauri, F. Superconductivity in C_6Ca explained. Preprint at <http://xxx.soton.ac.uk/PS.cache/cond-mat/pdf/0506/0506082.pdf> (June 2005).
- Hannay, N. B. *et al.* Superconductivity in graphitic compounds. *Phys. Rev. Lett.* **14**, 225–226 (1965).
- Koike, Y., Suematsu, H., Higuchi, K. & Tanuma, S. Superconductivity in graphite-alkali metal intercalation compounds. *Physica B+C* **99**, 503–508 (1980).
- Belash, I. T., Bronnikov, A. D., Zharikov, O. V. & Pal'nichenko, A. V. Superconductivity of graphite intercalation compound with lithium C_2Li . *Solid State Commun.* **69**, 921–923 (1989).
- El Makrini, M., Guérard, D., Lagrange, P. & Hérol, A. Intercalation of rare earth metals in graphite. *Physica B* **99**, 481–485 (1980).
- Emery, N. *et al.* Superconductivity of bulk CaC_6 . *Phys. Rev. Lett.* **95**, 087003 (2005).
- Moon, R. M., Koehler, W. C., Child, H. R. & Raubenheimer, L. J. Magnetic structures of Er_2O_3 and Yb_2O_3 . *Phys. Rev.* **176**, 722–731 (1968).
- Guérard, D., Chaabouni, M., Lagrange, P., El Makrini, M. & Hérol, A. Insertion de métaux alcalino-terreux dans le graphite. *Carbon* **18**, 257–264 (1980).
- Kopelevich, Y. *et al.* Reentrant metallic behaviour of graphite in the quantum limit. *Phys. Rev. Lett.* **90**, 156402 (2003).
- Uher, C., Hockey, R. L. & Ben-Jacob, E. Pressure dependence of the c-axis resistivity of graphite. *Phys. Rev. B* **35**, 4483–4488 (1987).
- Al-Jishi, R., Dresselhaus, M. S. & Chaiken, A. Theory of the upper critical field in graphite intercalation compounds. *Phys. Rev. B* **44**, 10248–10255 (1991).
- Al-Jishi, R. & Dresselhaus, M. S. Superconductivity in graphite intercalation compounds. *Phys. Rev. B* **45**, 12465–12469 (1992).
- Belash, I. T., Bronnikov, A. D., Zharikov, O. V. & Pal'nichenko, A. V. On superconductivity of graphite intercalation compounds with sodium. *Solid State Commun.* **64**, 1445–1447 (1987).
- Baskaran, G. Resonating-valence-bond contribution to superconductivity in MgB_2 . *Phys. Rev. B* **65**, 212505 (2002).
- Suzuki, S., Maeda, F., Watanabe, Y. & Ogino, T. Electronic structure of single-walled carbon nanotubes encapsulating potassium. *Phys. Rev. B* **67**, 115418 (2003).

Acknowledgements

We acknowledge M. Baxendale and M. Laad for their comments, suggestions and discussions. In the preliminary development of the sample preparation we are indebted to C. Gallagher, J. Goodyer and S. L. Molodtsov (Dresden TU). We thank K. S. Lee (London Centre for Nanotechnology, UCL) and the Institute of Archaeology, UCL for scanning electron microscopy/energy dispersive X-ray spectroscopy studies on the final samples. We are also grateful to the Eastman Dental Institute for cutting of graphite samples. We are thankful to G. Aeppli, G. Csányi, A. H. Harker, A. Kusmartseva, D. F. McMorrow, A. H. Nevidomskyy, C. Pickard, P. B. Littlewood, G. G. Lonzarich, J. Loram, S. Özcan, Ch. Renner, S. Rowley and B. D. Simons for useful discussions. We would also like to thank the EPSRC, CCLRC (ISIS), The Royal Society and Jesus and Trinity Colleges of the University of Cambridge for financial support.

Correspondence and requests for materials should be addressed to M.E. or S.S.S.

Competing financial interests

The authors declare that they have no competing financial interests.

Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>