

Mechanism of ferromagnetism in TDAE-C₆₀ : ESR study under pressure

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Abstract

The low-frequency electron spin resonance (ESR) under hydrostatic pressure has been studied in the soft-ferromagnet TDAE-C₆₀, where TDAE is tetrakis-dimethylamino-ethylene. A demagnetising field causes ESR line shift proportional to the spontaneous magnetisation. The pressure dependence of T_C deduced from the ESR line shift is found to follow a relationship of $T_C(P) \approx T_C(0)[1 - (\frac{P}{P_C})^2]$, where $T_C \approx 16$ K and $P_C \approx 9$ kbar. The antiferro-orbital-ordering model of Jahn-Teller distorted C₆₀⁻ is investigated as a possible mechanism for the ferromagnetism. With the realistic magnitudes of parameters a prediction of this model is in good quantitative agreement with the data. The pressure above 10 kbar promotes an irreversible phase change; a reduced lattice constant along *c*-axis, a reduced ESR line width, an increased number of spins and an increased *g*-shift. From the *c*-lattice constant of 9.17 ± 0.07 Å, we concluded that a new β -phase induced by pressure is a [2+2] cycloadditive 1D polymer phase, where the spin revives on TDAE⁺, missing in the ferromagnetic α -phase.

Key words: Electron spin resonance, Magnetic measurements, Magnetic phase transition, Fullerenes and derivatives

1. Introduction

The ferromagnet TDAE-C₆₀ with the highest transition temperature $T_C \approx 16$ K in the pure organic substances has attracted a lot of researchers to reveal a mechanism of the ferromagnetism [1]. According to the susceptibility with ESR intensity [2–4] and SQUID [4–6], the number of $S = \frac{1}{2}$ unpaired spins contributed to the ferromagnetism is considered to be ≈ 1 spin per one TDAE-C₆₀ unit. The location has been assigned to C₆₀ from the ESR *g*-value of ≈ 2.0005 that is nearby ≈ 2.0000 for C₆₀⁻, but far from ≈ 2.0037 for TDAE⁺ radical. This means a missing spin problem on TDAE⁺ with one unpaired electron, not solved yet [7]. The present finding of polymerization by pressure accompanied by a revival of the spin on TDAE⁺ has provided new information on this issue. On the na-

ture of the ferromagnetism, ESR study over wide frequency range suggested that this system is an ideally soft ferromagnet with the anisotropy field of several tens of Gauss [8]. On the magnetic ordering mechanism, an importance of orbital ordering of Jahn-Teller distorted C₆₀⁻'s is suggested in both theoretically and experimentally [3,9–13].

2. Results and discussion

Figure 1 shows an effect of pressure on T_C determined from temperature dependences of the resonance field shift due to a demagnetising field of the spontaneous magnetisation. The solid curve demonstrates a theoretical prediction with realistic parameters based on the antiferro-orbital-ordered structure of the Jahn-Teller distorted C₆₀'s [14]. The good agreement with the data suggests a realistic possibility in this model to be a

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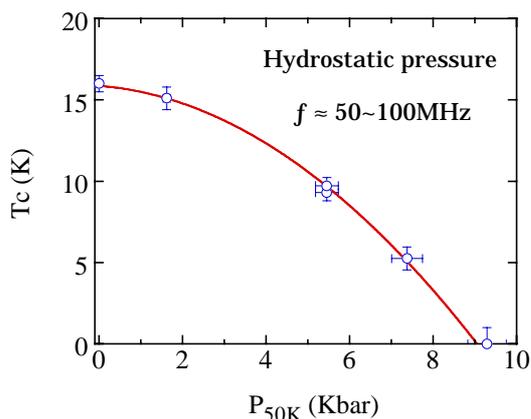


Fig. 1. The pressure dependence of T_C . The solid curve indicates a prediction of theoretical model of orbital ordering [11,12,14].

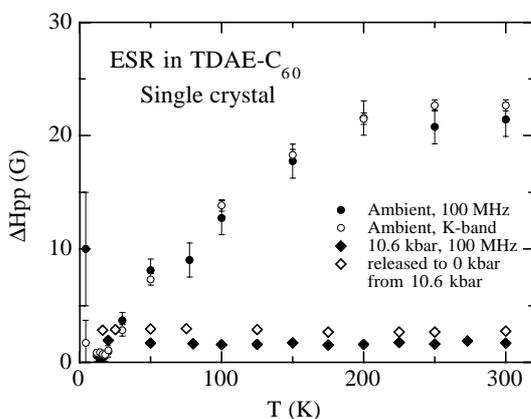


Fig. 2. The temperature dependence of ESR line width at several experimental conditions. Note that an irreversible change of the line width after pressure release of 10.6 kbar.

mechanism of the ferromagnetism.

Figure 2 demonstrates an irreversible change of the ESR line width, after application of the pressure more than 10 kbar. X-ray data shown in Table 1 suggest an occurrence of [2+2] cyclo-polymerization of C_{60} 's along the c -axis, the nearest neighbor direction. This table also shows a change of the number of unpaired spins and g -value from the ferromagnetic phase, indicating a revival of the missing spin on $TDAE^+$, probably because of disappearance of $TDAE^+$ pairing [15].

Acknowledgement - K.M. would like to express sincere thanks to Prof. M. Yamashita, and Dr. T. Ishii for their kind help in X-ray experiment. This work was partly supported by Grant-in-Aid for Scientific Research on the Priority Area "Fullerenes and Nanotubes" by the Ministry of Education, Science, Sports and Culture of Japan.

Table 1

The shortest distances r_1 between C_{60} 's and the lattice constants, r_2 and r_3 at 89 K for the new 1D polymer β -phase of TDAE- C_{60} , together with o - Rb_1C_{60} [16] for comparison. N_S , the number of $S = \frac{1}{2}$ unpaired spins per (counter cation + C_{60}) unit and g -values are also listed.

	r_1 (Å)	r_2 (Å)	r_3 (Å)	N_S	g -value
TDAE-C_{60}					
·New β -phase	9.17 ± 0.07	13.69	15.70	≈ 2	2.0028
· α -phase (Ferro)	9.99	13.00	15.86	≈ 1	2.0005
[2+2] polymer					
o - Rb_1C_{60}	9.138	10.107	14.173	≈ 1	2.0012

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