Superconductivity in the Graphite Intercalation Compound BaC_6

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Among many two-dimensional (2D) high T_C superconductors, graphite intercalation compounds (GICs) are the most famous intercalation family, which are classified as typical electron-phonon mediated superconductors. We show unambiguous experimental facts that BaC_6, the superconductivity of which has been missing for many years so far among various alkaline earth metal (Ca, Sr, and Ba) intercalted GICs, exhibits superconductivity at $T_C = 65$ mK. By adding this finding as the additional experimental point, a complete figure displaying the relationship between T_C and interlayer distance (d) for GICs is now provided, and their possible superconducting mechanisms raised so far are revisited. The present study settles a long-running debate between theories and experiments on the superconductivity in the first stage GICs.

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Since the discovery of superconductivity in Hg [1], tremendous effort has been devoted to realizing higher T_C. Various 2D layered superconductors, such as cuprates (the highest $T_C = 164$ K of $HgBa_2Ca_2Cu_3O_{8+\delta}$ under pressure) [2], iron pnictides (the highest $T_C = 55$ K of $Sm[O_{1-x}F_x]FeAs$) [3], and hafnium nitrides (the highest $T_C = 25.5$ K) [4], some of which can be categorized as unconventional high T_C superconductors, have been discovered and studied in detail in materials science. In addition, Ginzburg [5] and Little [6] have proposed that carbon related materials can be good candidates for high T_C superconductors. In particular, consequently, GICs (the highest $T_C = 11.5$ K for CaC_6) [7,8], organic charge-transfer complexes (the highest $T_C = 14.2$ K for β'-$(BEDT\text{-}TTF)_2ICl_2$ under pressure) [9], and doped C_{60} (the highest $T_C = 38$ K for Cs_3C_{60} under pressure) [10] have been extensively studied recently.

GICs are good 2D model materials for studying the phonon-mediated mechanism of superconductivity, due to its layered structure and variable d. Superconductivity in the first stage alkali metal GICs, the T_C values of which were much lower than 1 K and depend on d, was first reported by Hannay et al. [11]. The recent discovery of the superconductivity of YbC_6 ($T_C = 6.5$ K) and CaC_6 ($T_C = 11.5$ K) has renewed interest in GICs, since T_C for CaC_6 is almost 2 orders of magnitude higher than that for KC_8 discovered nearly 40 years ago. Moreover, a report was made on the possibility that a grain control of GIC via chemical modifications gives an order higher T_C than that of the conventional GICs even for alkali metal intercalations [12].

T_C for GICs has been considered as being closely related to d, and it actually increases with a decrease in d as a function of chemical and physical pressure [11,13,14], and the superconducting mechanism of GICs has been described using a phonon-mediated BCS scenario with s-wave pairing symmetry [15–17]. The T_C of 1.65 K for SrC_6 has been reported to be lower than that for CaC_6 due to chemically tuned negative pressure effects [13], which cause a decrease in the electron-phonon coupling strength for both in-plane and out-of-plane phonon modes of the intercalant and the carbon. In the case of BaC_6, however, d is much larger, as shown in Fig. 1, and therefore, the superconductivity is significantly suppressed. At present, several reports have suggested the absence of superconductivity down to extremely low temperatures on the basis of experimental evidence [13,18,19]. On the other hand, *ab initio* calculations within the framework of the density functional theory (DFT) predicted that BaC_6 exhibits superconductivity within the experimental accessible temperatures [20,21]. Whether BaC_6 can be superconducting or not is a long-lasting question for understanding the intrinsic picture of GIC superconductors.

Here, we report that BaC_6, isostructural to SrC_6 and YbC_6, shows bulk superconductivity with T_C of 65 mK. A complete description of the relationship between T_C and d is given to provide an important clue towards an intrinsic understanding of GIC superconductors.

BaC_6 samples were prepared from flakes of highly oriented pyrolytic graphite (HOPG ZYA grade, NT-MDT Co.) and Ba metal (99.95% purity, Furuuchi Co Ltd.) by a conventional vapor phase reaction. Thermal treatment was performed in a furnace at 773 K for several weeks. Powder x-ray diffraction (XRD) measurements were carried out using RIGAKU SmartLab equipped with a monochromator and a Cu$K\alpha$ radiation source to confirm the stage number of the BaC_6 samples. ac magnetization measurements were

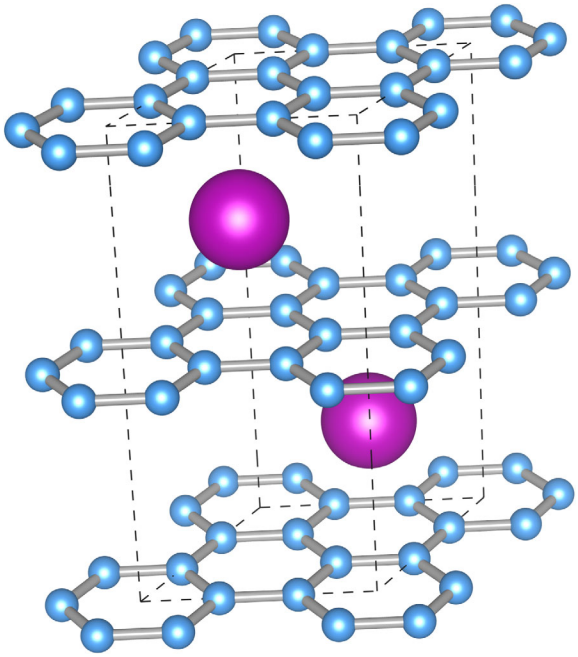

FIG. 1 (color online). Schematic crystal structure model of hexagonal BaC_6. Ba ions and C atoms are depicted as red and blue spheres, respectively.

performed in a dilution refrigerator down to 31 mK. A copper rod with a fine Cu wire bundle mounted at one end was used as the sample cell. The bundle was encapsulated in an airtight jacket made of STYCAST 1266 epoxy. BaC_6 specimens (the total sample weight was 8.9 mg in a typical case) were covered with Apiezon N grease and were inserted into the bundle. The ab plane of specimens was set parallel to the external magnetic field. The other end of the copper rod was connected to the mixing chamber of the dilution refrigerator. A small piece of pure indium (99.999%), which was used as a reference, was placed beside the specimens. All procedures were carried out in an Ar glove box. The sample temperature was monitored with carbon and RuO_2 resistance thermometers, which were calibrated to the PLTS-2000 temperature scale by using a ^{3}He melting curve thermometer [22]. The sample was first cooled to 31 mK under zero magnetic field, and then the magnetization was measured by an ac inductance bridge method in a magnetic field of 6 mOe from peak to peak and a frequency of 200 Hz. The obtained magnetic signals were calibrated with the superconducting transition signal of the indium reference, and the difference in the demagnetization factor was neglected.

Figure 2 shows an XRD profile of BaC_6. The color of the HOPG changed from black to metallic gold, as shown in the inset photograph of Fig. 2. No 00l with higher stage GICs was observed. The d of BaC_6 was estimated to be 5.25 Å from the positions of the 00l reflections, and the increase in d reflects the large size of the Ba ions, and is consistent with a previous report [23]. The stacking

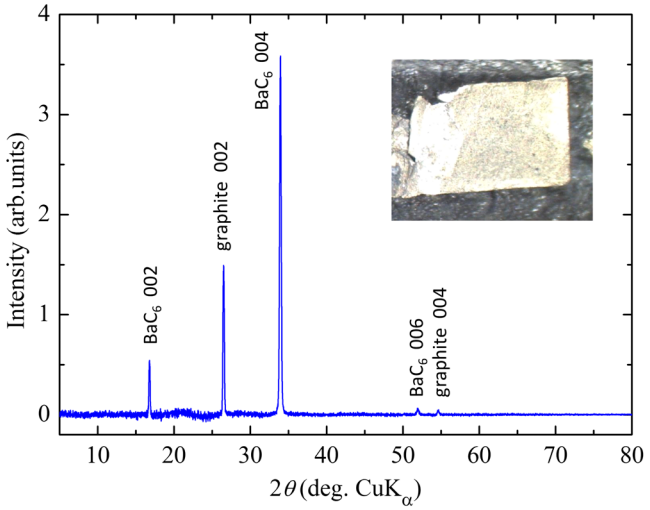

FIG. 2 (color online). XRD profile of BaC_6. The inset photograph shows a typical BaC_6 specimen.

sequence of BaC_6 was $A\alpha A\beta A$, where A corresponds to a graphene layer and the α and β are the intercalant layers, and the space group was determined to be $P6_3/mmc$ by using refinement similar to that used for SrC_6 [13,23]. Ba atoms occupy the graphite interlayer sites on the $2c$ Wyckoff position of the carbon honeycomb lattice, as shown in Fig. 1. Among the MC_6 (M = Ca, Sr, Ba, Yb) systems, only the crystallographic structure of CaC_6 has been reported to have rhombohedral $R\bar{3}m$ symmetry with a stacking sequence of $A\alpha A\beta A\gamma$.

The temperature dependence of the ac susceptibility of BaC_6 under various applied static magnetic fields is shown in Fig. 3. The ac susceptibility under the zero magnetic field showed an unambiguous drop below 65 mK, which defined

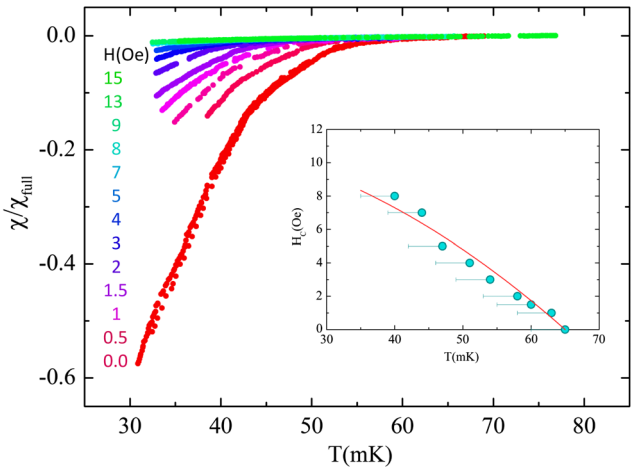

FIG. 3 (color online). Temperature dependence of ac susceptibility of BaC_6 under various applied magnetic fields. The inset shows the upper critical fields (H_{c2}). H_{c2}(T) is defined as the magnetic field and temperature where ac susceptibility becomes zero. The $\{1\text{-}(T/T_C)^2\}$ fitting curve (red line) is also drawn.

the onset temperature of the superconducting transition (T_C^{onset}). The diamagnetic signal increased gradually below T_C^{onset}. The superconducting shielding fraction was estimated to be 55% at the lowest temperature in the present measurements. As the magnetic field increased, T_C^{onset} shifted to lower temperatures and the superconducting transition became broader. These observations under ambient pressure unambiguously show the intrinsic bulk superconductivity. From anisotropic Ginzburg-Landau theory, the upper critical field parallel to the ab plane, $H_{c2}^{\parallel}(T)$, can be estimated by using $H_{c2}^{\parallel}(T) = \phi_0/[2\pi\xi_{\parallel}(T)\xi_{\perp}(T)] = \phi_0/[2\pi\xi_{\parallel}(0)\xi_{\perp}(0)\{1\text{-}(T/T_C)^2\}]$, where ϕ_0 denotes the quantum magnetic flux and $\xi_{\perp}(T)$ and $\xi_{\parallel}(T)$ are the coherence length perpendicular and parallel to the ab plane, respectively. From the $1\text{-}(T/T_C)^2$ fitting shown in the inset of Fig. 3, the upper critical field, $H_{c2}^{\parallel}(0)$, for the type-2 superconductor was estimated to be 11.7 Oe by extrapolating the fitting curve to the $T = 0$ K limit. Thus, $\xi(0)$ was estimated to be 5300 Å, assuming $\xi_{\parallel}(0) = \xi_{\perp}(0)$. Both values are similar to those for KC_8 [24].

Figure 4 shows the behavior of T_C as a function of d for GICs, including BaC_6. T_C drastically decreased with an increase in d. T_C plots for MC_6 (M = Ca, Sr and Ba) follow a trend similar to those of XC_8 (X = K and Rb), suggesting that the superconducting mechanism of GICs can be interpreted systematically regardless of the valence charge (Z) of intercalant ion. Many advanced DFT calculations were proposed in order to explain the mechanism of superconductivity in GICs and their T_C values for various intercalants in the framework of the conventional phonon mediated electron paring mechanism [20,21]. Calandra and Mauri have proposed that BaC_6 has a

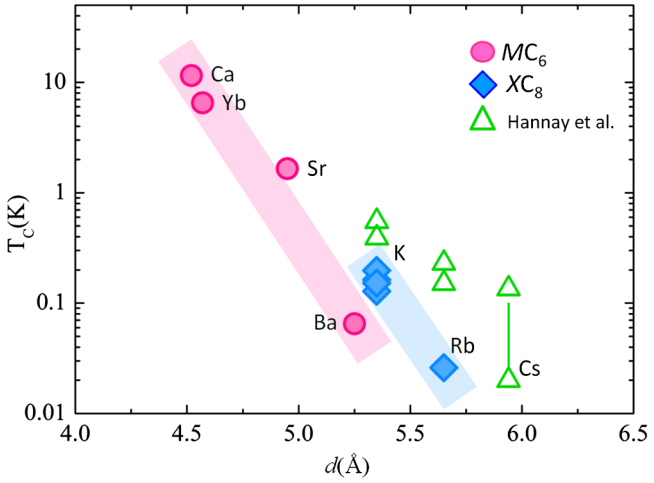

FIG. 4 (color online). T_C vs d for two types of GICs: MC_6 (M = Ca, [7,8] Sr, [13] Ba, and Yb [7], solid red circle) and XC_8 (X = K [24,25] and Rb [26], solid blue rhombus) from HOPG. Open green triangles are the values reported by Hannay *et al.* [11]. The line is a guide for the eye.

2D-like Fermi surface and CaC_6 has a three dimensional (3D) like surface [20]. They predicted that T_C of BaC_6 was estimated to be 0.23 K, which is 1 order of magnitude larger than our experimental value, and that the electronic density of states at the Fermi level for BaC_6 is similar to that for CaC_6. Actually, as for BaC_6, the large d prevents an interlayer band shift near the Fermi surface and suppresses the electron-phonon interactions. Thus, the superconductivity of BaC_6 appears at a quite low temperature compared to that of CaC_6.

It is still difficult to explain the difference between alkali and the alkaline earth metal series. Our results suggest that some other factors are still important for a full understanding of the mechanism of GIC superconductors. Takada proposed a unified model for the superconductivity in GICs using the pertinent gap equation on the basis of first principles calculations [27,28]. In this model, there are three important controlling parameters for determination of T_C in superconducting GICs with the chemical formula NC_x with $x = 2$, 6, and 8 (N = alkali or alkaline earth metals). The first is the Z, the second is the atomic mass (N_M) of the intercalant ion, and the third is the effective mass (m^*) of the itinerant electrons in the interlayer state. Electrons are transferred from intercalants to the graphite bands with 2D characters or to the nearly isotropic 3D bands composed of orbitals from the intercalants and the graphite interlayer states. The fractional factor f between 2D and 3D electrons is defined as the branching ratio Zf: $Z(1\text{-}f)$ in the proposed model. The 3D electrons feel a large electric field of the polarization wave derived from the oscillations of positively charged intercalant ions M^{Z+} and negatively charged carbon ions $C^{-fZ/x}$. Both out-of-phase optic and in-phase acoustic phonons can provide strong phonon mediated attractive interactions. The electrons on the 2D Fermi surface screen the polar coupling, causing a decrease in T_C with an increase in f [28], whereas intercalant atoms with a large Z cause a decrease in f. In fact, T_C for CaC_6 can be well reproduced with $m^* = 2.8m_e$ and $f = 0.16$, where m_e is the mass of a free electron. On the other hand, T_C for KC_8 can be described using $m^* = m_e$ and $f = 0.6$, indicating that the dimensionality of the Fermi surface is a very crucial parameter. T_C for BaC_6 have not been presented.

It is noted that other intriguing results about phonons in GICs were reported by Raman spectroscopy [29], inelastic x-ray scattering study [30], and first-principles calculation [31]. Our results give further information for understanding previous reports. Our experimental findings provide not only the last missing piece, but also a deep insight of the mechanism of GIC superconductors.

In summary, superconductivity in BaC_6 with T_C of 65 mK was successfully detected for the first time, and these essential data give a complete picture of GIC superconductors. A relationship between T_C and d is now perfectly clarified, from which a systematic and clear

understanding of the superconductivity in GICs can be argued. There was a drastic decrease of T_C in BaC_6 due to the changes in the dimensionality of the Fermi surface and suppression of the electron-phonon interactions. The present systematic picture not only settles a long-running debate, but also helps one to develop a new layered superconductor.

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