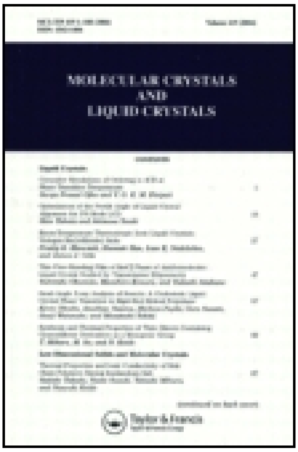

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Ferromagnetic Interaction in C_{60} Charge Transfer Complexes

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Version of record first published: 05 Dec 2006.

To cite this article: B. Gotschy , R. Gompper , H. Klos , A. Seidl , A. Schilder , W. Schütz & G. Völkel (1995): Ferromagnetic Interaction in C_{60} Charge Transfer Complexes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 272:1, 51-56

To link to this article: http://dx.doi.org/10.1080/10587259508055273

Mol. Cryst. Liq. Cryst., 1995, Vol. 272, pp. 51–56
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FERROMAGNETIC INTERACTION IN C_{60} CHARGE TRANSFER COMPLEXES

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Abstract C_{60}[TDAE] was the first and so far the only C_{60} CT complex which exhibits molecular ferromagnetism with a Curie temperature of about 16 K [1]. Despite extensively investigated a convincing access to the origin of the low temperature phase of this C_{60} CT complex is still missing. The 3 fold degeneracy of the C_{60} HOMO is lifted by a change of the C_{60} conformation, and we find a transition from a static low temperature Jahn-Teller distortion to a dynamic one at about 140 K. The excess electron is concentrated in a belt around the equator of the C_{60}^-. The distorted C_{60} molecules have a spin density distribution with an axial symmetry and are aligned along the crystallographic axes. This orientational ordering of the C_{60}^- molecules is the necessary precursor to a ferromagnetic spin glass type ordering in C_{60}[TDAE] which was interpreted in terms of spin polarisation between $C_{60}^{-\bullet}$ and $TDAE^{+\bullet}$ by Yamaguchi et al [2].

INTRODUCTION

The fullerene charge transfer complex $C_{60}^{-\bullet}$[tetrakis(dimethylamino)ethylene]$^{+\bullet}$, abbreviated as C_{60}[TDAE], was the first and so far the only C_{60} molecular ferromagnet with a Curie-temperature of about 16 K [1]. Stimulated by the experimental findings the properties of C_{60}[TDAE] were interpreted in the first report in terms of itinerant ferromagnetism. Recently conductivity studies of Schilder et al have ruled out the presence of itinerant moments [3]. Later a spin glass model was discussed extensively by Blinc and co-workers [4]. Meanwhile a number of different interpretations were given for the low temperature phase of C_{60}[TDAE]. Anyhow, none of the proposed theories is capable, to explain all the experimental observations published in a consistent way, and the real nature of the low temperature phase of C_{60}[TDAE] is still a matter of discussion. Furthermore there is still some discrepancy between data of C_{60}[TDAE] from different groups. For example Suzuki et al reported evidence for spontaneous magnetisation and a small hysteresis in C_{60}[TDAE] below 15 K [5] in contrast to Allemand et al [1], who claimed a very soft ferromagnetism without hysteresis. The main problem so far is that C_{60}[TDAE] is the only C_{60} ferromagnet discovered, and the lack of ferromagnetic C_{60} systems with varying lattice constants prevents the test of any theoretical model. In addition C_{60}[TDAE] is a very air and moisture sensitive powder, and sample preparation may easily influence its properties.

An alternative way is electrocrystallisation yielding bulk single crystals of C_{60} radical anion salts. One such salt is $C_{60}I[P(C_6H_5)_4]_2$. The synthesis of this air stable salt was first reported by Pénicaud et al. [6]. Here we will show, that this salt is an excellent model system for the ferromagnetic C_{60}[TDAE] and a good tool, to study the spin and molecular dynamics of C_{60} mono-anions in the solid state. Furthermore $C_{60}X[P(C_6H_5)_4]_2$ with X=I, Cl is an exception among the fullerides, since the temperature dependence of the Jahn-Teller distortion, predicted for ionic C_{60} [7], can be directly monitored.

RESULTS

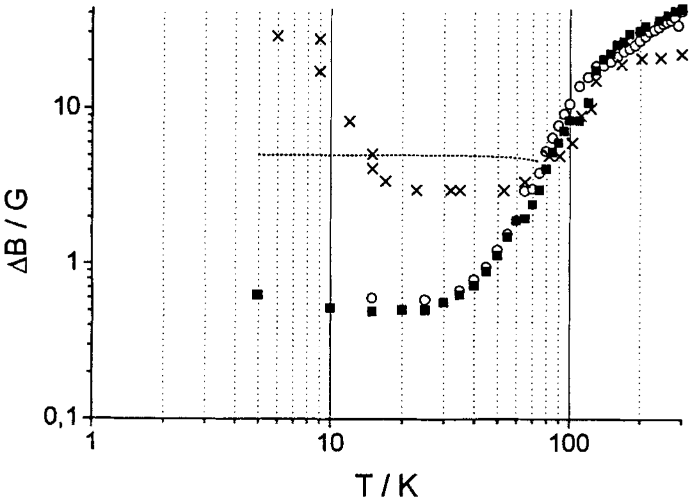

Figure 1: EPR line width ΔB vs. temperature in a single crystal of $C_{60}I[P(C_6H_5)_4]_2$ at 34 (O) GHz and 9.7 (■) GHz; ···· powder sample; ΔB(T) of C_{60}[TDAE] (×) from [8].

The EPR line width ΔB of C_{60}[TDAE] [8], C_{60} mono-anions in frozen solutions in low concentration [9] and powder samples of $C_{60}I[P(C_6H_5)_4]_2$ [10] exhibits an uniform temperature dependence (figure 1). At high temperatures ΔB(T) varies only slightly. At about 140 K ΔB(T) levels off, and below about 70 K a plateau is observed with a width of the EPR spectrum between 3 G and 4 G in all three cases. On the other hand pulsed EPR studies [9, 11] reveal that the homogeneous line width is an order of magnitude smaller. So we have to conclude that the observed powder EPR line is dominated by a g-tensor anisotropy which is the same in all three cases. However a g-tensor anisotropy in a frozen (amorphous) solution means, that it must have a molecular origin. Thus a lot of the electronic properties of mono-anionic fullerene solids are simply mono-molecular properties, i.e. due to the largeness and high symmetry of the C_{60}^-. In this case $C_{60}X[P(C_6H_5)_4]_2$ is the ideal candidate, to study C_{60}^- in the solid state, since it is a single crystalline and air stable material. The following will not be dedicated to a discussion of the ferromagnetic phase of C_{60}[TDAE] which was extensively done in the literature, but we will concentrate on the molecular and spin dynamics studied by EPR of $C_{60}I[P(C_6H_5)_4]_2$ [10] and then discuss its relevance for the ferromagnetic ordering in C_{60}[TDAE].

Obviously the single crystal line width (figure 1) is an order of magnitude smaller than the width of the powder spectrum and coincides with the homogeneous line width determined by pulsed EPR [11]. This allows an accurate determination of the elements and the symmetry of the g-tensor.

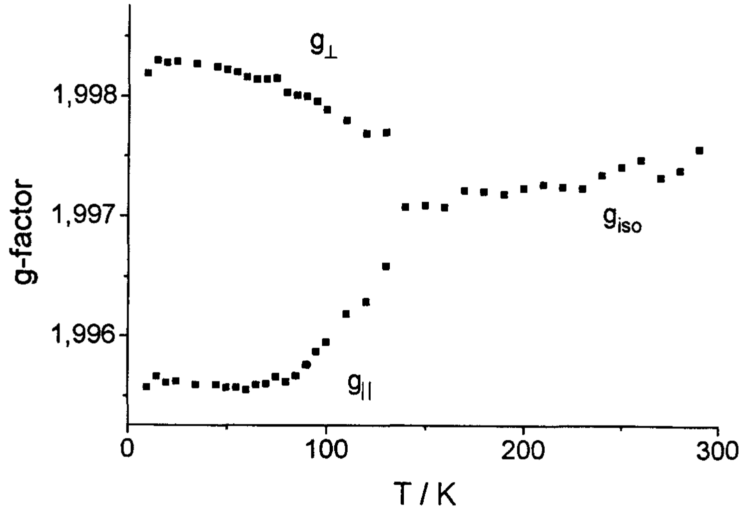

Figure 2: g-factor vs. temperature in a single crystal of $C_{60}I[P(C_6H_5)_4]_2$. The crystal was aligned along the [001] direction.

Above 140 K the EPR is isotropic, and we find only one EPR line. Below 140 K even in single crystals the EPR line splits, and two EPR lines with nearly equal intensities evolve. The splitting increases with decreasing temperature and finally reaches a value of 20 G in Q-band below about 70 K. The electronic g-factor is at all temperatures smaller than the free electron value g_0. This is caused by spin-orbit coupling, indicating that the angular momentum of the C_{60} single occupied MO (L = 1 [7]) is not completely quenched.

The low temperature data $\Delta g = g_{\perp} - g_{\|}$ can be described in a first, heuristic approach in analogy to a motional narrowing process:

$$\Delta g(T) = \sqrt{\Delta g(0)^2 - \frac{c}{\tau_c^2}}\ , \quad T << 140K$$

$\tau_c = \tau_0 \cdot \exp(E_a/kT)$ is the correlation time of the motion. $\Delta g(0) \approx 7 \cdot 10^{-3}$ corresponds to the splitting at the lowest temperatures, and c is a constant. The best fit gives $E_a/k = 142 \pm 2$ K.

The fit of $\Delta g(T)$ suggests a phase transition at 140 K which was not seen in the specific heat, and we will not claim a symmetry breaking of the C_{60}^- geometry at 140 K. However about 140 K the two lines collapse and Δg vanishes within experimental resolution, and we find an isotropic g-factor above 140 K. The g-factor of both lines has the common angular dependence of a system with axial symmetry below 140 K, and $g_{\perp}$ and $g_{\|}$ are equal for both lines. We attribute the two EPR lines to two different oriented C_{60} molecules as suggested by extensive X-ray work [6]. As mentioned above $g_{\perp}$ and $g_{\|}$ are molecular properties of the C_{60}^-, and the line width can not be determined by g-factor anisotropy. We want to anticipate that the fact that we found only two lines under a rotation around the [001] axes, which is the axes of crystal growth, could be a hint for strain. It is well established that strain significantly influences the EPR of Jahn-Teller distorted ions [12].

The first idea is that a rotation of the C_{60}^-, well known from NMR on C_{60} [13], is the reason for this motional narrowing of the EPR. Anyhow, a $\Delta g(0)$ of 20 G at 34 GHz corresponds to $\omega_c = 3.5 \cdot 10^8$ rad/s, and a mechanism which averages out Δg must have a correlation time of $\tau_c = 1/\omega_c = 2.8 \cdot 10^{-9}$ s. Our ^{13}C NMR data of $C_{60}I[P(C_6H_5)_4]_2$ (figure 3) [14] indicate that the C_{60}^- rotates free above 180 K. Below 180 K the C_{60}^- motion slows down very fast and "*freezes out*" at about 140 K. Thus, in the temperature domain where the g-anisotropy begins to decrease and finally vanishes, the molecular rotation cannot be encountered for the motional averaging of Δg. These NMR data are similar to measurements on C_{60} [13]. Furthermore, we want to emphasise that the onset of the molecular rotation above 180 K is not sufficient, to affect the EPR and to cause a significant decrease of the EPR line width.

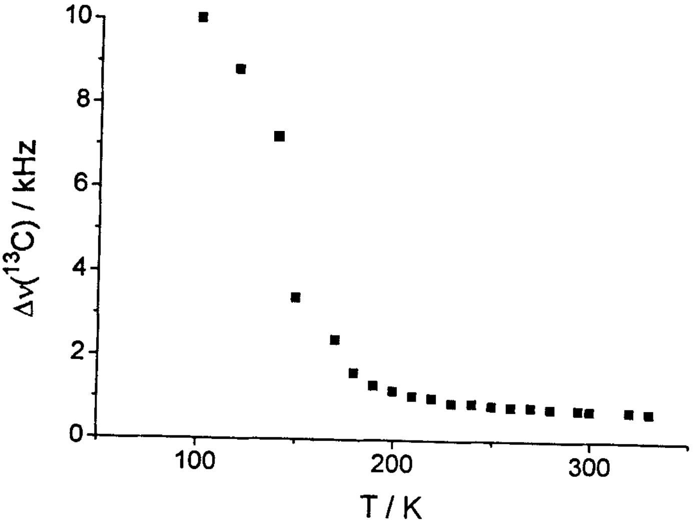

Figure 3: ^{13}C NMR line width of the C_{60}^- in $C_{60}I[P(C_6H_5)_4]_2$.

DISCUSSION

C_{60} anions will be subjected to a Jahn-Teller (JT) distortion [7]. The orbital energetic degeneracy of the SOMO is lifted, the C_{60}^- symmetry is reduced from I_h to D_{3d}, and the distribution of the radical π-electron density is concentrated in a belt around the equator [7], giving rise to an axial symmetric spin density distribution and a net magnetic moment along the long axes of the molecule, i.e. perpendicular to the equator.

In $C_{60}I[P(C_6H_5)_4]_2$ below 70 K the JT-distortion is static. Between 70 K and 140 K the g-factor anisotropy, due to the JT-distortion, is averaged out by a dynamic change of the C_{60}^- conformation (not by rotation). Above 140 K the JT distortion becomes completely dynamic with an isotropic g-factor. In this full dynamic limit the distorted C_{60}^- recovers its spherical shape, and we get an isotropic spin density distribution.

From the similarities in the EPR results of $C_{60}I[P(C_6H_5)_4]_2$ and C_{60}[TDAE] we conclude that the same symmetry reduction happens to the C_{60} mono-anions in the later system as well and that the distorted C_{60}^-, which have the form of a stretched rotational ellipsoid, are aligned with the molecular symmetry axes along the crystal axes. Probably the monoclinic unit cell of C_{60}[TDAE] [15] in this way favours the building of domains, where C_{60} molecules are oriented along the long axes of the unit cell. However in the absence of any coupling between the spins on different C_{60}^- molecules a simple paramagnet will result. Recently Yamaguchi et al [2] suggested that due to the close contact between the methyl groups of the $TDAE^{+\bullet}$ molecule and the $C_{60}^{-\bullet}$ a dynamic spin polarisation could be the driving force for ferromagnetic ordering. However such a mechanism cannot be understood without the lowering of the C_{60}^{-} symmetry which is accompanied by an anisotropic spin density distribution with a net magnetic moment perpendicular to the C_{60} equator. Thus in the domain, where the JT distortion is completely dynamic (isotropic limit), the Yamaguchi mechanism will not work, and ferromagnetic ordering will be in any case restricted to the temperature domain below 70 K (completely static JT limit).

As a last point we want to mention that the interpretation of the low temperature phase of C_{60}[TDAE] in terms of a spin glass behaviour [4] indicates that it is a system with pronounced orientational disorder of the C_{60}^{-}. Anyhow a short range orientational ordering of the C_{60} anions will be the necessary precursor for the ferromagnetic order.

Acknowledgement - Fruitful and stimulating discussion with M. Schwoerer and E. Rößler (Bayreuth/Germany) is acknowledged. This work was supported by Fond der Chemischen Industrie and BASF/BMFT 03M4067-6.

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