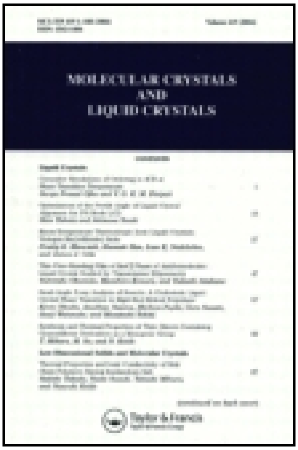

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A Search for New Ionic C_{60} Charge Transfer Complexes

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A SEARCH FOR NEW IONIC C_{60} CHARGE TRANSFER COMPLEXES

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Abstract As one of the strategies to obtain ionic C_{60} charge transfer complexes, a doping of alkali metals to neutral CT complexes has been attempted under a mild condition. Superconductivity has been detected by magnetic measurements in OMTTF·C_{60}·benzene doped with potassium or rubidium, where OMTTF is octamethylene-tetrathiafulvalene.

INTRODUCTION

Although nearly five years have passed since the discovery of the superconductivity in K_3C_{60},[1] the variation of the C_{60} compounds itself has been limited in almost a few families of alkali-, alkaline earth-, or tetrakis(amino)ethylene derivatives-C_{60}. Regarding C_{60} molecule as one component of charge transfer (CT) complexes, the C_{60} CT complexes with new crystal structures and/or new electronic states must be obtained by using a variety of components, especially by using molecular donors. It is also important to use organic or molecular donors as one of the counterparts of new C_{60} CT complexes, because (1) it could construct characteristic crystal structures not obtainable by mere spherical components and (2) the bigger counterpart is preferred to increase T_c of superconductor according to the density of states consideration. Since it is already known that C_{60} has an ability to give the three-dimensional superconductors, the above point (1) intends to produce the superconductors of two- or one-dimensional nature, and to make clear the correlation between superconductivity and dimensionality.

The C_{60} molecule is a weak electron acceptor comparable to 2, 5-dibromo-*p*-xyloquinone or 1, 2, 4, 5-tetracyanobenzene as has been demonstrated by the $h\nu_{CT}$ and redox potential measurements in solution phase.[2] As a result, C_{60} yields the CT complexes of neutral ground state with conventional organic TTF-type donors (OMTTF, BEDO-TTF, EDT-TTF, etc.). However, the anionic species of C_{60} seems to be essential to the realization of some fascinating solid state properties such as ferromagnetism or superconductivity in C_{60} compounds.

Within the framework of the two-component CT complexes composed of donor and C_{60}, strong electron donating ability of the donor is needed to ionize C_{60} in solid state, as represented by TDAE·C_{60}[3]. Based on a phase diagram of C_{60} CT complexes,[2] the molecular donors of redox potential $E_{redox} < -0.05$ V vs. SCE are required for partial or ionic CT complexes. We have investigated some metallocene donors, decamethylferrocene (Cp^*_2Fe) ($E_{redox} = -0.086$ V), nickelocene (0.00 V) for the CT complex preparation and obtained dark brown products. The dark brown solid obtained by a rapid dry-up of 2:1 toluene solution of Cp^*_2Fe and C_{60} at room temperature showed a charge transfer absorption at $h\nu_{CT} = 9.5 \times 10^3$ cm^{-1}. In one batch of this CT complex, a coercive field of about 20 G and a saturation of magnetization of about 0.4 emu/g were observed at 5 K and even at 300 K.[4]

As another strategy to prepare ionic C_{60} CT complexes, a doping of alkali metal to the neutral CT complexes (namely, three-component system) has been attempted. The doping was conducted under a mild condition to avoid possible decomposition of the CT complexes. At the beginning of our project, superconductivity was first detected by low field microwave absorption (LFMA) in OMTTF·C_{60}·benzene ($T_c = 16$ K) or BEDO-TTF~C_{60} ($T_c = 15$ K) doped with potassium.[5] Also we have observed superconductivity by SQUID magnetization measurements in potassium-doped OMTTF~C_{60} complex prepared from carbon disulfide solution ($T_c = 17$ K). The details on LFMA and EPR studies will be presented elsewhere.

In this paper, we describe the preparation of the samples, the results of magnetization measurements by a SQUID magnetometer on potassium- or rubidium-doped OMTTF·C_{60}·benzene, together with EPMA and a part of single crystal x-ray structure analysis on the potassium-doped sample. The pristine OMTTF·C_{60}·benzene is a neutral CT complex containing 1:1:1 of each component in one unit cell (Fw = 1111.29, $\rho_{calc} = 1.640$ g·cm^{-3}). This black crystal shows its lowest CT band at 10.9×10^3 cm^{-1} and is insulating (10^{-8} S·cm^{-1} at room temperature). From the single crystal structure analysis, at least two sets of atomic coordinates of the C_{60} molecule are determined at room temperature on the same spherical surface indicating an orientational disorder (R = 0.135).[2]

RESULTS AND DISCUSSION

Sample Preparation

The pristine neutral complex of OMTTF·C_{60}·benzene crystals was obtained by a direct mixing and slow evaporation method in benzene solution.[2] In a typical run, 55.0 mg

(0.176 mmol) of OMTTF and 51.0 mg (0.0708 mmol) of C_{60} were mixed with 100 cm^3 of dry and degassed benzene (distilled over P_2O_5) followed by ultrasonic dissolving at room temperature. After filtered into a 200 cm^3 beaker, the reddish brown solution was stored under dark at room temperature. Black plates started to crystallize when the volume of the solution was concentrated to about 50 cm^3. When the solution was concentrated further to about 25 cm^3 (about 10 days after the first mixing), the black shiny crystals were separated by filtration from the remaining OMTTF rich orange solution, washed with cold dry benzene, and dried *in vacuo* (58.2 mg, 74 % yield based on C_{60} used).

The quartz sample tubes of 5 mm diameter for EPR experiments were used for the doping and the subsequent SQUID measurements. About 3 mg of the pristine OMTTF·C_{60}·benzene was put into the bottom of the sample tube, then excess amount of alkali metal was sublimed into the other side of the tube and sealed off in a diffusion pump vacuum line (10^{-4} -10^{-5} torr). The sealed tubes of about 10 cm long were "warmed" in a horizontal dual-type furnace in which the OMTTF·C_{60}·benzene side was kept at slightly higher temperatures (T_s) than the alkali metals side (T_d) to prevent the alkali metals condensing on the source complex. The typical conditions were T_s/T_d = 67℃/64℃ for 19 days in the rubidium doping, and T_s/T_d = 55℃/50℃ for 11 days~1 month in the potassium doping , respectively (the decomposition temperature of OMTTF·C_{60}·benzene itself is higher than 150℃). After the doping treatments mentioned above, the appearance of the source complex did not changed so much. In most cases, the outer shapes of the crystals were kept unchanged though a slight roughening of the crystal surface was observed under a microscope. No sign was observed by appearances that OMTTF was squeezed out to the crystal surface or to the inside wall of the sample tube. The excess alkali metal remaining in the sample tube did not disturb the subsequent measurements since it had been condensed at the opposite end of the tube.

To examine whether the loss of benzene included in the crystal can easily occur under the doping condition, 4.4065 mg of the pristine OMTTF·C_{60}·benzene crystals were put into a glass cell and warmed at 65-68℃ under a dynamic vacuum (the base pressure measured near the oil diffusion pump head was $6\text{-}9 \times 10^{-6}$ torr) for 8.5 days. After this treatment, the mass decreased to 4.3964 mg (using an ultramicro balance, we can discuss the difference of 10 μg safely in this case) corresponding to 0.23 % loss in mass. Considering that the mass ratio of benzene/(OMTTF·C_{60}·benzene) is 7.0 %, and assuming that the observed loss in mass was due to a loss of benzene, the ratio of the benzene deficiency would be 0.03 %. This small value suggests that the selective loss of benzene does not occur at least in this condition (in the absence of alkali metal). On the other hand, something seemed to evaporate actually because a slight coloration of the liquid nitrogen glass trap (purple, brown, yellow, and white bands) was observed at the end of this experiment. Then, the small loss in mass (0.23 %) might be a result of the material migrations connected with dissociation of the CT complex under the dynamic vacuum, however, the same phenomenon would not necessarily proceed in the sealed tubes of relatively limited and static vacuum. In fact , any sign of coloring nor contamination of the inside wall near the source CT complex was not observed in the sample doping tube, as mentioned above.

Similar doping treatment by cesium changed the color of the crystals to brownish. Superconductivity has not been observed by the cesium doping so far.

Magnetization Measurements

The dc magnetization was measured by two SQUID magnetometers (Quantum Design MPMS-2) and by two different persons at Okazaki and Kyoto. In making

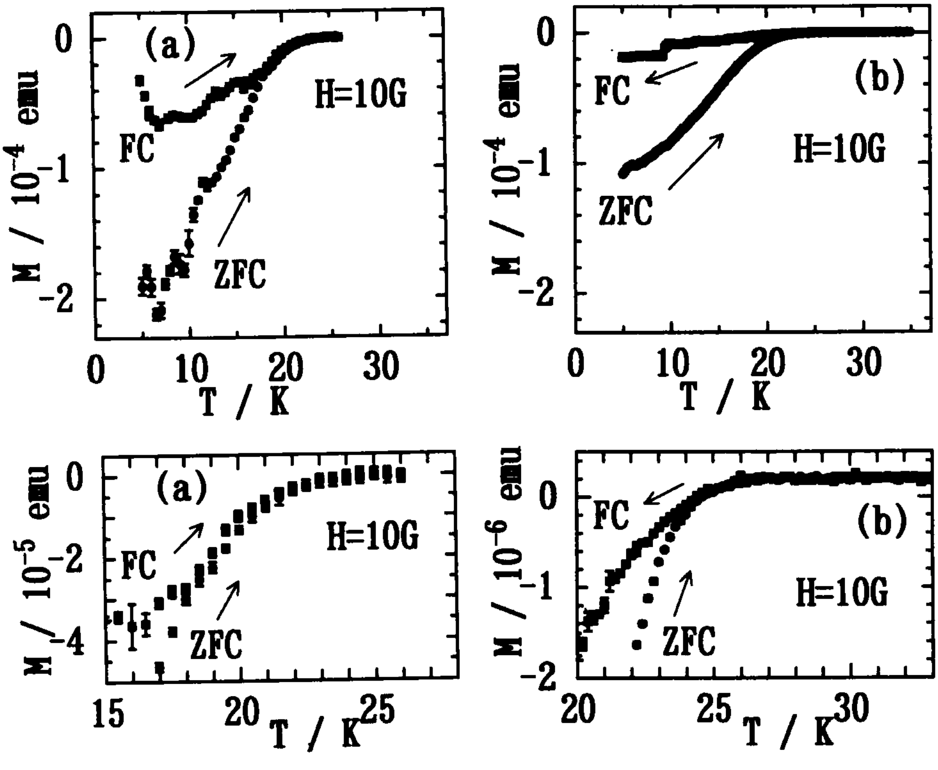

FIGURE 1 Temperature dependence of magnetization of the rubidium-doped-OMTTF·C_{60}·benzene (sample N2), see the text.

measurements, care was not taken to unify the precise magnetic field conditions such as field uniformity, remanence and the earth fields between the two machines. Though this prevents us from delicate discussion on some differences between the data sets measured with respective machine and from the inspection concerning the flux state of the sample, the presented conclusions are not affected.

Figure 1 shows the temperature dependence of magnetization of rubidium-doped OMTTF·C_{60}·benzene (sample N2). From the absolute value of the observed shielding diamagnetic moment at 5 K and 10 G (corresponds to about 10 % (Figure 1a) of the perfect diamagnetism without demagnetization correction) and the clear Meissner effect, we have interpreted that superconductivity has occurred in the sample N2 (with the highest T_c of 23-26 K).

Figure 1a shows the as made first measurement in which some anomalous structures are obvious at around 12 K and 8 K in the zero field cooling run (ZFC). These lower temperature structures suggest the possible coexistence of the multiphase superconductors with different T_c's, though the reproducibility of the magnitudes of

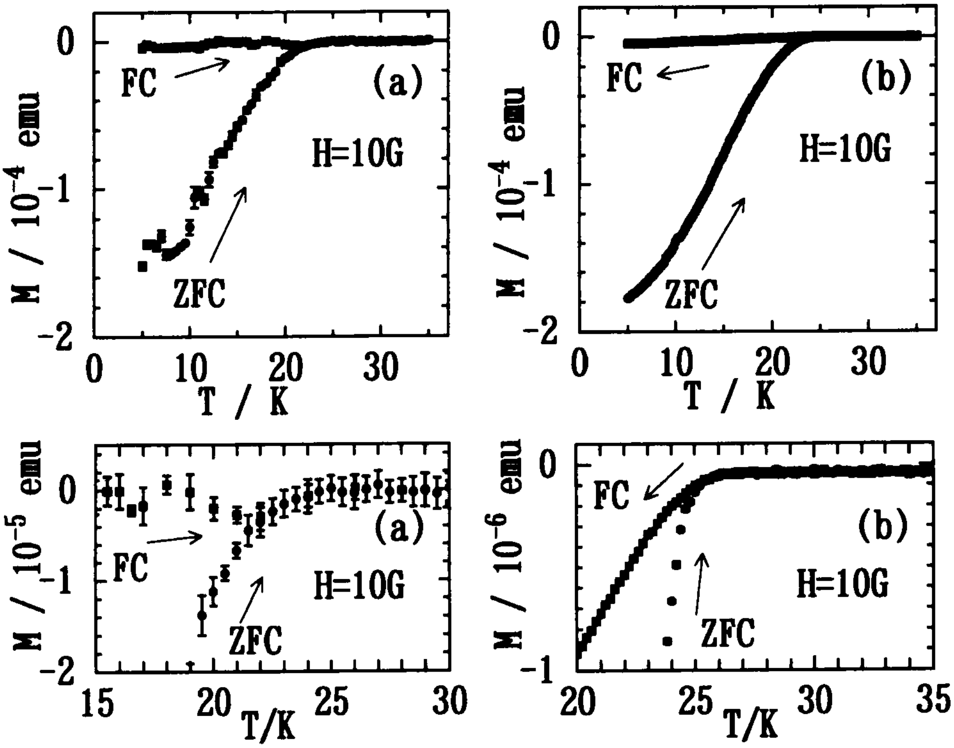

FIGURE 2 Temperature dependence of magnetization of the rubidium-doped-OMTTF·C_{60}·benzene (sample N3), see the text.

the lower temperature structures is not sufficient (and these lower temperature structures tended to be easily suppressed by the larger magnetic field e.g. 15 G). When the additional doping of 1.5 days was performed, those lower temperature structures became less pronounced without change in the highest T_c and the magnitude of the diamagnetic moment at 5 K (not shown).

After the above doping (total 19+1.5 days), the sample N2 was stored at room temperature for about 9 months. Figure 1b shows the measurement on the stored N2 sample. The magnitude of the diamagnetic signal at 5 K became smaller and the structures at around 8 K and 12 K in ZFC became scarcely observable compared with Figure 1a, though the highest T_c clearly remained (or rather elevated). These changes must be related to the chemical and thermal stability of the (multiphase) sample. It is likely that the highest T_c phase is thermally more stable than the lower T_c ones, and that during the 9 months the doping and annealing process has proceeded to some extent even at room temperature.

The sample N3 is the another batch of the rubidium-doped OMTTF·C_{60}·

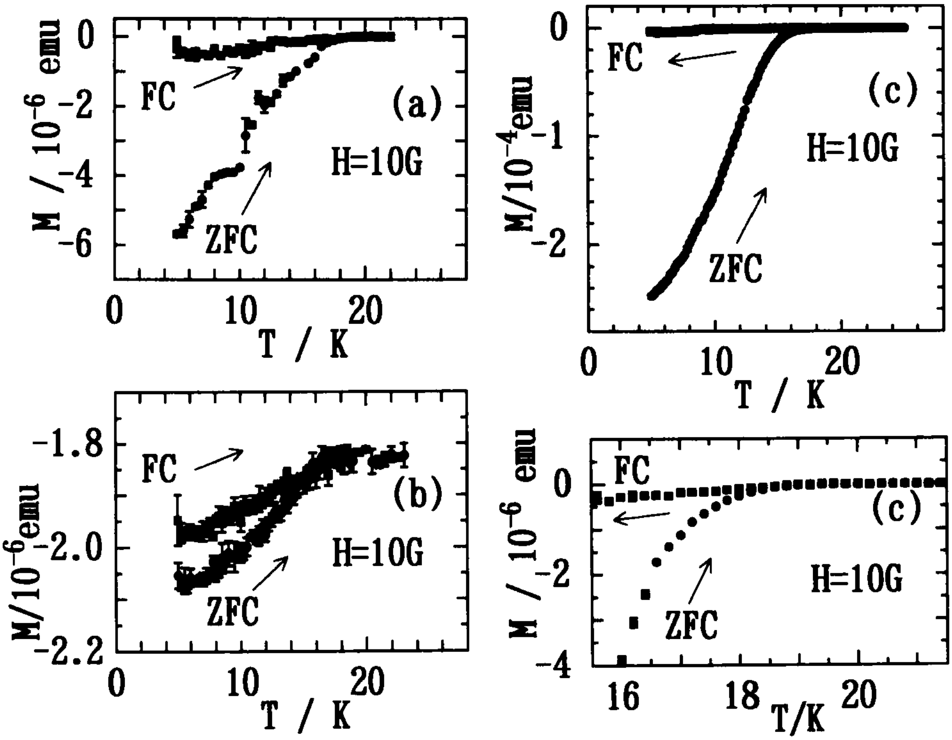

FIGURE 3 Temperature dependence of magnetization of the potassium-doped- OMTTF·C_{60}·benzene , see the text.

benzene treated similarly as the sample N2 except for the absence of the additional 1.5 days doping. Figure 2a shows its first measurement and Figure 2b the 9 months stored N3 sample. As shown in Figure 2a, the lower temperature structures were also observed like Figure 1a. These structures easily disappeared under the H = 15 G measurement at that time (not shown). Similar to the sample N2, relatively smooth curves were observed after 9 months (Figure 2b). The highest T_c also exists at 23-26 K as the sample N2.

In the case of the potassium doping, the obtained results so far have been rather scattered. Figure 3a shows the measurement on the sample doped for 11 days. The onset of the diamagnetic shielding signal can be determined at about 17 K, but the

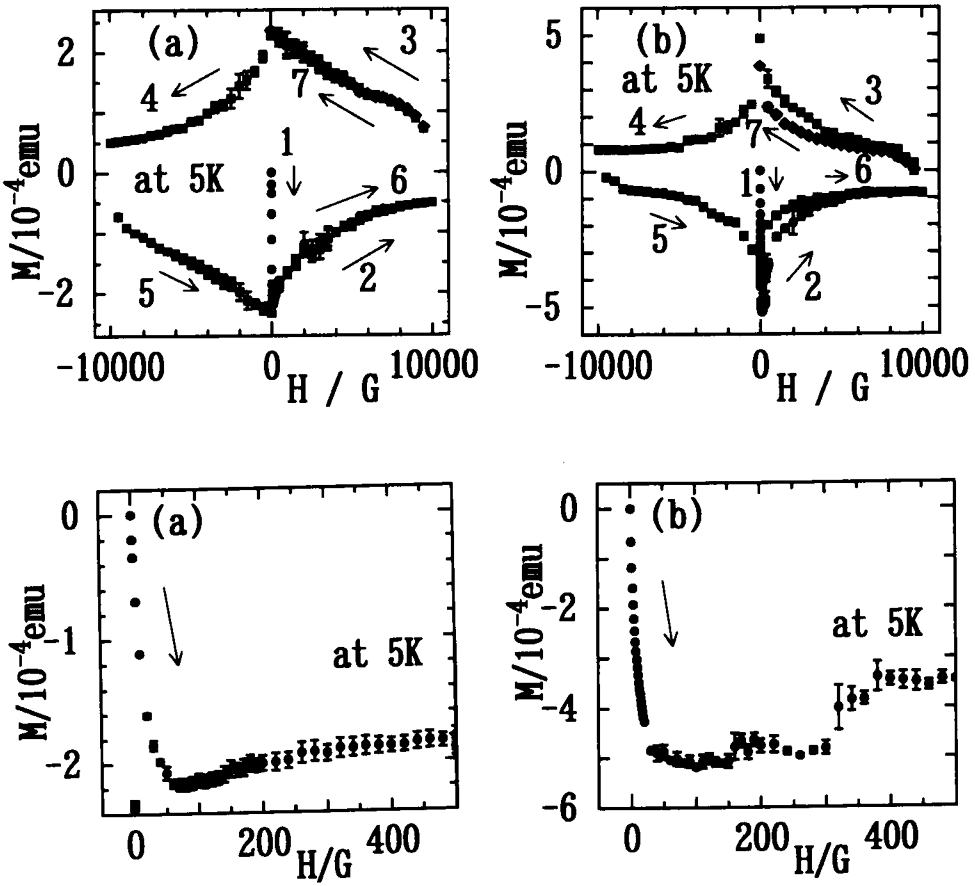

FIGURE 4 Magnetic field dependence of magnetization for the rubidium-doped (a) and the potassium-doped (b) OMTTF·C_{60}·benzene at 5 K, see the text.

magnitude of the moment is definitely small. What one should notice in ZFC of Figure 3a is the appearance of some structures at around 8 K and 12 K like the rubidium-doped samples (Figures 1a, 2a). Being different from the rubidium-doping case, further 7 days doping of the same sample drastically diminished the magnitude of the diamagnetic moment at 5 K as well as the lower temperature structures (Figure 3b). Comparing Figure 3b with 3a, the background diamagnetic moment appears to have been enhanced by the further doping. After the sample of Figure 3b was exposed to air, the superconductivity was almost completely lost indicating its air-sensitivity. During that degradation in atmosphere, the magnetization of about the half amount of the Figure 3b sample was measured at 10 G below 30 K. The magnetization slowly changed its sign from diamagnetic (-3.4×10^{-7} emu) to paramagnetic (7.0×10^{-7} emu) in a period of 3 months. On the other hand, a different batch of the potassium-doped OMTTF·C_{60}·benzene (doped for about 1 month) showed a large diamagnetic shielding signal with onset T_c of 18.8 K (Figure 3c). In Figure 3c, the shielding curve is smooth and the lower temperature structures are not obvious.

To ensure the character as a type II superconductor, magnetic field dependence of the magnetization was measured at 5 K for the rubidium-doped (Figure 4a, the same sample shown in Figure 1b) and the potassium-doped (Figure 4b, the same sample shown in Figure 3c) OMTTF·C_{60}·benzene. In each data, a clear hysteresis loop is shown indicating the presence of substantial flux pinning. Since it is difficult to define a so-called flux penetration field without ambiguity, we only show the nominal magnetic field at which the initial magnetization reached the maximum. As shown in the low field regions of Figure 4, 80 G for the rubidium-doped sample and 100 G for the potassium-doped one can be defined. Another sample (the rubidium-doped, the N3) showed the maximum at around 200 G. These values can be compared with the H_{c1} values (120 G for Rb_3C_{60} and 130 G for K_3C_{60})[6] reported for A_3C_{60}, though the anisotropic nature expected in the doped OMTTF compounds should be properly treated.

As seen in Figures 1-3, the transitions observed were broad and generally did not saturate even at 5 K. It is necessary to examine whether this situation comes from some intrinsic nature or from an insufficient quality of the sample.

It is difficult to distinguish only by the SQUID data whether the origins of the observed superconductivity contain new phases or not. One of the authors (AAZ) has confirmed that the LFMA signal on a single crystal of the rubidium-doped OMTTF·C_{60}·benzene shows a clear angular dependence (namely, anisotropy) at around 5 K. This result strongly suggests that new phase of anisotropic nature with $T_c \geqq 5$ K exists.

EPMA

As for the chemical composition of the material revealing the superconductivity above, we expect that some amount of rubidium or potassium cations must be intercalated into the pristine OMTTF·C_{60}·benzene crystal as a result of the doing process. To confirm the existence of the alkali atoms in the doped crystals, EPMA (and SEM) measurements were performed on a few crystals selected from one batch of the potassium-doped OMTTF·C_{60}·benzene (after the measurement of Figure 3b). The crystals for EPMA/SEM were exposed to the air before the analyses when they were taken out from the sample tube. The lustrous surface appearance of the crystals was changed to the dully one at that time maybe due to the reaction between potassium and oxygen or water in the air. Since the potassium must remain with the crystal even after such a chemical reaction, we can deduce the ratio of (potassium) to (OMTTF·C_{60}·benzene) from the obtained atomic percentage on carbon, sulfur, and potassium.

According to the SEM photographs, some crystals showed very rough surface (probably the effect of the air exposure) and some other crystals' surface remained smooth. Some particles with higher content of potassium were observed on every crystal. These facts indicated that in this batch the distribution and the concentration of potassium were inhomogeneous from crystal to crystal and even in one crystal. Table I shows the calculated atomic ratios of carbon , sulfur, potassium, and oxygen (if detected) based on the observed EPMA results obtained from the surface of a relatively well doped crystal.

TABLE I Atomic ratio of the potassium-doped OMTTF·C_{60}·benzene measured by EPMA. The numbers in the left end column denote the different place and area analyzed. The values have been normalized as the sulfur becomes 4 for convenience to know the ratio of potassium to the complex ($C_{80}H_{22}S_4$), see the text.

	C	S	K	O
1-0	103	4	1.6	4
1-3	39	4	0.1	0.5
2-0	97	4	1.3	2.7
2-3	116	4	1.8	0
3-0	96	4	1.3	0
3-3	117	4	1.6	3.3

In spite of some scatter of data in Table I, we can evaluate the nominal ratio of (potassium) to (OMTTF·C_{60}·benzene) as 1.8:1 at the most. In another crystal, the highest concentration of potassium (C:S:K = 47:4:5.1) was observed from a particle on the crystal surface, however, such a point-like localization would not dominate the total composition. This measurement was made on the air-exposed sample, meaning that some change in specific distribution of potassium might occur. If such a migration of potassium from inside to surface of the doped crystals was the case, the above derived ratio would be overestimated.

In relation to the contents of alkali atoms in the doped OMTTF·C_{60}·benzene, we have tried to observe the Raman spectra of the intramolecular modes of C_{60} between 1200 and 1600 cm^{-1} with a 488 nm argon laser excitation. In the alkali-doped C_{60} solids, it has been well established that the A_g mode of C_{60} appears in the range of 1430-1458 cm^{-1} depending on the charge of C_{60} (the A_g mode shifts linearly at 5 cm^{-1} /e^-).[7] It is required to confirm or remake the calibration curve to know the charge on the C_{60} in these lattice of lowered symmetry (e.g. OMTTF·C_{60}·benzene and the potassium-doped one both belong to triclinic). Unfortunately, any meaningful spectra have not been obtained so far and still in progress.

X-ray Crystal Structure Analyses

The pristine neutral crystal of OMTTF·C_{60}·benzene exhibits a relatively loose two-dimensional sheet of the C_{60} molecules,[2] which can be intercalated by small alkali cations and should give new arrangements of C_{60} anions other than cubic lattices. Figure 5 shows the ac plane projection of the pristine OMTTF·C_{60}·benzene crystal.

X-ray crystal structure analyses have been carried out for the potassium-doped OMTTF·C_{60}·benzene single crystal (after the measurement of Figure 3b). Despite its

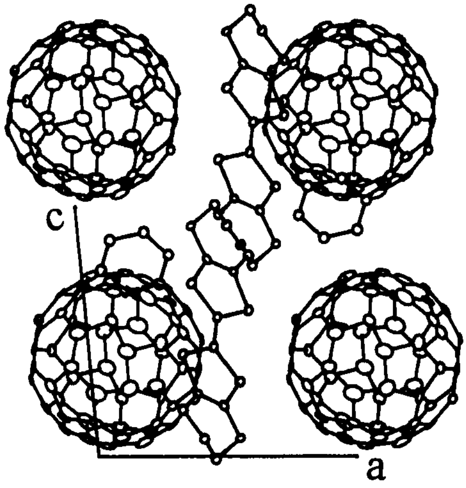

FIGURE 5 Crystal structure of the pristine OMTTF·C_{60}·benzene projected onto the ac plane.

air-sensitive nature, we could determine the lattice parameters of one crystal out of the five tried at ambient atmosphere. The diffraction data for structure analyses were subsequently collected at room temperature by use of a four-circle diffractomerter with Mo radiation. The obtained lattice parameters were listed in Table II together with those of the pristine complex.

TABLE II Lattice parameters of OMTTF·C_{60}·benzene before and after the potassium doping.

	Before potassium doping[2]	After potassium doping
a/Å	10.320(1)	10.342(3)
b	13.676(1)	13.706(4)
c	10.024(1)	10.018(3)
α/°	95.68(1)	95.64(2)
β	95.74(1)	95.71(2)
γ	125.42(1)	125.33(2)
V/Å^3	1125.4(3)	1131.3(6)

Although these two sets of lattice parameters listed above were determined by different diffractometers with different radiations (Cu radiation was used for the pristine complex), almost the identical results have been obtained for the same potassium-doped crystal by use of other different two diffractometers (Mo radiation). We have interpreted that this crystal has expanded by the potassium doping (5.0-6.8 Å^3 increase in volume). The volume of 6 Å^3 corresponds to about 0.6 particles of potassium cation (K^+) in volume by using the ionic radius of potassium (1.33 Å)[8]. As mentioned in the EPMA results, it is likely that the degree of doping should have a distribution. Since the diffraction data should reflect the bulk nature of the sample, we can conjecture that the ratio of the potassium to OMTTF·C_{60}·benzene in this one crystal would be about 0.6:1 as an average.

The structure determination has not completed (R = 0.197), but it has been confirmed that the basic packing is equal to that of the pristine complex. It is noteworthy that the c-axis length shrinks whereas the a- and the b- axes expand. These changes correspond to the d-space expanding and shrinking (d_{100}+0.36 %, d_{010}+0.37 %, d_{001}-0.021 %). Remembering that the c-axis length is the shortest C_{60} to C_{60} distance in the pristine complex, the dimensionality of the intermolecular interaction was lowered to more one-dimensional by the potassium doping.

To find the electron density of potassium in the doped crystal, the data set collection of better quality is now in progress.

CONCLUSIONS

By mild doping of potassium or rubidium to the neutral charge transfer complex of OMTTF·C_{60}·benzene, bulk superconductivity was observed by SQUID measurements with T_c at 23-26 K for the rubidium doping, 17-18.8 K for the potassium doping, respectively. In both doping, the possible existence of lower T_c's of 8 K and 12 K were also shown in the shielding measurements on a SQUID magnetometer. Although the EPMA/SEM showed the inhomogeneous potassium doping, K:(OMTTF·C_{60}·benzene) = x:1 ($x \leq 1.8$) of the composition ratio was observed in the crystal examined. The single crystal x-ray structure studies on a potassium-doped OMTTF·C_{60}·benzene indicated that the lattice expanded with doping. The volume expanded corresponded to about 0.6 potassium adding per complex. The dimensionality of the crystal seemed to be lowered by the doping though the basic packing was not altered.

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