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Superconductivity in $K_3Ba_3C_{60}$

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We report superconductivity of ternary fulleride synthesized by intercalation of potassium into Ba_3C_{60}. Bulk superconductivity with the onset temperature at 5.6 K was observed in $K_3Ba_3C_{60}$, which forms a body-centered-cubic (bcc) lattice with the cell parameter of $a = 11.24$ Å. Naive electron counting predicts that the Fermi level of $K_3Ba_3C_{60}$ is at the center of the t_{1g}-derived band, in sharp contrast with also superconducting Ba_6C_{60}. This result indicates that the superconductivity of fullerides occurs at the half-filled states both of the t_{1u}- and t_{1g}-derived bands. [S0163-1829(96)00846-6]

The lowest two unoccupied molecular orbitals of C_{60} are both triply degenerate, having t_{1u} and t_{1g} symmetry. Superconductivity in fullerides appears when electrons are introduced by intercalation of alkali or alkali-earth metals into the next lowest t_{1g} level, as well as into the lowest t_{1u} level.[1,2] The former superconductors are realized in the alkali-earth-metal intercalated compounds, such as Ca_5C_{60} (Ref. 3), Ba_6C_{60} (Ref. 4), and Sr_6C_{60} (Ref. 5). Occurrence of superconductivity in such a high reduction state is one of the most unique properties of fullerides. Nontheless, understanding of the ''t_{1g} superconductors'' is extremely poor in comparison with the well-known t_{1u} superconductors, that is the alkali intercalated C_{60} having a $(C_{60})^{3-}$ reduction state, in other words the half-filled state of the t_{1u}-derived band. This is partly because of the difficulty in synthesis of samples. From this point of view, synthesis of new materials having partially filled t_{1g} state and easy to synthesize can be a breakthrough to global understanding of fullerene superconductivity.

Recently, synthesis of multinary complex fullerides involving not only alkali metals but also neutral molecules or alkali-earth metals enables us to control the crystal structure and band filling (electron numbers on the t_{1u} level) independently. The former example is intercalation of NH_3 molecules into A_3C_{60}-type materials.[6–8] The latter is the A_2BaC_{60} and ABa_2C_{60}-type compounds, where A denotes alkali metals. In these compounds, one can change the valence of C_{60} without significant structural modification,[9] because a simple electron counting with monovalent alkali and divalent alkali earth holds for all compounds synthesized. These multinary complex fullerides might provide an opportunity to study the relation between the C_{60} valence state and the electronic properties or superconductivity.

The idea of complex fullerides is applicable to the highly reduced fullerides. Particularly, complex fullerides containing alkali and alkali-earth metals are promising materials for the study of the band-filling effect of the t_{1g} band. As a first step of this strategy, we tried intercalation of alkali metals into Ba_3C_{60} (Ref. 10). We chose this host material having an $A15$ structure because of two reasons. First, the simple ionic crystal model predicts that the t_{1u} level is fully occupied and the t_{1g} level is empty. Second, the $A15$ structure involves three unoccupied interstitial sites per C_{60}. Potassium is the best intercalant since the ionic radius of K^+ (1.33 Å) is close to that of Ba^{2+} (1.38 Å). Here we report synthesis and structure of $K_3Ba_3C_{60}$, which displays superconductivity with the onset temperature at 5.6 K. A naive electron count indicates that $K_3Ba_3C_{60}$ is in the half-filled state of the t_{1g}-derived band in sharp contrast with the almost filled t_{1g}-derived band in Ba_6C_{60}.

Starting Ba_3C_{60} powders were synthesized by reacting stoichiometric amount of powders of Ba and C_{60}. A quartz tube with mixed powders inside was sealed under high vacuum at about 2×10^{-6} torr, and heated at 600 °C for three or four days. This reaction reproducibly yielded a single phase of $A15$ Ba_3C_{60}. The reaction of potassium and Ba_3C_{60} was made in a similar manner to that of potassium doping into pure C_{60}. A piece of potassium metal and Ba_3C_{60} powders were loaded in a Pyrex tube, which was sealed under 2×10^{-6} torr and heated at 260 °C for three days. Reaction at 400 °C or longer annealing time at 260 °C tends to result in a phase separation into Ba_6C_{60} and K_6C_{60}.

Although Ba_3C_{60} does not show any superconducting signal, potassium-intercalated materials superconduct with the onset temperature at 5.6 K. Figure 1 shows the temperature dependence of dc magnetization measured at 10 Oe for samples of the nominal composition at $K_{3.5}Ba_3C_{60}$. The shielding fraction reached 30% at 2 K, indicating the bulk nature of the superconductivity. In a separate experiment, we

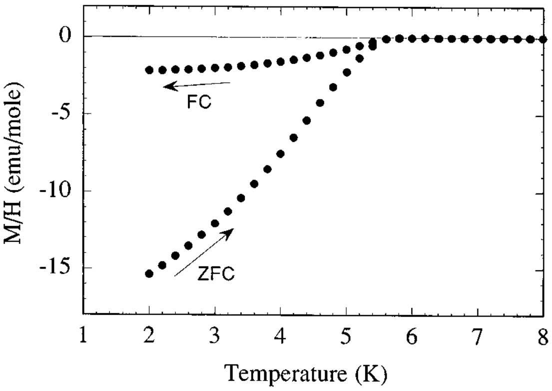

FIG. 1. Temperature dependence of magnetization of nominal $K_{3.5}Ba_3C_{60}$ at a field of 10 Oe.

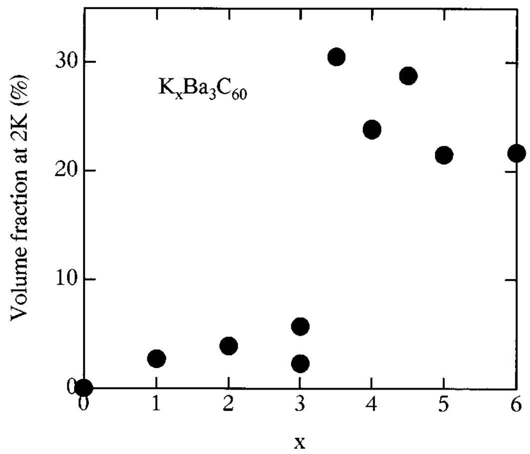

FIG. 2. Shielding fraction measured at 2 K by a zero-field cooling as a function of nominal potassium concentration x.

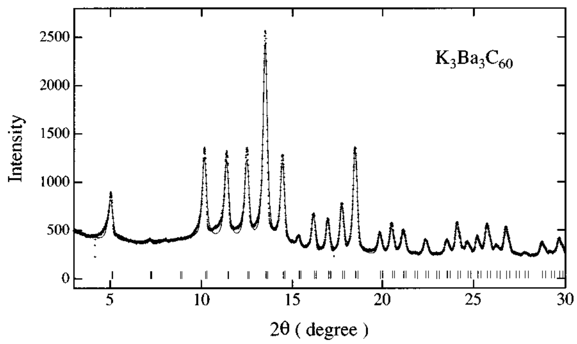

FIG. 3. X-ray-diffraction pattern of nominal $K_{3.5}Ba_3C_{60}$ collected with Mo $K\alpha$ radiation. The crosses are experimental points and the solid line is a Rietveld fit to the model $K_3Ba_3C_{60}$ in the space group $Im3$. Ticks mark the positions of the allowed Bragg reflections taking the $K\alpha_1$ and $K\alpha_2$ radiations into account.

have synthesized Ba_6C_{60} in the same way as Ba_3C_{60} and checked the superconducting properties. The Ba_6C_{60} sample, which showed a bcc pattern in the x-ray diffraction (XRD) measurement, displayed 24% shielding at 2 K and the onset temperature at 7 K. This onset temperature is consistent with the literature[4] and definitely differs from what we observed in potassium-doped samples (Fig. 1). We also note that, in the phase-separated samples annealed at 400 °C, bulk superconductivity was not observed, even from Ba_6C_{60}. This is possibly due to the narrow range of Ba concentration that is favorable for the superconductivity.[4]

Figure 2 shows the shielding fraction at 2 K against the nominal composition x of potassium. Above $x=3$, the shielding signal jumps to over 30%, keeping high fraction to $x=6$. This trend is in sharp contrast with that for Ba_xC_{60} which forms an extremely narrow peak at $x=6$. The high volume fraction observed in a wide range of nominal potassium content indicates that the superconducting phase is considerably stable as the case of alkali intercalated C_{60}. Since the T_c was constant at 5.6 K for all K-doped samples in Fig. 2, there is only one superconducting phase at around $x=3$–4.

XRD measurements were performed on all samples in Fig. 2. Samples with $x=1$ and 2 show similar patterns to that of $A15$ phase. At $x\geqslant 3$, we find a drastic change to a single phase bcc pattern with the cell parameter $a=11.24\pm 0.01$ Å. Although the bcc structure was kept unchanged to $x=6$, peaks are broadened and a tiny additional peak from potassium metal is sometimes observed at $x\geqslant 4.5$, indicating that the bcc is a saturated phase. Figure 3 shows the XRD pattern of the nominal $x=3.5$ sample collected by Mo $K\alpha$ radiation on a 12 kW rotating anode generator. The pattern is similar to that for the well-known bcc structure found in A_6C_{60} [A is K, Rb, Cs (Ref. 11), and Ba (Ref. 4)]. All the observed peaks are indexed as a single phase bcc of $a=11.246$ Å, which is close to the averaged value of the cell parameters for Ba_6C_{60} (11.17 Å) and K_6C_{60} (11.39 Å). This result strongly indicates that the superconducting phase is $K_3Ba_3C_{60}$, which is a solid solution of Ba_6C_{60} and K_6C_{60}.

We have carried out a Rietveld refinement of the structure using the RIETAN package (F. Izumi). The solid line in Fig. 3 shows fitted data to a model of the bcc structure (space group $Im3$). C_{60} molecules are assumed to have equal C-C bond lengths. Carbon positions are allowed to move only radially to preserve the shape of the C_{60} molecules. The refinement converged rapidly to the R factors of $R_{wp}=8.55\%$ and $R_p=6.61\%$, and $S=6.4$ at the following coordinates; $C1$ at 0.06407, 0.0, 0.3112; $C2$ at 0.1281, 0.1037, 0.2716; $C3$ at 0.06407, 0.2074, 0.2319; and K and Ba at 0.0, 0.5, 0.2798, and at isotropic thermal factors of $B=1.4$ and 2.3 (Å^2) for C and Ba(K), respectively. Here the occupancies of K and Ba are both fixed at 0.5. We have tried a refinement of the composition x of K to the model $K_xBa_3C_{60}$ and $K_xBa_{6-x}C_{60}$. Both refinements gave $R_{wp}=8.55\%$ at $x=3.0$ (4). These results led us to conclude that the ideal composition of the superconducting phase is $K_3Ba_3C_{60}$. Figure 2 indicates that a slight excess of potassium in the nominal content is necessary to obtain a high shielding fraction in $K_3Ba_3C_{60}$ superconductor.

We have also succeeded to prepare $Rb_3Ba_3C_{60}$ by the same method as $K_3Ba_3C_{60}$. The sample showed an XRD pattern that is indexed as a single phase bcc with the lattice constant of 11.32 Å. This value is also close to the mean value of Ba_6C_{60} and Rb_6C_{60}. This compound, however, did not superconduct down to 2 K. Occurrence of superconductivity in $K_3Ba_3C_{60}$ ($a=11.24$ Å) and absence of superconductivity in $Rb_3Ba_3C_{60}$ with the larger cell is a notable feature that differs from that in t_{1u} superconductors.

The relation between T_c and the lattice parameter is in controversy. Kortan *et al.* showed that T_c increases with increasing the intermolecular distance,[5] as in the case of t_{1u} superconductors. Meanwhile, Schirber *et al.* showed T_c increases with pressure in Ca_5C_{60} (Ref. 12), suggesting an opposite trend. This issue should be discussed on the isoelectronic materials. In this sense, the isoelectronic and isostructural group of $A_3Ba_3C_{60}$ provides a new opportunity.

The position of the Fermi energy in $K_3Ba_3C_{60}$ is another important issue. Many experiments such as electrical resistivity[13] and photoemission[14] measurements clearly showed that the superconductivity in alkali-earth–metal-doped C_{60} occurs when carriers are introduced into the t_{1g} level (the next lowest unoccupied molecular orbital) of

C_{60}. However, precise electronic structures of Ba_6C_{60} are unclear. For instance, Raman measurements on Ba_xC_{60} were unsuccessful,[9] and Baenitz suggested that the true superconducting phase is not Ba_6C_{60} (Ref. 15). A calculation by a local-density approximation[16] (LDA) shows that the alkali earth and C_{60} orbitals are significantly hybridized and that the Fermi level of Ba_6C_{60} is located close to the top of the t_{1g}-derived band, resulting in a semimetallic character. The position of the Fermi energy derived from the LDA calculation is not far from the simple electron counting, except for the strong hybridization of the t_{1g} band with Ba orbitals. This result suggests that the simple counting is still useful. Thus speculated energy scheme indicates that $K_3Ba_3C_{60}$ is a metal in which the t_{1g}-derived band is half-filled, in contrast with Ba_6C_{60}. (Here, we must note that the conduction band is formed by a strong hybridization of the t_{1g} level of C_{60} and Ba orbitals.) Superconductivity in $K_3Ba_3C_{60}$ as well as in Ba_6C_{60} and Ca_5C_{60} indicates that superconductivity at the t_{1g}-derived band is not restricted to the specific reduction state. In this sense, the comparison with the A_3C_{60}-type superconductors is of significant interest. A recent experiment[9] shows that the superconductivity on the t_{1u} band occurs only near the half-filled state, in contrast with the t_{1g} superconductors. The role of electron-phonon and electron-electron interactions on the superconductivity might be significantly different between the t_{1u}- and t_{1g}-derived bands.

Recently, superconductivity of rare-earth metal intercalated C_{60} was reported on $R_{2.75}C_{60}$ ($R=$ Yb and Sm).[17,18] The authors suggest that rare-earth metals are divalent in these compounds, indicating that the Fermi level is still on the t_{1u}-derived band close to the upper edge of this band. Although the hybridization effect between C_{60} and metal ions cannot be neglected in this system, it is another interesting example of superconductors from the viewpoint of valence state of C_{60}.

In summary, we have synthesized a superconductor $K_3Ba_3C_{60}$, with $T_c=$ 5.6 K. This compound has a bcc structure which is regarded as a 1:1 solid solution of K_6C_{60} and Ba_6C_{60}. The new material indicates that the superconductivity occurs at the half-filled state of the t_{1g}-derived band in the bcc lattice. Existence of the solid solution $K_3Ba_3C_{60}$ suggests that a variation of synthesis routes might produce a solid solution of $K_xBa_{6-x}C_{60}$. This system will hopefully enable us to control electron counts on the t_{1g}-derived band without changing the bcc structure, providing an interesting opportunity to investigate the effects of the valence state of C_{60} on the electronic properties and superconductivity.

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