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Magnetism and analysis of the halogen doped C_{60}

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The IBr (1:1 compound of iodine and bromine) doping into a fullerne C_{60} powder brought about a hysteresis in the magnetization curve and difference between field-cooled MT (magnetization versus temperature) curves and zero-field-cooled MT curves as well as a lattice transformation from f.c.c. to b.c.o.. Some discussions are made for them.

1. INTRODUCTION

A variety of studies on chemical and physical properties have been made for fullerenes since the synthesis of macroscopic amounts of C_{60} and C_{70}[1-4]. The discovery of superconductivity in C_{60} doped with alkali metals has also stimulated the studies on fullerens[5-7]. However, attempts to dope elements of electron acceptors such as Br(bromine) and I(iodine) has been scarcely reported[8,9]. Here, we report about the magnetism and analysis of the halogen-doped C_{60}. We found that the simultaneous doping of iodine and bromine into C_{60} brought about a hysteresis in MH curves (magnetic moment versus magnetic field curves) accompanied by a transformation below about 30K from f.c.c. to b.c.o.. The hysteresis became clear when the molar ratio of IBr to C_{60} exceeded about 2.5. The clear difference of field-cooled MT curves (moment versus temperature curves) and zero-field-cooled MT curves were also observed. The magnetic behaviour seems to correspond to the spinglass, the mictomagnetism or the mixed phase of ferro- (or ferri-) magnetism and paramagnetism.

It would be regarded as significant that a new fundamental property of C_{60} have been revealed in this study. It could also be expected for this material to be applied to new devices such as a memory at a low temperature.

2. EXPERIMENTAL PROCEDURE

C_{60} (30mg) and various amounts of IBr (1:1 compound of iodine and bromine) (from 3mg up to 50mg) were sealed in a quartz tube of 5 mm in diameter under about 10^{-1} Torr of helium. They were heat treated at 250°C for 5 minutes, cooled down in the furnace naturally (about 50°C per hour) and then heat treated at 200°C for 20h. About 10 samples were prepared in each condition to check the reproducibility. Both MH and MT curves were measured using a SQUID magnetometer within the quartz tube while X-ray diffraction have been performed in the air.

For obtaining the MT curves, the samples were first cooled to 5K in zero field and data were taken in 80 Oe field as warming the samples up to 150K(ZFC) The samples were also measured by applying 80 Oe field at room temperature, then they were cooled to 5K and were measured as warming in order to obtain the field cooled curves (FC). For the MH curves, the samples were first cooled to 5K, 15K and 30K in zero field, and after 30 minutes, magnetic field was swept from -4000 Oe to 4000 Oe with the temperture fixed. For a few samples, the MH curves were measured in the field range of -50000 Oe to 50000 Oe. The X-ray diffraction was performed for the same samples in the air after the magnetization measurements.

3. RESULTS AND DISCUSSION

The results of the dc magnetization measurements of both ZFC and FC MT curves with the SQUID magnetometer are shown in Fig. 1. The nominal ratio of IBr to C_{60} was about 3 and the applied field was 80 Oe. It is

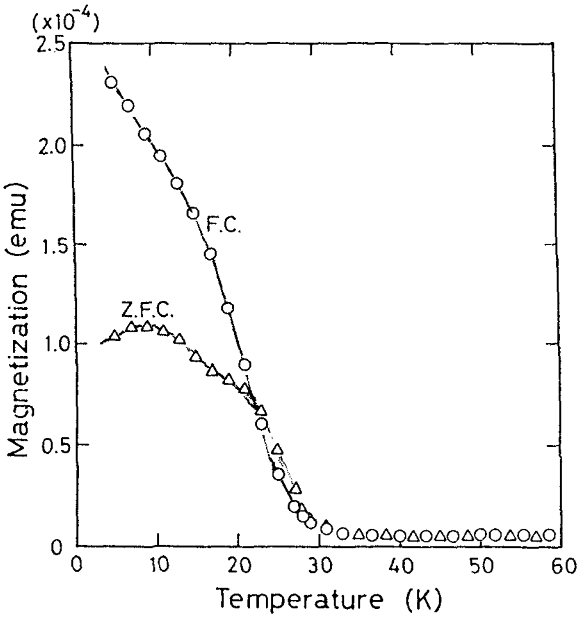

Figure 1 Results of dc magnetization measurements of both ZFC and FC MT curves.

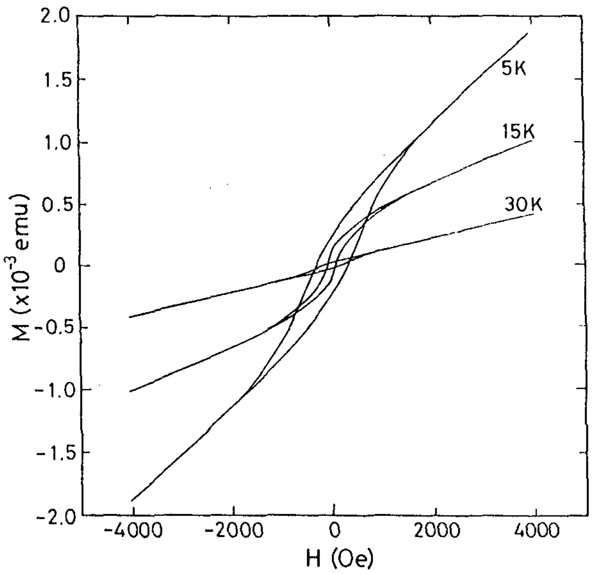

Figure 2 The MH curve measured for the same specimen as shown in Fig. 1.

noteworthy that the ZFC MT curve and the FC MT curve seperate at a temperature below 20K-30K. Figure 1 also shows that the magnetic moment suddernly inceases at a temperature around 28K with decreasing temperature. These results indicate a possibility that a magnetic phase transition from paramagnetism to ferromagnetism or the freezing of spin (spinglass) occurs with decreasing temperature below 30K.

Figure 2 shows the result of the MH curve measurement at 5K, 15K and 30K for the same specimen as shown in Fig. 1. In Fig. 2, a hysteresis is clearly seen in the field range from -1800 to 1800 Oe at 5K. However, the MH curve aproaches a linear curve with increasing absolute value of the magnetic field around 4000 Oe. The width of the hysteresis decreases with increasing temperature.

These results seem to indicate two possibilities. One is a mixed phase consisting of ferromagnetic and paramagnetic phases. Another possibility may be the spin freezing (spinglass). The discussion will be made later on.

Figure 3 shows the average magnetic moment per C_{60} versus the nominal molar ratio of IBr to C_{60}. In Fig. 3, the average Bohr magneton per C_{60} increases up to $5.2 \times 10^{-3}\ \mu_B$ until the molar ratio exceeds about 2.5. The optimization of heat treatment conditions is being made to increase the average magnetic moment.

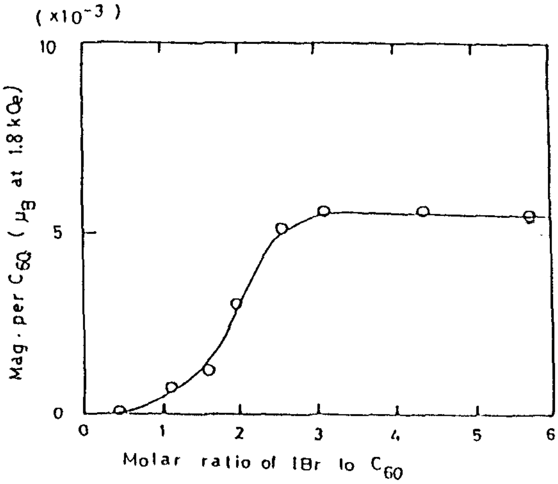

Figure 3 The average magnetic moment versus the nominal molar ratio of IBr to C_{60}.

To check the difference of magnetic behaviour below and above 30K, we measured an MT curve under a strong magnetic field of 1T, sweeping temperature from 5K up to 160K. The reult is shown in Fig. 4. this indicates that a strong interaction between spins exists below 30K.

For a few samples, the MH curves were measrued in the wide field range from -50000 to 50000 Oe at 5K and 30K. The results are shown in Fig. 5. The MH curve at 5K indicates two different cases. One is the mixed phase of ferromagnetic and paramagnetic phases. Another would be the spinglass.

We tried to decompose the two contributions, i.e. paramagnetic and ferromagnetic ones, in the MH curves in Fig. 2. The former can be estimated from the the slope of the linear fitting of the data in

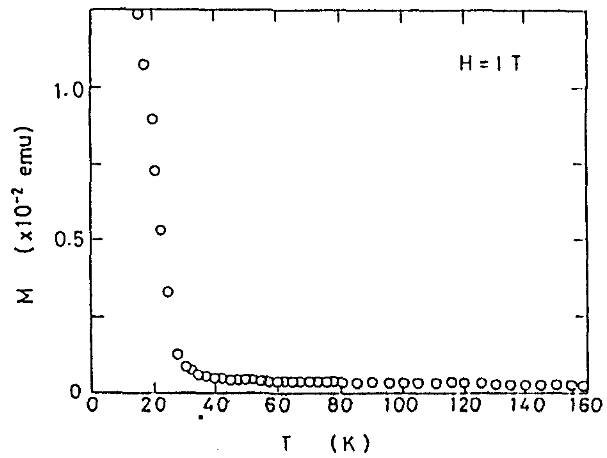

Figure 4 The MT curve measured at 1T at temperature from 5K to 160K.

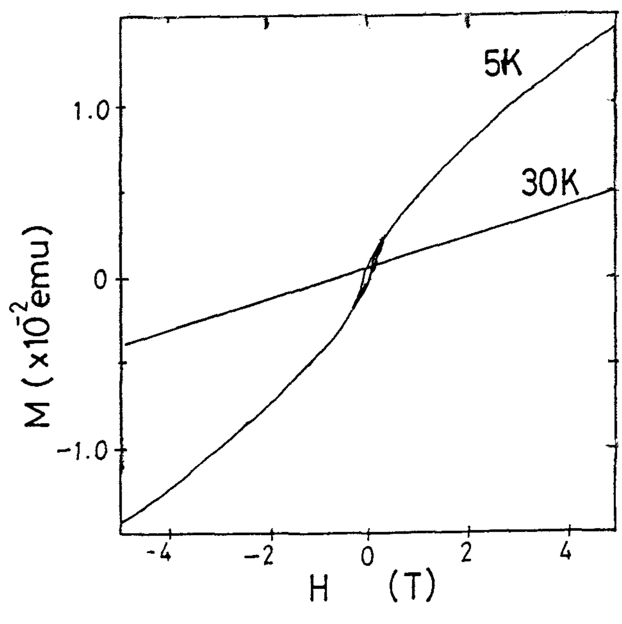

Figure 5 MH curves measured in the wide field range from -5T to 5T at 5K and 30K.

high fields, and the latter (saturation magnetization can be estimated from the intercepts between the two linear components extrapolated from positive and nagative field directions. Figure 6(a) shows the paramagnetic susceptibility χ(emu/G.mol) as a function of temperature. This shows a typical Curie-Weiss curve. Figure 6(b) shows the ferromagnetic saturation magnetization as a function of temperature. These figures indicate the existence of ferromagnetic phase.

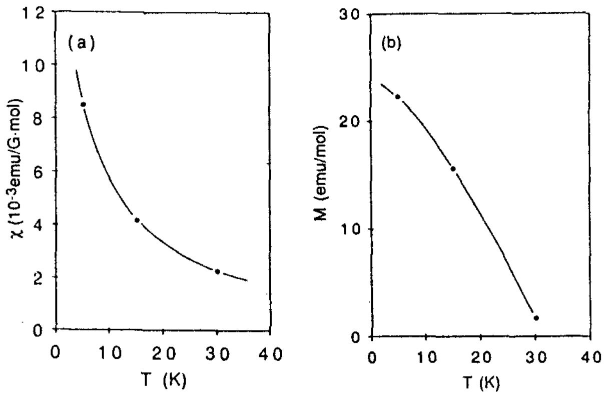

Figure 6 (a) Paramagnetic susceptibility versus temperature.
(b) Ferromagnetic saturation moment versus temperature

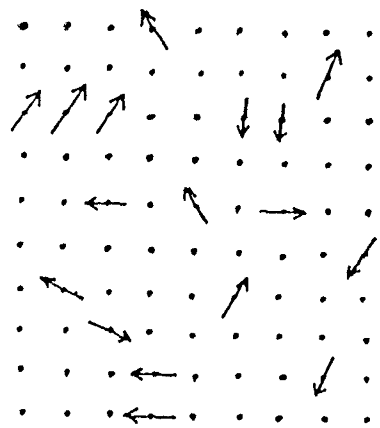

Figure 7 An illustration of spinglass

Figure 7 illustrates a model of spinglass. Spins of diluted magnetic impurities freeze in the random direction in a non magnetic matrix, due to exchange interactions of various directions. A small peak just above 5K observed in the ZFC MT curve in Fig. 1 seems to support the latter case.

The data is not enough to decide which model is more probable for this material. The optimization of the formation conditions and more precise investigations would be necessary for the conclusion.

Figure 8 (a) and (b) show the x-ray charts of the undoped and doped specimens, respectively. The results of the X-ray diffraction indicated a lattice transformation from f.c.c. to b.c.o., similarly to the structural model of iodine-doped C_{60} proposed by M.Kobayashi et al[10]. In our material, the transformation occurs when the nominal ratio of IBr to C_{60} is

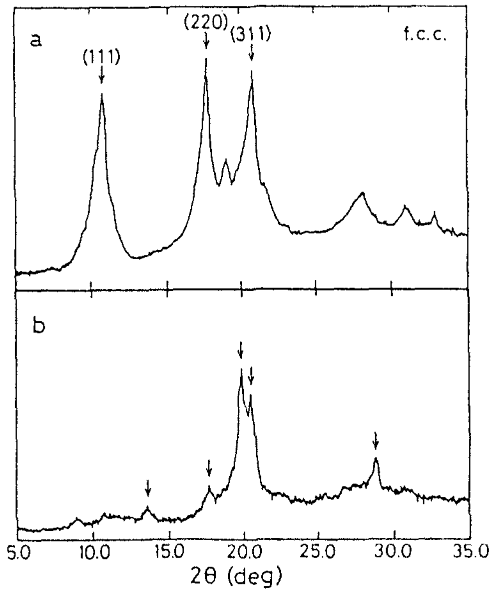

Figure 8 X-ray diffraction charts of (a) the undoped specimen and (b) the specimen doped with IBr.

about 1.5, and the majority of the lattice is converted from f.c.c. into b.c.o. when that ratio exceeds about 2.5. The lattice transformation as well as the magnetic behaviour indicate the intercalation of bromine and /or iodine into the C_{60}.

4. CONCLUSION

The doping of IBr into C_{60} brought about a hysteresis in the MH curve, difference of FC and ZFC MT curves and the lattice transformation from f.c.c. to b.c.o.. Our results of magnetic behaviour and structure study indicate that bromine and/or iodine certainly intercalated into the C_{60} lattice and probably either of them created holes instead of electron carriers. Although there may be a possibility of obtaining superconductivity by halogen doping by a long term heat treatment at a relatively low temperature or by some other technique, we in this study focused ourselves on obtaining magnetic materials which show a hysteresis with a good reproducibility .

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