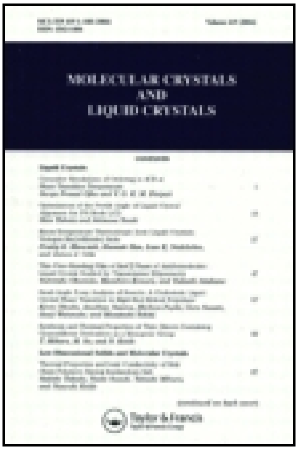

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ALKALI METAL DOPING TO C_{60} CT COMPLEXES

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Abstract In order to ionize C_{60} in a different packing manner other than A_3C_{60}, alkali metals were doped to neutral charge transfer complexes under a mild condition. Bulk superconductivity has been detected by magnetic measurements in OMTTF·C_{60}·benzene doped with potassium or rubidium, where OMTTF is octamethylene-tetrathiafulvalene. Although an expansion of unit cell volume has been observed in the case of the potassium doping, such a detection of apparent change in the single crystal x-ray diffractometry has not succeeded yet by the rubidium doping. After the x-ray experiments on the rubidium-doped crystals, however, SQUID measurements showed superconductivity in one crystal out of the three examined.

INTRODUCTION

C_{60} yields the charge transfer (CT) complexes of neutral ground state with conventional tetrathiafulvalene (TTF) -type organic donors (OMTTF, BEDO-TTF, EDT-TTF, etc.), because C_{60} molecule is a weak electron acceptor comparable to 1, 2, 4, 5-tetracyanobenzene as has been demonstrated by the CT energy and redox potential measurements in solution phase.$^{1)}$ On the other hand, the anionic species of C_{60} seem to be essential to realize fascinating solid state properties such as superconductivity or ferromagnetism in C_{60} compounds.

It is important to use organic or molecular donors as one of the counterparts of new 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 superconductivity in the framework of the density of states consideration.

As one of the strategies to obtain the molecular donor-C_{60} CT complexes of ionic ground state, a doping of alkali metal to the neutral CT complexes has been attempted under mild condition. The "mild condition" is required to prevent the decomposition of the complex, and is favorable to preserve the basic packing manner of the pristine complex. In the pristine neutral complex of OMTTF·C_{60}·benzene single crystal, C_{60} molecules form a two-dimensional layer which is sandwiched by the layers of OMTTF and benzene molecules. By the doping of potassium or rubidium to the neutral CT 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, accompanied by the possible existence of lower T_c's of 8 K and 12 K in the shielding measurements on the both compounds.[2] 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 etc. were described in the previous paper.[2] In this report, the single crystal x-ray diffractometry was performed on the rubidium-doped OMTTF·C_{60}·benzene followed by the re-measurements of the temperature dependence of magnetization.

EXPERIMENTAL

The crystals used for the x-ray experiments were selected from the batches which had already given the SQUID magnetization data. As reported previously, about 3 mg of OMTTF·C_{60}·benzene and excess amount of rubidium were sealed in a sample tube (5 mm diameter, 10 cm long) followed by 19 days warming (crystal side 67 °C, rubidium side 64 °C). Two different batches of samples N2 and N3 had shown almost the

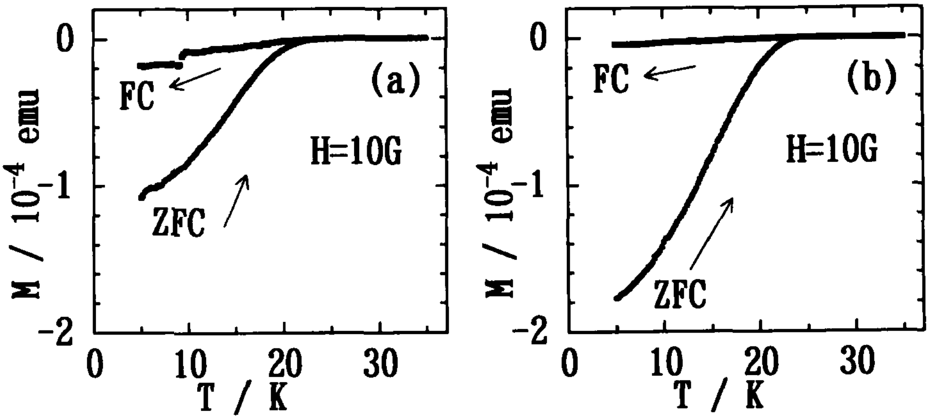

FIGURE 1 Temperature dependence of magnetization of the rubidium-doped OMTTF·C_{60}·benzene,[2] sample N2 (a) and sample N3 (b). The sample mass was about 3 mg in each case.

same results of the temperature dependence of magnetization each other (Figure 1)2).

Since it had been demonstrated that the superconductivity of the potassium-doped OMTTF·C_{60}·benzene was lost by an exposure to the air,2) the selection and the loading of the crystals into the capillary tubes for x-ray diffraction were conducted in a well controlled atmosphere of an argon grove box (<3 ppm oxygen approx. at least). Five crystals from each ampoule (N2 and N3, total ten crystals) of good-looking quality were selected under a microscope, loaded into glass capillary tubes (0.7 mm diameter, 0.01 mm thick), fixed by silicone grease (Toray Silicone, 111) or Torr Seal® (Varian), and sealed by Torr Seal®. The distance of the crystal from the ends of the capillary was about 1 cm.

The x-ray diffraction data for single crystals after the rubidium doping were collected at room temperature by a Rigaku automated four-circle diffractometer with Cu radiation. The final lattice parameters were refined by 19-25 reflections of $47^\circ < 2\theta < 59^\circ$ after the full data collection for structure analyses. No degradation of the intensity and shape of the reflections during the measurements was observed.

Temperature dependence of magnetization under the applied magnetic filed of 10 G or 1 G was measured by a SQUID magnetometer (Quantum Design MPMS-2) for the rubidium-doped crystals after the x-ray data collection. The x-ray capillary tube containing the crystal was put into the bottom of quartz sample tube (5 mm diameter, 10 cm long) and sealed with 10 torr of helium gas. Another empty quartz tube (5 cm long, the both ends open) was placed beneath the sample tube to cancel the signal from the quartz wall.

RESULTS AND DISCUSSION

Among the ten crystals tried, only three from the N3 ampoule were most suitable for

TABLE I Lattice parameters of OMTTF·C_{60}·benzene before and after the alkali doping. Three crystals of N3-1, N3-3, N3-5 were selected from the same ampoule of N3 after the measurement of Figure 1b.

	Before	After K	After Rb doping		
	doping1)	doping2)	N3-1	N3-3	N3-5
a/Å	10.320(1)	10.342(3)	10.319(2)	10.325(3)	10.325(3)
b	13.676(1)	13.706(4)	13.678(2)	13.687(3)	13.685(4)
c	10.024(1)	10.018(3)	10.025(1)	10.016(2)	10.017(1)
α/°	95.68(1)	95.64(2)	95.69(1)	95.69(2)	95.68(2)
β	95.74(1)	95.71(2)	95.76(2)	95.70(2)	95.73(2)
γ	125.42(1)	125.33(2)	125.42(1)	125.34(2)	125.38(2)
V/Å^3	1125.4(3)	1131.3(6)	1125.5(4)	1127.4(6)	1126.5(6)

the data collection for structure analyses. Table I summarizes the obtained lattice parameters together with those of the pristine complex[1] and those of the potassium-doped one.[2]

The structure determinations including difference Fourier treatments are still in progress, but it has been confirmed that the basic packing of the three rubidium-doped crystals is equal to that of the pristine and the potassium-doped complexes. Different from the case of the potassium doping, apparent changes in the lattice parameters after the rubidium doping could not be recognized though the ionic radius[3] of rubidium (1.47 Å) is more than 10% larger than that of potassium (1.33 Å). The relative intensities of several reflections (without absorption correction) were quite similar to each other (Table II), however, it is actually difficult to know how obviously the intensity would be altered by very subtle transformation expected for these cases.

TABLE II Relative intensities of the $|F_O|$ value of several reflections of OMTTF·C_{60}·benzene before and after the alkali doping (normalized by the $|F_O(1\ \text{-}1\ 3)|$ value, and absorption correction was ignored). The data of the potassium-doped crystal were measured with Mo radiation. Asterisk means the Friedel pair of the reflection listed in the left end column. $|F_O|/\sigma(F_O)$ of the listed reflections was ranged in 77-581.

	Before doping	After K doping	After Rb doping		
			N3-1	N3-3	N3-5
1 -1 3	1.00	1.00	1.00	*1.00	1.00
-2 3 0	0.74	0.63	*0.59	0.72	0.66
1 1 1	0.51	0.52	0.52	*0.45	0.39
0 2 1	0.51	0.52	0.51	0.43	0.31
1 0 -2	*0.49	*0.44	0.54	*0.44	0.42
2 1 -2	*0.45	*0.42	0.45	*0.37	0.46
0 1 3	0.41	0.40	0.47	0.43	0.35
3 -7 2	0.38	0.38	0.34	*0.37	0.34
0 3 1	0.37	0.37	0.34	0.32	0.25
2 0 -3	*0.34	*0.31	0.36	*0.30	0.29
2 -3 2	0.33	0.30	0.34	*0.33	0.32
2 -3 3	0.24	0.25	0.25	*0.26	0.26

To confirm that the individual crystal used for the x-ray measurement would show superconductivity or not, SQUID magnetization measurement was preliminary performed for the three crystals (N3-1, N3-3, N3-5). Although the sample setting arrangement was unfavorable to observe a weak diamagnetic signal in this measurement (; the spatial position of the center of the crystal was not coincided with that of the sample holders including x-ray glass capillary and Torr Seal®), some reliable diamagnetism by superconducting single crystal should be detected judging

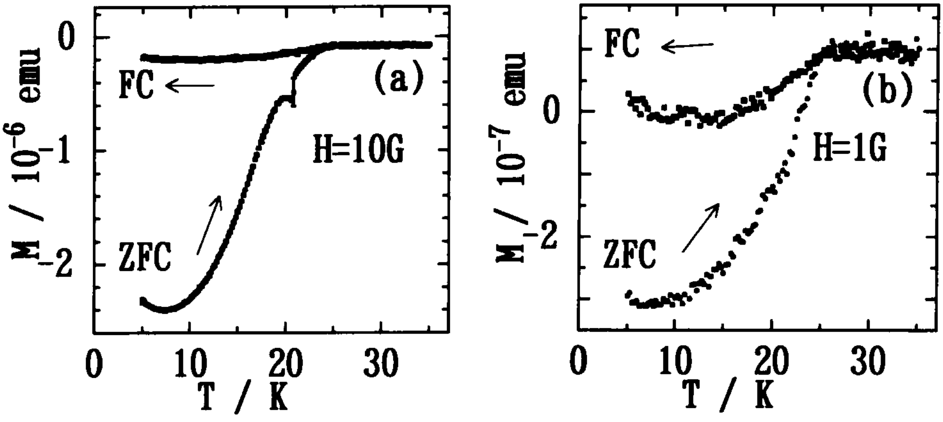

FIGURE 2 Temperature dependence of magnetization of the rubidium-doped OMTTF·C_{60}·benzene crystal after the x-ray diffraction experiment (the crystal N3-5). The applied magnetic field was 10 G (a) or 1 G (b). The earth field was not canceled. The background coming from x-ray glass capillary, silicone grease, Torr Seal®, etc. was not subtracted. See the text.

from Figure 1b. Figure 2 shows the results of the N3-5 crystal measured under the different two applied magnetic fields. The N3-5 crystal showed a diamagnetic signal ascribable to superconductivity below around 25 K. The size of the N3-5 crystal ($0.6\times0.6\times0.2$ mm^3) corresponds to about 3% of the total amount of the N3 ampoule in Figure 1b. Distinct from the case of N3-5, diamagnetism by superconductivity was not detected for the N3-1 ($1\times0.5\times0.1$ mm^3) nor the N3-3 ($0.4\times0.6\times0.1$ mm^3) (not shown).

Considering that the N3 sample actually showed the superconductivity of about 10% volume fraction as a whole (Figure 1b),2) it is likely that the doping was not uniform in an ampoule. In the potassium doping, EPMA/SEM showed a distribution of the potassium contents within each crystal as well as among the crystals.2) We assume at present that the silicone grease, Torr Seal®, or x-ray irradiation does not degrade the doped sample completely. It is possible, however, that the less doped crystals might be selectively examined for the single crystal x-ray experiments followed by the SQUID measurements in this work as a result. The SQUID magnetization will be measured on the individual seven crystals (N2-1~N2-5, N3-2, N3-4) which did not show good quality by the x-ray diffraction.

Some close investigations are still in progress. The LFMA (low field magnetic absorption) measurements will also detect the traces of superconductivity for the x-ray examined crystals, because this method is superior to SQUID in the coexistence of the x-ray capillary, silicone grease, Torr Seal®, etc., near the sample. EPR and optical studies will clarify the valence of the C_{60} in the doped crystal. Care should be taken to dope the crystals more uniformly, for example by shaking the ampoule sometimes during the doping. The doping runs in which only one single crystal is loaded in an ampoule are now in progress, to complete many measurements by the individual single crystal.

CONCLUSIONS

From two batches of superconducting sample of rubidium doped OMTTF·C_{60}·benzene, ten crystals were selected in a grove box for four-circle x-ray diffractometry to determine the lattice parameters and crystal structure of the rubidium-doped sample. Although three crystals of the ten showed the quality fit for diffraction data collection, the obtained lattice parameters were not distinguishable from those of the pristine crystal. Magnetization (SQUID) was measured for the three x-ray examined crystals. Diamagnetism by superconductivity was detected in one crystal, but not in the other two. It was interpreted that the doping was not uniform.

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