Magnetism of C_{60} induced by photo-assisted oxidation

Y. Murakami* and H. Suematsu

Department of Physics, School of Science, University of Tokyo,
Hongo, Bunkyoku, Tokyo 113, Japan.

Abstract
The C_{60} crystals which are exposed to light in oxygen show a ferromagnetic magnetization with a small hysteresis of the coercive field Hc = 10^{-2} T and a saturation magnetic moment (Ms) of 10^{-3} μ_B per C_{60}. The most striking feature is that Ms remains up to Tc = 800 K, an extraordinarily high critical temperature. The small Ms indicates that only a small part of the sample contributes to the ferromagnetism, but the ferromagnetic part can be enriched by dissolution of pure C_{60} into toluene; a residue substance has a larger Ms of 10^{-1} μ_B/C_{60}. The x-ray powder diffraction and the Raman scattering measurements reveal that the residue has a crystal structure close to pure C_{60} crystal although a broadening of line width in the diffraction spectrum and a small shift of Ag and Hg vibrational modes to a lower energy are observed. The mechanism of the ferromagnetism will be discussed in relation to oxidization and polymerization of C_{60} molecules.

1. Introduction

Organic ferromagnets have been attracting much attention from both the chemical and physical sciences because of the novel properties, and actually have been found so far in several materials such as free radical organics and carbon-based materials. A typical of the former case is p-nitrophenyl nitronyl nitroxide (p-NPNN) in which a ferromagnetic transition occurs at Tc = 0.60 K for β-phase while an antiferromagnetic transition does at 0.65 K for γ phase [1,2]; both magnetic orderings come from the exchange interaction between unpaired electrons on radical molecules. Recently C_{60}(TDAE) have been found to be a ferromagnet below 16 K [3]; the mechanism is not well understood at present. In case of carbon materials, carbon-based polymers, when heat-treated at about 1000 ºC in Ar gas, show a spontaneous magnetization at room temperature and have an Ms of 10.5 emu/g [4]. A similar ferromagnetism has been observed in activated carbon fiber [5]. These magnetic materials attract much interest in practical applications, but the origin of the magnetism has not been studied intensively.

In this paper we present the ferromagnetism of C_{60} induced by light in existence of oxygen. The C_{60} crystal is well known to absorb a large amount of oxygen gas, which shows a large paramagnetism at low temperature due to the nature of oxygen molecules [6]. However, if the crystals are exposed to light in oxygen gas, they show strong evidences of ferromagnetism, i.e., a typical ferromagnetic magnetization process with a magnetic hysteresis and the Curie temperature of about 800 K, an extraordinary high temperature. We will report the results of x-ray diffraction and Raman scattering measurements as well as the magnetic measurements, and discuss a possible mechanism for the magnetism.

* Present address : National Laboratory for High Energy Physics (KEK), Tsukuba, Ibaraki 305, Japan.

2. Experimental Procedures

Pristine crystals of C_{60} were prepared by sublimation method from powder crystals in order to remove any contamination in source material. The magnetization measurements were made by a squid magnetometer with a high temperature oven (MPMS system, Quantum Design Inc.).The x-ray powder diffraction measurements were performed by using a monochromatic synchrotron radiation x-ray at Photon Factory, KEK, Tsukuba.

3. Experimental Results and Discussion

We first describe a process to obtain a ferromagnet phase in C_{60} crystals. The pristine crystals show a diamagnetism ($\chi_0 = - 3.2 \times 10^{-7}$ emu/g) independent of temperature even at low temperatures as shown in Fig.1 : This indicates that no magnetic impurity was included in the sample. When exposed to oxygen gas of about 100 kPa, the sample shows a steep increase of susceptibility χ at low temperatures, which obeys the Curie law (see the inset). This fact means that oxygen physisorbs in the form of an O_2 molecule and gives the paramagnetism. The amount of absorbed oxygen is determined from the Curie constant and is 4 mol% per C_{60} in the present case, but it depends on grain size of crystals and reaches 20 mol% at most for fine powder crystals. Oxygen molecules are known to occupy the octahedral sites of the C_{60} fcc crystal. The absorbed oxygen can be desorbed completely by evacuation at a temperature T > 500 K [6, 7]. At high temperatures the Curie paramagnetism of O_2 molecules decreases negligibly and the diamagnetism of C_{60} takes a predominant role.

When the crystal was in light irradiation of a xenon lamp in presence of oxygen, the susceptibility changes remarkably as shown in Fig.2. For the light irradiation for 2.5 hours the sample shows a positive χ in the whole temperature region, and a much more change for 3 months exposure in air. These changes can be seen more drastically in the magnetization curve in Fig.3. We observe a non-linear magnetization process at a low field, which is typical of a ferromagnet. This indicates that the sample contains a small amount of a ferromagnetic material.

After exposed to light and oxygen for 2.5 hr we made a heat-treatment of the sample at 400 °C in vacuum in order to remove physisorbed oxygen. We observed an increase of the ferromagnetic part while the paramagnetic part decreases (Fig.3(c)). At
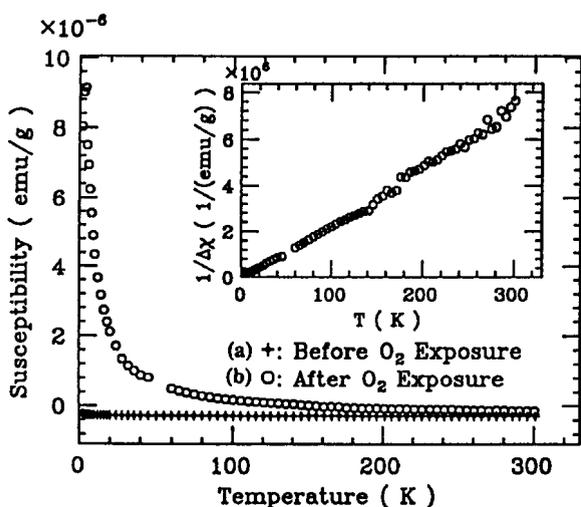

Fig.1 The temperature dependence of χ for (a) pure C_{60} crystals and (b) the O_2 absorbed sample.   Inset; T-dependence of inverse of $\Delta\chi$, the difference of (a) and (b).
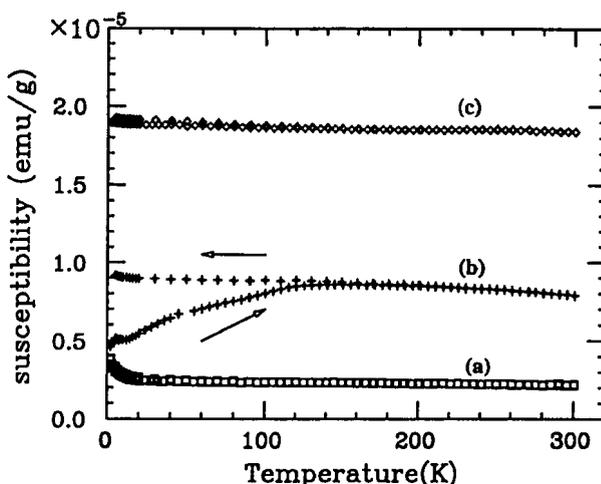
Fig.2 The temperature dependence of χ for samples (a) exposed to light in O_2, (b) baked at 400 °C for 14 hours, and (c) exposed in air for 3 months.
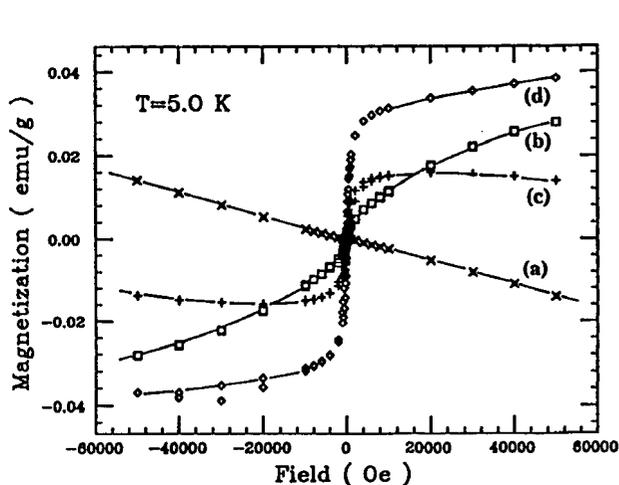
Fig.3 The field dependence of magnetization at T=5 K for (a) the pristine C_{60} crystal, (b) the sample exposed to light in oxygen for 2.5 hours, (c) baked at 400 °C for 2.5 hours, and (d) exposed in air for 3 months.
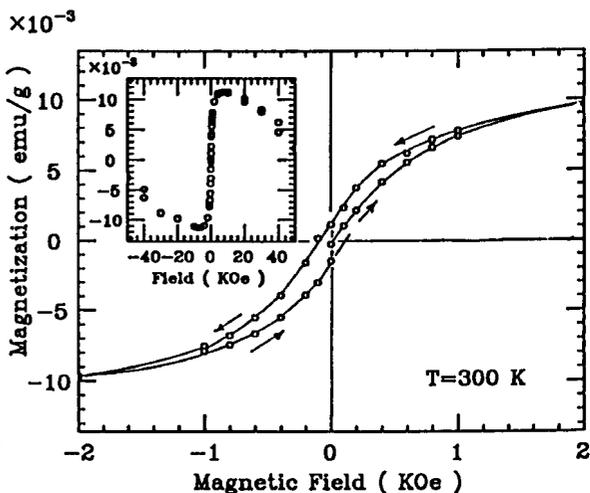
Fig.4 A detail of the magnetization process at low fields (T=300 K, Sample (c)). Inset; M(H) in a larger scale of field.

T< 90 K we observed a difference of χ between the value for field cooling(upper branch) and that measured after zero-field cooling (lower branch), but we have no explanation for it.

The magnetization processes M(H) observed in these samples can be described by the sum of the diamagnetic and paramagnetic terms and the ferromagnetic nonlinear term as follows,

$$M\ (H) = \chi_o\ H + \frac{C}{T\text{-}T_o}\ H + f\ (H)\ ,$$

(1)

where the first term is the diamagnetism of C_{60} crystals, the second comes from the Curie paramagnetism of O_2 molecules, and the last the ferromagnetic term. At high fields of H >> 1 T the first two terms are dominant, and the Curie paramagnetism rules at low temperatures while the diamagnetism does at high temperatures. The ferromagnetic term is remarkable at low fields. Fig. 4 shows the detail of M(H) at low fields, in which we observe a hysteresis below about 0.2 T and the coercive force of 10^{-2} T. The observed small hysteresis loop can be understood in terms of the fine particle effect. Ms is obtained from the zero-field extrapolation of M from high fields as 1.4 x10^{-2} emu/g (cf. the inset of Fig. 4), which corresponds to 10^{-3} μ_B/C_{60}, a very small value. So, the sample is considered to be a mixture of the minor ferromagnetic material and the major C_{60} crystals absorbing oxygen.

A most striking feature is the temperature dependence of Ms. Fig. 5 shows the T-dependence of M measured at 1 T , which is approximately equal to Ms since the first two terms in eq.(1) are small at the field. Ms remains finite up to Tc = 800 K, an extraordinarily high Curie temperature. The plateau below 120 K corresponds to Ms of about 10^{-3} μ_B per C_{60}. A steep increase of M below 40 K corresponds to the increase of the Curie term.

In order to extract the ferromagnetic part from the mixture we made a toluene solution of the sample, and found that the ferromagnetic part remains unresolved while the pristine C_{60} crystal is soluble in toluene. The fact of no solubility of the ferromagnetic part is deduced from that Ms of the residue material is almost the same as that
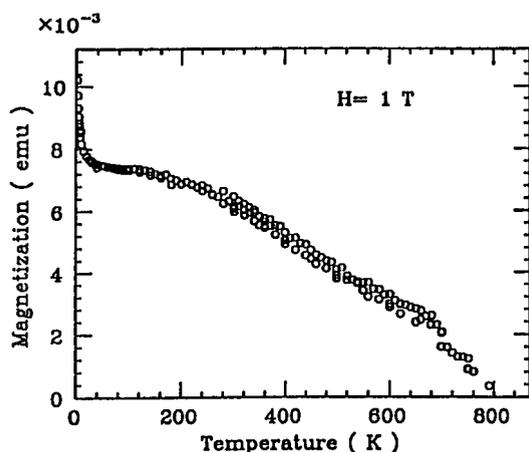
Fig.5 The temperature dependence of
saturation moment Ms (Sample (c)).
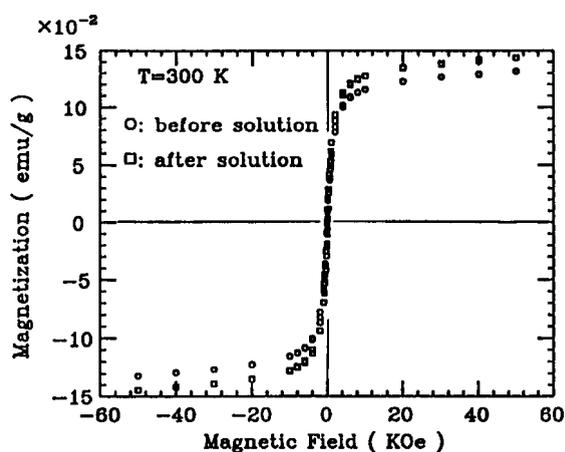Ms remains up to Tc=800 K.

Fig.6 The M(H) curve of the ferromag-
netic residue compound (Square).

of the original mixture (Fig. 6). By this procedure of enrichment the ferromagnetic
moment per weight increases by a factor of 100, so that the magnetic moment becomes
0.1 μ_B per C_{60}. This means that there is one spin per 6 carbons in average.

In order to inspect whether the ferromagnetism comes from light irradiation only,
we exposed the sample to xenon light in vacuum for 21.5 hours. However we observe no
appreciable difference in χ from the pristine crystals at the whole temperature region
studied. Thus, we conclude that the ferromagnetism should come from the combined
effect of light and oxygen.

The x-ray diffraction measurement reveals that the spectrum of the residue mate-
rial has diffraction angles and relative intensities closely similar to those of pure C_{60},
but the peaks broaden to a large extent as compared with a pure C_{60} crystal in Fig. 7. In
the Raman scattering measurements we also observe the spectrum characteristic of the
C_{60} crystal, such as the Hg and Ag modes, as shown in Fig. 8, but the peaks shift slightly
toward a lower frequency and have a broader line width than pure C_{60}. These structural
results indicate that the ferromagnetic residue has the structural framework very close
to the pure C_{60} crystal, but the crystalline quality is much worse and the bonding force
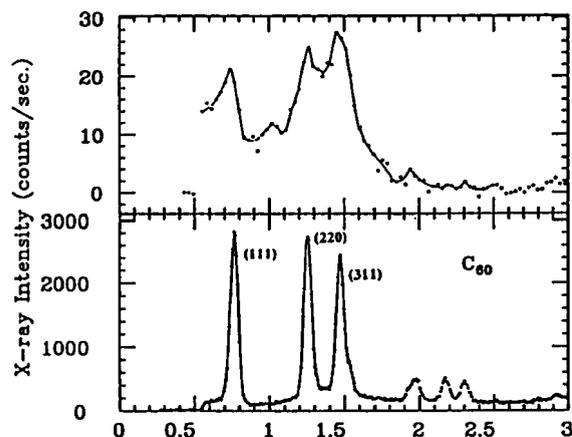between carbon atoms reduces appreciably.

Fig.7 The powder x-ray diffraction spectra
of the ferromagnetic residue compound
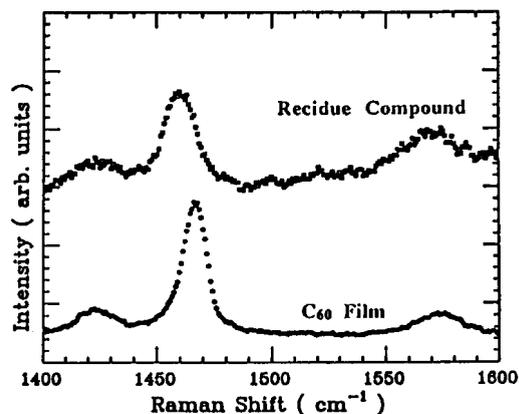(upper) and the pure C_{60} crystal (lower).

Fig.8 The Raman scattering spectra of
the ferromagnetic residue compound
(upper) and the pure C_{60} film(lower).

Now we discuss the origin of the ferromagnetism in our case. For realizing the ferromagnetism we assume both the existence of unpaired spins and an interaction between them. A possible mechanism to introduce spins is oxidization of carbons, which may realize easily for double bonded carbons on C_{60} cage. The O_2 molecule dissolves by light irradiation to make a pair of $> C -- O ^-$, which have each an unpaired electron. For these spins we expect an exchange interaction, and the interaction is possibly strong for those on the same cage (J in Fig. 9) enough to explain the observed high Tc. Rao et al reported the photo-induced polymerization of C_{60} crystal by strong light irradiation [8], and if such an effect occurs simultaneously in our case the interaction between spins on neighboring C_{60} cages (J') becomes strong : Fig. 9 depicts the radicals on the polymerized C_{60}. In connection to polymerized networks of carbons Shima and Aoki's theoretical work is very interesting, who pointed out a possibility of ferromagnetism for a correlated electron system in honeycomb superlattices of graphite network [9].
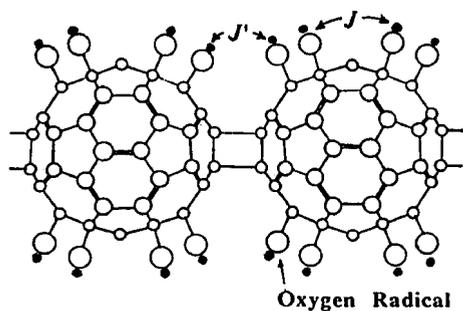

Oxygen Radical

Fig.9 A schematic model for the ferromagnetic interaction between oxygen radicals.

In conclusion we have studied the ferromagnetic properties of C_{60} crystals irradiated by light in oxygen. Ms is 10^{-3} μ_B per C_{60}, the small moment indicating that the sample is a mixture of the minor ferromagnetic phase and the major C_{60} crystals. The enriched sample shows a larger moment of 10^{-1} μ_B/C_{60}. The x-ray powder diffraction and the Raman scattering measurements reveal that the ferromagnetic phase has a crystal structure close to the pure C_{60} crystal, but a broadening of line width in the diffraction and Raman spectra and a small shift of Ag and Hg vibrational modes to a lower energy are indicative of modifications of the pristine structure. The origin of the ferromagnetism is discussed in relation to the oxidization and polymerization of C_{60} molecules.

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