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# Magnetic properties of the fullerene organic compounds in strong magnetic fields

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**Abstract**

Magnetisation 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 spectroscopy of the molecular complex $(ET)_2C_{60}$ at $T = 1.8$ K for the frequency range 60–90 GHz in magnetic field up to 32 T provide the experimental evidence that a paramagnetic centers with the reduced $g$-factor values $g < 1$ control magnetic properties of these solids. Anomalous $g$-factor values may be caused by dynamic Jan-Teller effect on the negative $C_{60}$ ions, which appear as defects in crystalline structure with a weak charge transfer.

*Keywords:* Fullerene; Molecular complexes; Magnetic properties; Anomalous paramagnetic centers

## 1. Introduction

Since the discovery of fullerenes and fullerene-based molecular complexes, most studies of magnetic properties of these materials were focused on the investigation of the superconducting or ferromagnetic compounds, i.e. materials with the pronounced magnetic properties [1]. The case of weakly magnetic $C_{60}$-based compounds has attracted much less attention so far. The magnetic response of the pure $C_{60}$ is believed to originate from the intrinsic diamagnetism of the neutral fullerene molecule and the paramagnetic contribution caused by oxygen impurity. Therefore, the magnetic susceptibility can be represented as a sum of two terms [1,2].

$$\chi(T) = \chi_{\mathrm{dia}} + \chi_{\mathrm{para}}(T) \tag{1}$$

where $\chi_{\mathrm{dia}}$ is negative and temperature-independent, and $\chi_{\mathrm{para}}(T) \sim 1/T$ is a Curie term. Eq. (1) suggests that it is possible to expect a temperature-induced inversion of the susceptibility sign, and this really meets the case for pure $C_{60}$. At first glance, this model should be valid for weakly magnetic $C_{60}$ molecular complexes where charge transfer is small and intrinsic diamagnetism can be connected with the completely filled electron orbitals of $C_{60}$ and other molecules in complex. As before, paramagnetic contribution may originate from some impurity, particularly oxygen. Indeed, aforementioned supposition is looks to be qualitative agreement with the experimental data for the complex $(ET)_2C_{60}$, where ET = bis(ethylenedithio)tetrathiafulvalene [3]. However, paramagnetic contribution to $\chi(T)$ in this compound is much smaller than for the pure $C_{60}$, as a result of which the experimental samples remain diamagnetic even at liquid helium temperatures [3,4].

Unfortunately, this simple view fails to provide a description of the field dependence of the low-temperature magnetisation $M(B)$ [3,4]. If the model of paramagnetic impurity works, than according to Eq. (1) the $M(B)$ will be constructed of the negative linear diamagnetic term and nonlinear Brillouin function representing magnetisation of paramagnetic impurity. A simple estimate shows that nonlinear shape of $M(B)$ should

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appear below 10 T [3]. Contrary to this expectation, for the complex $(ET)_2C_{60}$ the field dependence of magnetisation remains linear up to 30 T and only slight curvature in the range $30\ T < B < 50\ T$ have been observed [3]. The similar result was obtained for pure $C_{60}$ where linear $M(B)$ dependence was found even for the paramagnetic state of the sample [4].

The observed discrepancy rules out the “oxygen impurity” model [1,2], or more precisely, the model of magnetic impurity with $g$-factor $g \approx 2$ [3,4]. Analysis of the field and temperature dependencies of magnetisation for the complex $(ET)_2C_{60}$ suggests that a consistent description of magnetic properties of this compound may be obtained assuming a very specific paramagnetic centers with $|g| \sim 0.14$ [3,4]. A possible candidate for this center could be negative ion $C_{60}^-$, for which a strong reduction of the effective $g$-factor up to $g \sim -0.1$ is expected as a consequence of the dynamic Jan-Teller effect [5]. In $(ET)_2C_{60}$, an excessive electron density is localised on the $C_{60}$ molecule [6] and therefore the defects like $C_{60}^-$ may likely appear.

Nevertheless, the hypothetical paramagnetic centers proposed for the explanation of magnetisation data for $(ET)_2C_{60}$ are rather exotic and therefore require more experimental studies to clarify their nature and check their possible presence in other fullerene-based molecular complexes. For this purpose, the aim of the present work was to investigate magnetic properties of molecular complex $C_{60}\cdot TMTSF\cdot 2CS_2$ and to try to find a usual paramagnetic centers in $(ET)_2C_{60}$ by direct magneto-optical spectroscopy means.

## 2. Magnetic properties of $C_{60}\cdot TMTSF\cdot 2CS_2$

The synthesis of $C_{60}\cdot TMTSF\cdot 2CS_2$ (where TMTSF is tetramethyltetraselenafulvalene) molecular complex is described in [7]. The structure of this complex possesses a layered structure representing a sequence of the homogeneous layers formed by TMTSF and inhomogeneous layers consisting of $C_{60}$ balls interleaved by $CS_2$ molecules; the bonding in the complex occur via zigzag ...–TMTSF–$C_{60}$–TMTSF–$C_{60}$–... chains which link layers together [7]. Similar to $(ET)_2C_{60}$, the charge transfer in $C_{60}\cdot TMTSF\cdot 2CS_2$ is small, but application of external pressure about 5 GPa induces transform of 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] for $(ET)_2C_{60}$ and $C_{60}$ magnetism.

Magnetisation $M(T,B)$ of the single-crystal $C_{60}\cdot TMTSF\cdot 2CS_2$ having weight of 6 mg was studied in the temperature range 2.5–130 K in magnetic field up to 8 T using Oxford Instruments vibrating sample magnetometer (VSM). The field dependence of magnetisation $M(B)$ in magnetic field up to 47 T at liquid helium temperatures was registered by induction technique in pulsed field magnet (pulse duration 20 ms). Special attention was paid on correct subtraction of the signal from the empty pick-up coil, which have allowed to provide measurements of the weak magnetic response of $C_{60}\cdot TMTSF\cdot 2CS_2$.

First we consider temperature dependence of magnetisation for the field $B = 8$ T which is for within the range of linear magnetic response for $C_{60}\cdot TMTSF\cdot 2CS_2$ (Fig. 1). The $M(T)$ curve resembles one obtained earlier for $(ET)_2C_{60}$ [3]; the onset of “paramagnetic” contribution below 40 K superimposed on diamagnetic background $M_{dia}$ is clearly visible. As in the case of $(ET)_2C_{60}$ for the studied compound, the low-temperature increase of magnetisation is less pronounced than in pure $C_{60}$, and $C_{60}\cdot TMTSF\cdot 2CS_2$ sample remain in diamagnetic state even at $T \sim 2.5$ K.

However, the quantitative analysis of $M(T)$ data shows an essential difference between two molecular complexes. Assuming the validity of Eq. (1), it is possible to write for magnetisation

$$M(B,T) = M_{para}(B,T) + M_{dia}(B) = \left[\frac{3\chi_{para}(T)k_B T}{(J+1)g\mu_B}\right] B_J\left(\frac{g\mu_B JB}{k_B T}\right) + \chi_{dia}B \qquad (2)$$

where $B_J(x)$ is the Brillouin function and $J$ the total angular momentum. In the diapason of linear response to magnetic field, Eq. (2) reduces to $M(B,T) = A/T + M_{dia}$, where both $A$ and $M_{dia}$ are constant in fixed magnetic field. In the case of $(ET)_2C_{60}$, the use of Eq. (2) provided an adequate description of both temperature and field dependencies of magnetisation [3,4]. At the same time for $C_{60}\cdot TMTSF\cdot 2CS_2$, the similar procedure gives a poor description of $M(T)$ shape (compare experimental data (Fig. 1, curve 1) with the best-fit (Fig. 1, curve 2) obtained using Eq. (2) in linear approximation).

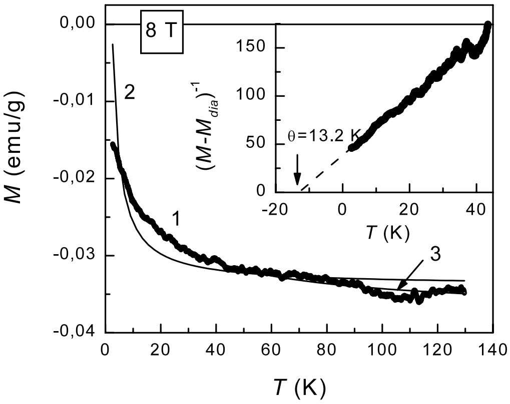

Fig. 1. Temperature dependence of magnetisation for $C_{60}\cdot TMTSF\cdot 2CS_2$. Points—experiment; lines—simulation using various models (see text).

Field dependence of $M(B)$ at $T = 4.2$ K for $C_{60}\cdot$TMTSF$\cdot 2CS_2$ also deviates from that reported previously [3,4]. The linear section of the $M(B)$ lasts up to 20 T (Fig. 2), i.e. about 10 T less than for $(ET)_2C_{60}$ [3,4]. Above 20 T, the experimental curve first deviates downwards from linear asymptotic (Fig. 2) that is in agreement with the model of paramagnetic center with reduced $g$-factor [3]. But when magnetic field reach the value $\sim 35$ T the magnetisation of the sample tends to saturate, which is in contrast to experimental data reported so far for the weakly magnetic fullerene-based compounds [3,4].

Now let analyse the application of the paramagnetic center model to $C_{60}\cdot$TMTSF$\cdot 2CS_2$ in more detail. Taking Eq. (2) as first approximation and following procedure described in detail in [3] for the separation of diamagnetic and paramagnetic contributions, it is easy to calculate field dependence of magnetisation from Fig. 1 assuming $g = 2$ and $J = 1/2$. The result is presented in Fig. 2, and it is obvious that a straightforward model of the oxygen-like impurity does not complain with the $M(B)$ data. Hereafter, we will consider the $J = 1/2$ case, as long as higher spin values does not change qualitatively the result for $g = 2$ and hence the possible reduction of the $g$-factor should play a key role [3]. Restricting further analysis to the interval $B < 35$ T, it is possible to estimate a renormalised reduced $g$-factor value $g \sim 0.3$ (Fig. 1, curve 2). This value is about two times higher than that find from a similar computation for $(ET)_2C_{60}$; the discrepancy is apparently due to the fact that the curvature of the $M(B)$ curve for $C_{60}\cdot$TMTSF$\cdot 2CS_2$ is more pronounced and appear in lower magnetic fields.

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 magnetisation (curve 2 in Fig. 1). Therefore, it is worth for a possible consistent description of the $M(B)$ and $M(T)$ data within the model of paramagnetic center with the renormalised $g$-value. We find that a best approximation of the $M(T)$ shape can be provided by the expression

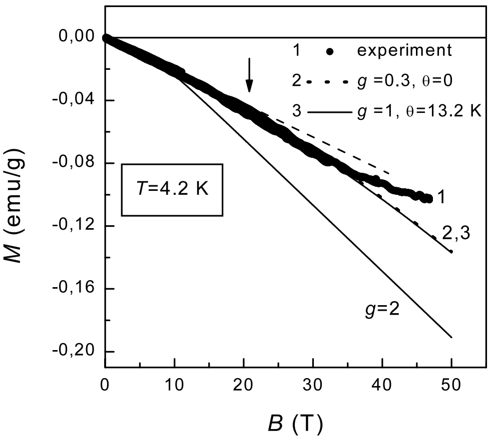

Fig. 2. Field dependence of magnetisation for $C_{60}\cdot$TMTSF$\cdot 2CS_2$. Points—experiment; lines—simulation using various models (see text). Arrow marks the region of linear response.

$$M(T) = \frac{A}{T + \theta} + M_{\text{dia}} \tag{3}$$

with $M_{\text{dia}}(B = 8\ \text{T}) = -0.0373$ emu g$^{-1}$ and $\theta = 13.2$ K (see inset in Fig. 1, where experimental data are plotted in coordinates $(M - M_{\text{dia}})^{-1} = f(T)$). It is interesting that the obtained $M_{\text{dia}}$ value correspond to an “intrinsic” diamagnetic susceptibility $\chi_{\text{dia}} \approx -4.7 \times 10^{-7}$ emu g$^{-1}$ which is approximately 34% higher than in $C_{60}$ [1]. As long as $C_{60}\cdot$TMTSF$\cdot 2CS_2$ have a lower concentration of fullerene molecules than pure $C_{60}$, the additional diamagnetism may be associated with the neutral TMTSF and $CS_2$ molecules. This situation agrees with the small charge transfer in the $C_{60}\cdot$TMTSF$\cdot 2CS_2$ complex.

Within a paramagnetic center model, the validity of Eq. (3) suggests an interaction between magnetic moments. It is worth to note that possible paramagnetic centers themselves in fullerene-based solids are very exotic and the magnitude of the magnetic moment of the center should be strongly damped with respect to free electron. Therefore, it is difficult to say how Curie law could transform to a Curie–Weiss behaviour. At present, a possible interaction mechanism is completely unknown and more theoretical work is required to reveal the origin of onset of unexpected $M(T)$ dependence (Fig. 1).

In the presence of interactions, Eq. (2) is no longer valid and therefore the obtained estimate of the $g$-factor is put into question. In order to check the possible change of the $g$-factor, we attempted to simulate both $M(T)$ and $M(B)$ data in Figs. 1 and 2 using model representation

$$M(B,T) = \chi_{\text{dia}} B + M_0 \tanh\left[\frac{g\mu_B B}{2k_B(T + \theta)}\right] \tag{4}$$

which corresponds to Eq. (3) in the linear limit and reproduces a saturation of the magnetic moment. Eq. (4) have two fitting parameters, $M_0$ and $g$, as long as $\chi_{\text{dia}}$ and $\theta$ are supposed to be known. The results of model calculations for $M(T)$ and $M(B)$ are presented by curve 3 in Figs. 1 and 2, respectively. It is visible that Eq. (4) may provide an adequate and consistent description of the field and temperature dependencies of magnetisation for $B < 35$ T; however, the found $g$-factor value is considerably higher: $g = 1$.

We see that analysis of the magnetisation 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 $g \sim$

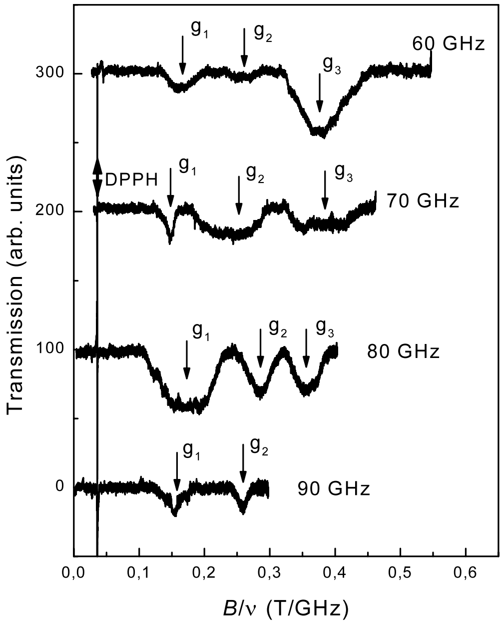

Fig. 3. ESR absorption lines in $(ET)_2C_{60}$ molecular complex at $T = 1.8$ K. Narrow line corresponds to a reference spectrum of DPPH.

0.14–1. This situation strongly demands the determination of this parameter by direct spectroscopic means.

## 3. Magneto-optical spectroscopy of $(ET)_2C_{60}$

Magneto-optical study of the mosaic sample prepared of single crystals of $(ET)_2C_{60}$ was carried out in pulsed magnetic field up to 32 T in the frequency range $\nu = 60$–90 GHz at $T = 1.8$ K. As a source of microwave radiation, a set of Gunn oscillators have been used. A transmission of the sample as a function of magnetic field has been recorded.

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. 3, where experimental data are presented as a function of reduced field $B/\nu$). At the same time, no ESR absorption in the sample was found around $g = 2$ (Fig. 3).

The obtained result qualitatively confirms predictions of [3,4] as well as results of the previous section. Moreover, the model of the $g$-factor renormalisation caused by dynamic Jan-Teller effect [5] may explain the 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. 3).

## 4. Conclusions

Summarising, we provide experimental evidence that a paramagnetic centers with the renormalised $g$-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 probably 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 Jan-Teller effect [3] and coupling to several phonon modes may cause the presence of several magneto-absorption lines.

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