Magnetizm of C_{60}-based molecular complexes: high field magnetization and magneto-optical study

© S.V. Demishev*,****, N.E. Sluchanko*, L. Weckhuysen**, V.V. Moshchalkov**, H. Ohta***,****, S. Okubo***, Y. Oshima*****, N.G. Spitsina******

* Low Temperatures Laboratory, General Physics Institute, Russian Academy of Sciences, 117942 Moscow, Russia
** Laboratorium voor Vaste-Stoffysica en Magnetisme, Katholieke Universiteit Leuven, B-3001 Heverlee, Belgium
*** Molecular Photoscience Research Center and Department of Physics, Kobe University, Rokkodai, Nada, Kobe 657–8501, Japan
**** Venture Business Laboratory, Kobe University, Rokkodai, Nada, Kobe 657–8501, Japan
***** Graduate School of Science and Technology, Kobe University, Rokkodai, Nada, Kobe 657–8501, Japan
****** Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow region, Russia

E-mail: demis@lt.gpi.ru

Magnetization study of the $C_{60} \cdot TMTSF \cdot 2CS_2$ molecular complex in magnetic field up to 47 T for the temperature range 1.8–300 K and ESR specrtoscopy of the molecular complex $(ET)_2C_{60}$ at $T = 1.8$ for the frequency range 60–90 GHz in magnetic field up to 32 T provide experimental evidence that a paramagnetic centers with the reduced g-factor values $g < 1$ control magnetic properties of these solids. A model is suggested where the renormalisation of the g-factor value is due to dynamic Jahn-Teller effect on the of the negative C_{60} ions which appear as defects in crystalline structure with a weak charge transfer.

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1. Since the discovery of fullerenes it is believed that for a weakly magnetic C_{60}-based compounds with a small charge transfer their magnetization can be represented as a sum of two terms [1,2]

$$M(B, T) = M_{\text{para}}(B, T) + M_{\text{dia}}(B)$$
$$= [3\chi_{\text{para}}(T)k_BT/(J+1)g\mu_B]B_J(g\mu_BJB/k_BT)$$
$$+ \chi_{\text{dia}}B, \quad (1)$$

where negative diamagnetic term χ_{dia} is connected with the completely filled electron orbitals of C_{60} and other molecules in complex, while $\chi_{\text{para}}(T) \sim 1/T$ is a Curie term originating from oxygen impurity.

Unfortunately, Eq. (1) fails to provide a description of the field dependence of the low-temperature magnetization $M(B)$ for the complex $(ET)_2C_{60}$, where ET = bis(ethylenedithio)tetrathiafulvalene as well as for pure C_{60} [3,4], and the observed discrepancy rules out any model of magnetic impurity with g-factor $g \approx 2$ [3,4]. Experimental data suggest that Eq. (1) may be used assuming a renormalized value $|g| \sim 0.14$ [3,4], which may be characteristic for the negative ion C_{60}^- where a strong reduction of the g-factor may originate from the dynamic Jahn-Teller effect [5].

It is worth to check the possible presence of these exotic centers in other fullerene-based molecular complexes. The aim of the present work was to investigate the magnetic properties of molecular complex $C_{60} \cdot TMTSF \cdot 2CS_2$ and to look for unusual paramagnetic centers in $(ET)_2C_{60}$ by means of magneto-optical spectroscopy.

2. Synthesis and structure of $C_{60} \cdot TMTSF \cdot 2CS_2$ (where TMTSF = tetramethyl-tetra-selenefulvalene) molecular complex are descrribed in [6,7]. Similar to $(ET)_2C_{60}$, the charge transfer in $C_{60} \cdot TMTSF \cdot 2CS_2$ is small. However, application of external pressure of about 5 GPa moves one electron from TMTSF to C_{60} molecule thus forming a complex based on C_{60}^- ion [8]. Therefore $C_{60} \cdot TMTSF \cdot 2CS_2$ seems to be a good candidate for checking models suggested in [3,4].

The temperature dependence of magnetization for the field $B = 8$ T is shown in Fig. 1, *a*. The $M(T)$ curve demonstrates the onset of "paramagnetic" contribution below 40 K superimposed on diamagnetic background M_{dia}. However, the use of Eq. (1) for $C_{60} \cdot TMTSF \cdot 2CS_2$ gives a poor description of $M(T)$ shaped (compare experimental data (curve in Fig. 1, *a*, *1*) with the best fit (curve in Fig. 1, *a*, *2*) obtained using Eq. (1)).

Field dependence of $M(B)$ at $T = 4.2$ K for $C_{60} \cdot TMTSF \cdot 2CS_2$ deviates from that reported previously [3,4]. The linear section of the $M(B)$ lasts up to 20 T, i.e., about 10 T less than for $(ET)_2C_{60}$ [3,4]. Above 20 T the experimental curve first deviates downwards from linear asymptote (Fig. 1, *b*), which indicates a possible presence of paramagnetic centers with reduced g-factor [3]. Taking Eq. (1) as first approximation and following [3], we calculated the field dependence of the magnetization from Fig. 1 assuming $g = 2$ and $J = 1/2$. The result is presented in Fig. 1, *b*, and it is obvious that a straightforward model of the "oxygen-like" impurity does not complain with the

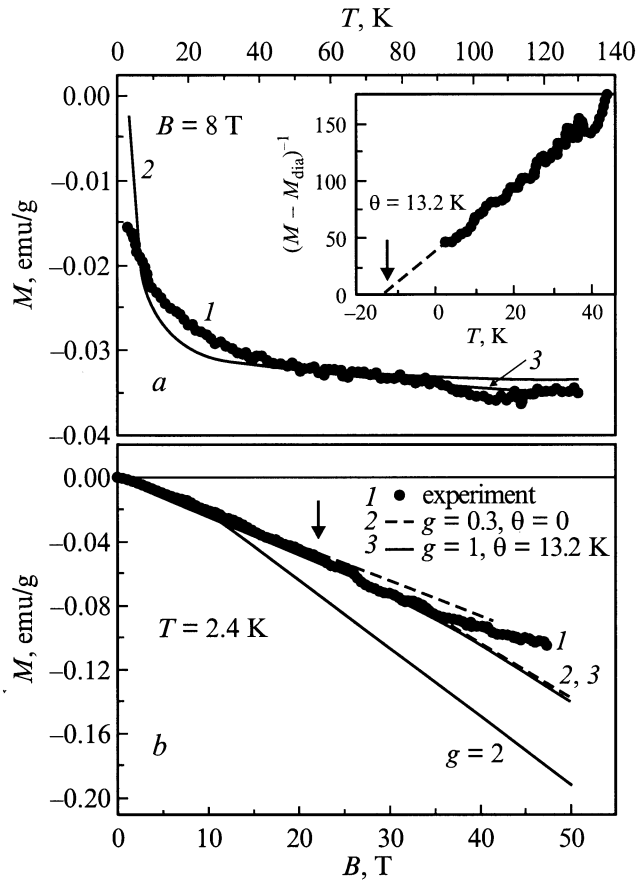

Figure 1. Temperature (a) and field (b) dependence of magnetization for $C_{60} \cdot TMTSF \cdot 2CS_2$. *1* — experimental data for $M(T)$ and $M(B)$, *2* — simulation of $M(T)$ and $M(B)$ using Eq. (1), *3* — simulation of $M(T)$ and $M(B)$ using Eq. (2). Inset in part (a) shows temperature dependence of magnetization in coordinates $(M - M_{dia})^{-1} = f(T)$.

$M(B)$ data. Assuming that a reduction of the g-factor plays a key role [3] and restricting further analysis to the interval $B < 35$ T, we find a renormalized reduced g-factor value $g \sim 0.3$ (curve *2* in Fig. 1, a).

Nevertheless the small g-factor (which "makes linear" the $M(B)$ data for $B < 8$ T) does not help to improve the simulation of the temperature dependence of magnetization (curve *2* in Fig. 1, a). A good approximation of the $M(T)$ shape can be provided by empirical expression

$$M(B, T) = M_{para}(B, T) + M_{dia}(B) = \chi_{dia}B + M_0 \tanh[g\mu_B B/2k_B(T + \theta)], \quad (2)$$

which corresponds to Curie–Weiss law in weak magnetic field and represents saturation of magnetic moment in strong magnetic field. Simulating both $M(T)$ and $M(B)$ data in Fig. 1 using model representation (2) we find $g = 1$, $M_{dia}(B = 8\,T) = -0.0373$ emu/g and $\theta = 13.2$ K (see also inset in Fig. 1, a). The results of model calculations for $M(T)$ and $M(B)$ are presented by curves *3* in Fig. 1, a and b respectively. It is clear that Eq. (2) provides an adequate and consistent description of the field and temperature dependences of magnetization for $B < 35$ T, however the found g-factor value is considerably higher than that in the model given by Eq. (1).

The analysis of the $M(B, T)$ data for $C_{60} \cdot TMTSF \cdot 2CS_2$ and $(ET)_2C_{60}$ leads to the following conclusions. First, the validity of Eq. (2) suggests an interaction between magnetic moments in $C_{60} \cdot TMTSF \cdot 2CS_2$. At present a possible interaction mechanism is completely unknown and more theoretical work is required to reveal the origin of the onset of unexpected $M(T)$ dependence (Fig. 1, a).

Secondly, the analysis of the magnetization data in fullerene-based complexes gives a very rough estimate of the effective g-factor, which depends on the type of the solid and model used, and may vary in a wide range $g \sim 0.14-1$. This situation strongly demands the determination of this parameter by direct spectroscopic methods.

3. Magneto-optical study of the mosaic sample prepared of $(ET)_2C_{60}$ single crystals was carried out in pulsed magnetic field up to 32 T in the frequency range $\nu = 60-90$ GHz at $T = 1.8$ K. The obtained transmission curves show three broad absorption lines corresponding to $g_1 = 0.43 \pm 0.03$, $g_2 = 0.27 \pm 0.02$ and $g_3 = 0.19 \pm 0.01$ (see Fig. 2, where experimental data are presented as a function of reduced field B/ν). At the same time, no ESR absorption in the sample was found around $g = 2$ (see Fig. 2 where narrow line for $g = 2$ correspond to the reference DPPH powder).

The obtained result qualitatively confirms predictions of [3,4] as well as results of the previous section. Moreover, the model of the g-factor renormalization caused by dynamic

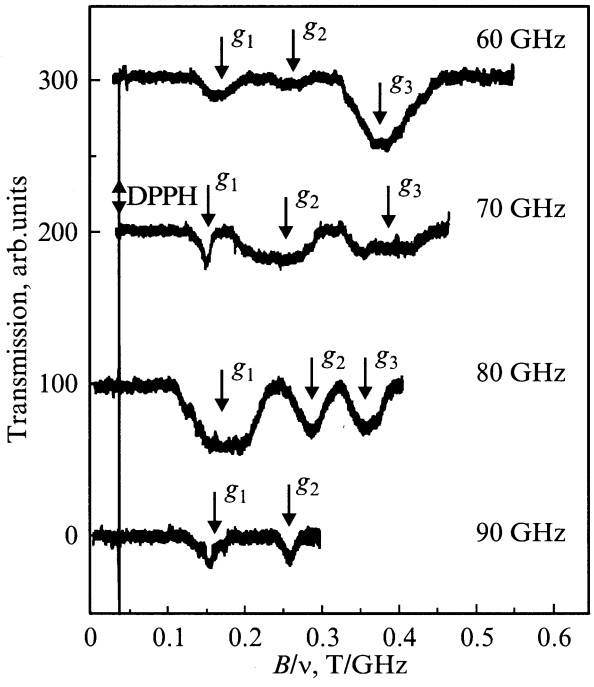

Figure 2. ESR absorption lines in $(ET)_2C_{60}$ molecular compex at $T = 1.8$ K.

Jahn-Teller effect [5] may explain presence of a several ESR absorption lines. As long as the origin of the g-factor reduction is a coupling to a phonon mode [5], the existence of a different strong modes in vibronic spectrum of a weakly magnetic complex may give rise to a several g-factor values which are observed experimentally (Fig. 2).

4. To summarize, we provide experimental evidence that the paramagnetic centers with the renormalized g-factor values $g < 1$ are (i) characteristic for the C_{60}-based weakly magnetic molecular solids and (ii) responsible for their magnetism. The presence of these centers may be associated with the negative C_{60} ions which appear as defects in crystalline structure with a weak charge transfer. In this model the reduction of the g-factor value is due to dynamic Jahn-Teller effect [3] and the presence of several magneto-absorption lines may be caused by coupling to several phonon modes.

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