Superconductivity of Bulk CaC_6

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We have obtained bulk samples of the graphite intercalation compound, CaC_6, by a novel method of synthesis from highly oriented pyrolytic graphite. The crystal structure has been completely determined showing that it is the only member of the MC_6, metal-graphite compounds that has rhombohedral symmetry. We have clearly shown the occurrence of superconductivity in the bulk sample at 11.5 K, using magnetization measurements.

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Graphite intercalation compounds (GICs) are synthesized by inserting foreign atoms or molecules between the hexagonal two-dimensional sheets of graphite, leading to ordered structures. Since graphite is a semimetal, the electrons accepted or donated by the intercalant modify the electronic properties of graphite, resulting in a metallic behavior in the final material. This process leads to a series of compounds with regular stacking of n graphite layers between two successive intercalant planes; n is referred to as the stage of the compound. Superconductivity in the first stage potassium-graphite donor compound KC_8, was reported years ago with a critical temperature, T_c, of 0.14 K [1]. It is interesting that neither of the constituents are superconducting by themselves. Superconductivity in GICs was the subject of extensive studies during the late 1980s and early 1990s, until the discovery of higher T_c in C_{60} compounds [2]. In particular, several first stage metal-graphite compounds were investigated in order to test the idea that T_c will increase with increasing metal concentration that is accompanied by a larger electronic charge transfer to the graphene planes [3]. However, it is a fact that LiC_6 is not a superconductor even though the charge transferred to the graphene layer is shown to be larger than in KC_8 [4]. Nevertheless, high-pressure syntheses, leading to metastable compounds with higher metal concentration, were successful in increasing superconductivity T_c up to 1.9 K for LiC_2 [5], and 5 K for NaC_2 [6] and KC_3 [7]. As a consequence, graphite has been demonstrated to be a convenient host for producing various two-dimensional ordered systems with promising electronic properties. These are not only related to electron charge transfer but also to other parameters such as changes in graphite layer spacing due to different intercalated species. It is also possible to intercalate three or even more layers of metals between two adjacent graphitic planes, leading, for example, to the $KTl_{1.5}C_4$ compound, with a 1.210 nm interlayer distance [8], exhibiting superconductivity at 2.7 K [9], up to now the highest among all the graphite intercalation compounds synthesized at ambient pressure.

Very recently, T_c of 6.5 K was discovered in YbC_6 as well as the suggestion of superconductivity at as high as 11.5 K in CaC_6, both of them synthesized at ambient pressure [10]. However, in the case of CaC_6, the intercalation was limited to surface layers, and, as a consequence, the transition temperature cannot be clearly determined since the Meissner effect measurement does not show a clear discontinuity but only a smooth change of magnetization with temperature. In addition, the lack of saturation of diamagnetism and the very small value of diamagnetic moment are attributed by Waller *et al.* [10] to "reduced sample quality." It is well known that the intercalation of alkaline earth metals into graphite is much more difficult than for any of the alkali metals. This is particularly true in the case of calcium. Indeed, the reaction between calcium vapor and pyrolytic graphite, as described in Ref. [11], leads only to an extremely superficial intercalation. For this reason, bulk CaC_6 was not obtained and, as a result, it was not possible to determine the structure of the first stage calcium-graphite compound until now. A high quality bulk sample is needed for both accurate structure determination and bulk superconductivity measurements.

We have succeeded in synthesizing bulk CaC_6 from highly oriented pyrolytic graphite [12]. The reaction is carried out for ten days between a pyrolytic graphite platelet and a molten lithium-calcium alloy at around 350 °C, under very pure argon atmosphere. The reactive alloy has to be very rich in lithium, with a composition between 70 and 80 at. % of Li. Despite such a low calcium concentration, no lithium is present in the final reaction product and calcium alone is intercalated into graphite.

The resulting bulk sample of CaC_6 permitted us to carry out the first structural study of this compound [12]. The characteristic texture of pyrolytic graphite used as the precursor in the intercalation process resulted in observing the $00l$ reflections in the x-ray diffraction diagram (Fig. 1). At the same time, there is an absence of $00l$ reflections due to graphite or to any other GICs. The shortest distance between two graphene sheets, i.e., the interlayer distance d_i, of this pure phase is obtained from the position of the reflection peak to be equal to 0.4524 nm. The stoichiometry of CaC_6 was confirmed using the x-ray $00l$ reflection intensities as well as by means of nuclear microprobe [13]. This stoichiometry [14] corresponds to an AA stacking of the successive graphene planes; i.e., all the carbon atoms in two successive layers are superimposed. Intercalant metal atoms in each layer are located in one out of three prismatic hexagonal sites denoted by α, β, and γ. As a result, three different **c**-axis stackings have to be thus considered [15]:

$$A\alpha A\alpha A\alpha A\alpha A\alpha \ldots \qquad A\alpha A\beta A\alpha A\beta A\alpha \ldots$$

$$A\alpha A\beta A\gamma A\alpha A\beta \ldots .$$

The first and the second stackings lead to hexagonal crystal symmetry, while the third corresponds to rhombohedral symmetry. For CaC_6, our experimental results demonstrate an $A\alpha A\beta A\gamma$ stacking, by the lack of reflections that obey the general diffraction conditions: $-h + k + l = 3n$, characteristic of this **c**-axis stacking. Indeed, detailed analysis of $00l$ and hkl reflections give a value of 1.3572 nm for the c parameter ($c = 3d_i$). Therefore, we conclude that the crystal structure of CaC_6 has been conclusively determined, and we have shown that, among the various MC_6 graphite intercalation compounds, CaC_6 is the only one to possess rhombohedral instead of hexagonal symmetry. The elemental unit cell is a rhombohedron belonging to the $R\bar{3}m$ space group with the following parameters: $a_R = 0.517$ nm and $\alpha = 49.55°$. It contains one calcium atom in site (0 0 0) and six carbon atoms in sites (1/6 5/6 1/2). However, it is often preferable to describe such a structure using a hexagonal unit cell, whose size is 3 times that of the rhombohedral cell (Fig. 2).

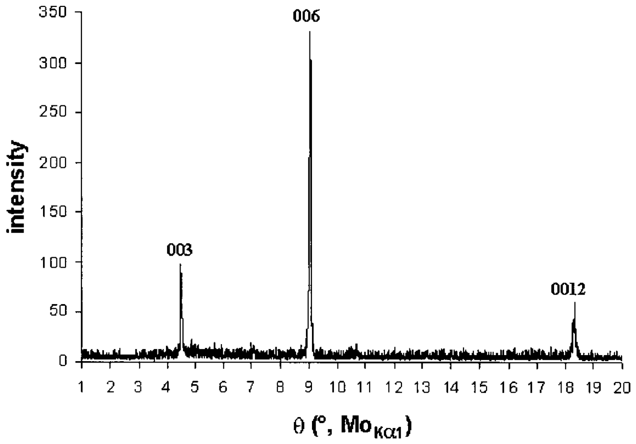

FIG. 1. The $00l$ diffraction pattern for CaC_6, using Mo $K\alpha_1$ x rays.

In addition, from measured dilation of carbon-carbon bond compared to pure graphite, we estimate the electron transfer between calcium and graphene plane, using the empirical Pietronero-Strässler rule [16]. It reaches the high value of 0.103 electrons per carbon atom and appears to be the highest charge transfer among all the MC_6 compounds.

In order to study the details of bulk superconductivity in CaC_6, its magnetization was measured as a function of temperature and magnetic field. Two different samples were used to perform two sets of measurements using a Quantum Design MPMS5 SQUID magnetometer. Since the **c** axes of all the crystallites forming the highly oriented graphite are parallel to each other, we are able to define the **c**-axis direction of the CaC_6 sample, while in the perpendicular direction the material is disordered, leading to an average of **a** and **b** directions, denoted as ab. Because of their chemical reactivity, the samples had to be kept in a closed cell, under helium atmosphere. The first sample, with a roughly rectangular shape of about 3.5×3 mm^2 and thickness of 0.3 mm, was measured with the magnetic field in the ab plane. The second sample was composed of 3 superposed platelets of about 8 mm^2 surface and 0.2 mm thickness each and was measured with the magnetic field along the **c** axis.

Magnetization as a function of temperature was measured for each sample at two different values of externally applied magnetic field. The samples were initially cooled to 2 K with the magnetic field switched off, and subse-

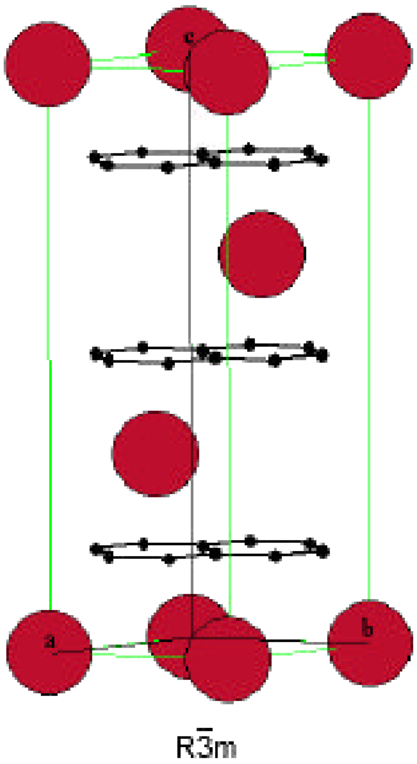

FIG. 2 (color online). Rhombohedral unit cell and the corresponding hexagonal cell of CaC_6.

quently the magnetization was measured with magnetic fields of 5 and 50 Oe, increasing the temperature up to 40 K. This is referred to as the "zero field cooling" experiment (ZFC). The same measurement was also carried by cooling the sample with the magnetic field applied, referred to as the "field cooling" experiment (FC). Figure 3 shows the results for both ZFC and FC measurements at 5 Oe and at intervals of 0.2 up to 20 K.

The ZFC results exhibit a sharp drop of the magnetization below 11.5 K, with 2/3 of the decrease occurring within 0.2 K. The strong diamagnetic signal shows a complete saturation below the superconducting transition temperature, indicating a true Meissner effect. The midpoint for the ZFC curve occurs at 11.1 K with a total transition width ΔT of 0.5 K, using temperatures corresponding to 90% and 10% of the diamagnetic signal. Moreover, a series of magnetization measurements versus the field were carried out at given temperatures around T_c, by steps of 0.1 K, allowing us to determine precisely that the diamagnetic signal completely disappears at $T_c^{\mathrm{onset}} = (11.46 \pm 0.04)$ K. The transition temperature appears as the highest transition temperature observed among all the graphite intercalated compounds.

The FC results show a similar sharp drop with the same onset of 11.5 K. However, the diamagnetic signal is strongly reduced compared to the ZFC. The superconducting volume fraction inferred from the diamagnetic signal is of 60%, with an error bar of 10%, obtained taking into account both demagnetization corrections and sample volume estimations. This value confirms the bulk intercalation and not only surface intercalation. Similar results were obtained for measurements at 50 Oe in the same direction and for 50 and 5 Oe with the magnetic field applied along the **c** axis.

Figure 4 shows the temperature dependence of the critical fields H_{c1} and H_{c2} obtained from the magnetization versus field, $M(H)$, measurements at a given temperature [the 6 K data are shown in the inset, with H_{c1} and H_{c2} defined as $M(H)$ minimum and zero crossing abscissas] and with the field oriented along the **c** axis. The material appears to be a type II superconductor. Note that the H_{c2} value at 2 K is a lower bound, since the measurements were performed only up to 2500 Oe and a very small diamagnetic signal (about 4×10^{-4} emu) was still present. The overall T dependence of H_{c1} and H_{c2} is compatible with the dependence derived by Helfand and Werthamer [17] within the BCS theory. In particular, in the region close to T_c, the dependence is roughly linear, in agreement with a Ginzburg-Landau picture, with an upturn at $T > 9$ K, possibly associated with fluctuation effects. The extrapolation of this tail is consistent with the measured $T_c^{\mathrm{onset}} = 11.5$ K. From similar measurements, with the field in the *ab* plane, we estimate a higher upper critical field H_{c2} of about 7000 Oe, indicating a sizable anisotropy of the critical field, as already observed in C_6Yb [10]. From the linear part of our measurements, we can evaluate the

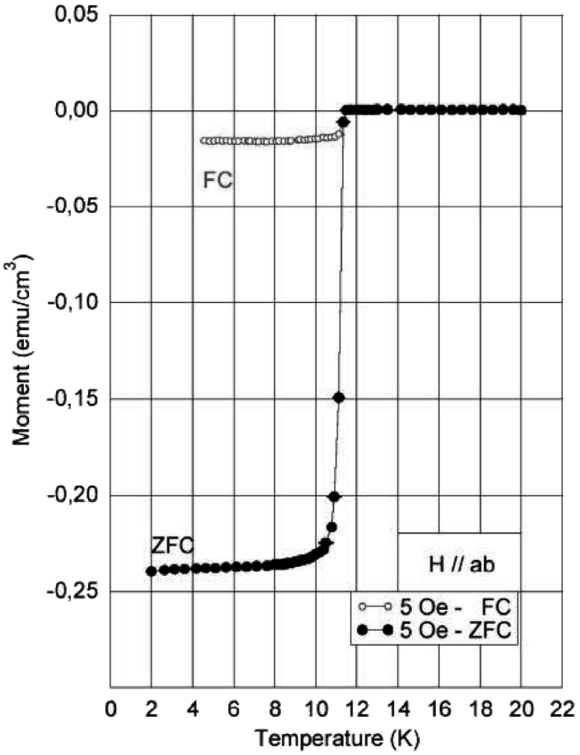

FIG. 3. Magnetization of CaC_6 as a function of temperature for an external magnetic field of 5 Oe under zero field cooling (ZFC) and field cooling (FC) conditions.

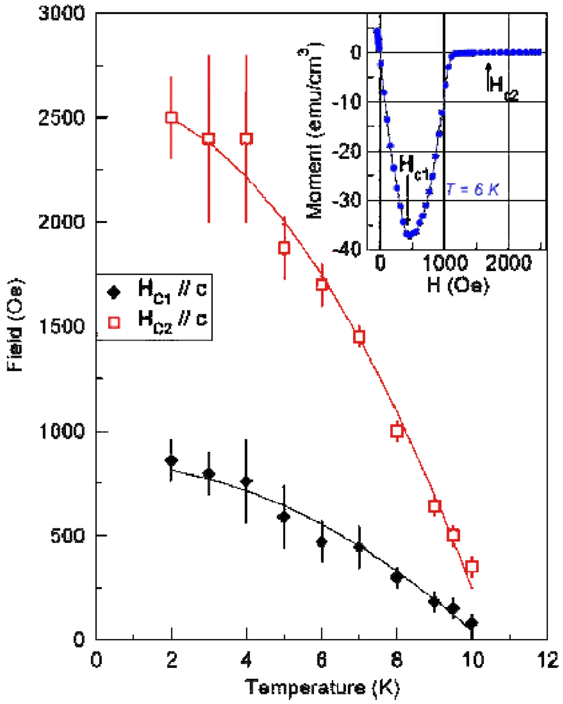

FIG. 4 (color online). Superconducting phase diagram of CaC_6 for the magnetic field along the **c** axis from $M(H)$ measurements at given T. The 6 K measurement is shown in the inset.

coherence lengths both in the *ab* plane and along the *c* axis, respectively, to be $\xi_{ab,0} = 35$ nm and $\xi_{c,0} = 13$ nm. This implies that the superconducting state of this material is anisotropic but clearly three dimensional in spite of the layered structure.

In order to find GICs exhibiting higher superconducting transition temperature than KC_8, two main paths have been previously followed: increasing the interlayer distance, d_i [9], and increasing the metal concentration [3]. The goal of both of these approaches was to obtain a well-localized high electronic density in the graphitic planes. In the present study of CaC_6, a transition temperature of almost 2 orders of magnitude larger than KC_8 [1] was obtained, and the measured interlayer distance in CaC_6 (0.452 nm) is smaller than 0.535 nm in KC_8, making the first approach unlikely to succeed. This is in contrast to the situation for the alkaline C_{60} compounds, another series of carbon-based intercalated compounds, where the alkali atom plays the role of spacer between the C_{60} molecules, and the superconducting temperature rises from 19.4 K for K_3C_{60} [2] to 32 K for $CsRb_2C_{60}$ [18] with an increase in the intercalant atom diameter. Similarly the maximum charge transfer, expected from CaC_6 stoichiometry, is equal to two electrons given by each Ca atom, i.e., one-third of the electron accepted by each carbon atom, the same as for KC_3, and lower than for LiC_2. Moreover, the estimated charge transfer of 0.1 electron per carbon atom for CaC_6 [12] is 3 times less than the largest possible value. As a result, the simple increase of charge transfer from the intercalant to graphite sheet appears to play a questionable role in this process. Recent calculations by Calandra and Mauri [19] indicate that the existence of a substantial amount of charge left on the metal plays a major role in the existence of superconductivity and magnitude of the transition temperature. In addition, the authors have noticed that the Ca rhombohedron in CaC_6 is close to the elementary cell of the fcc Ca pure metal, leading to a sizable 3D character of metallic bands in the intercalated compound. This result is supported by the low anisotropy of the coherence lengths ξ_{ab} and ξ_c, obtained from our measurements.

In conclusion, we have unambiguously demonstrated the existence of bulk superconductivity in CaC_6 both by the sharpness of the measured magnetization versus temperature and by the saturation of the diamagnetic signal. Our novel and efficient method for the preparation of high quality bulk CaC_6 played a crucial role in accurate measurement of the superconducting temperature as well as the width of the transition. We have also shown that among the various MC_6 graphite intercalation compounds, CaC_6 is the only one with the rhombohedral instead of the hexagonal symmetry as postulated elsewhere [10].

The three families of carbon-based materials, graphite intercalated compounds [1], doped fullerenes [18], and doped diamond [20], have all exhibited superconductivity. However, the present case of CaC_6 is particularly significant since it represents an increase of T_c by almost 2 orders of magnitude, at ambient pressure, over that of KC_8, discovered 40 years ago. This has led to renewed interest in taking advantage of the wide variety of intercalant species and structures in carbon-based materials. Furthermore, we have shown that the simple models existing until now are insufficient to predict the magnitude of the superconducting transition in these materials.

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