

EPR DETECTION OF PRESUMABLE MAGNETOELECTRIC INTERACTIONS IN THE LIQUID-CRYSTALLINE STATE OF AN IRON MESOGEN

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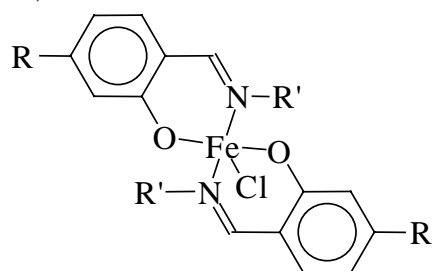
We report about unusual properties of recently synthesized [1] paramagnetic bis-chelate iron FeClL_2 complexes possessing a smectic mesomorphism.

Solid phases of FeClL_2 mesogenic complexes have been studied earlier [2] by EPR, magnetic susceptibility, and Mossbauer spectroscopy methods. It has been shown [2] that Fe(III) ions are in the high-spin state (d^5 , $S=5/2$), and FeClL_2 mesogenic complexes are organized in a low-dimensional (1d) magnetic subsystem, where iron ions are coupled by chlorine atoms in linear chains with weak antiferromagnetic interactions between iron ions, these linear chains forming smectic layers.

We have also investigated the dielectric behavior of FeClL_2 complexes in the smectic liquid-crystalline state [3]. An anomalous dielectric behavior of the static dielectric permittivity in the smectic mesophase (typical for a smeared ferroelectric phase transition) has been revealed [3]. This anomaly is evidently caused by local ordering of Fe-Cl dipole moments along the chains in smectic layers, and the observed dielectric relaxation is associated with the chlorine jumps within the Fe—Cl \cdots Fe bond (between two sites in the double-minimum potential) correlated along the chains.

It would be interesting trying to reveal the influence of the internal electric field obliged to the local ordering of Fe-Cl dipoles on the magnetic properties of the complex. An influence of the external electric field on the magnetic properties of the magnetic crystals (known as the magnetoelectric effect) has been investigated experimentally and theoretically [4]. The effect consist in the creation of an additional magnetization by the applied electric field. We have a chance to observe a similar effect in our samples, if the internal electric field plays the role of the external one.

Here we report the results of EPR studies for two paramagnetic bis-chelate iron FeClL_2 complexes (**1**, **2**) with Schiff's bases,

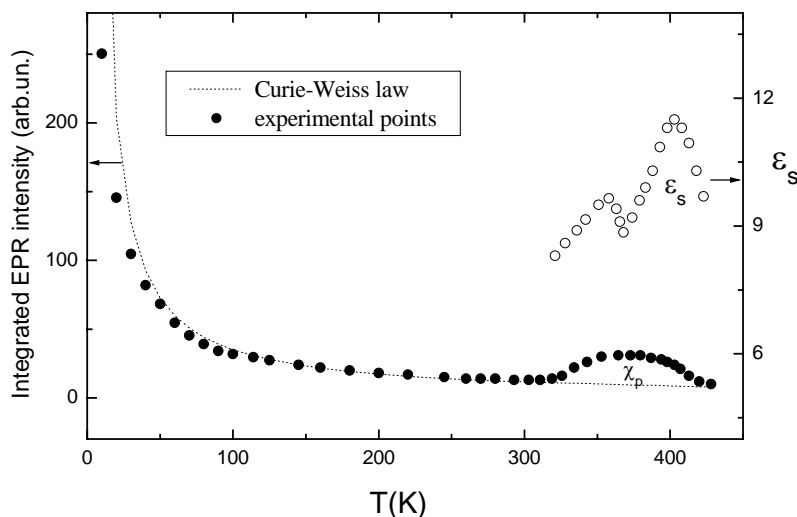


where $R = C_7 H_{15} O\text{-Ph-COO}$, $R' = -C_{12} H_{25}$ for complex **1**, and $R = C_{10} H_{21} O\text{-Ph-COO}$, $R' = -C_{12} H_{25}$ for complex **2**. The complexes exhibit following phase sequences: C 343 S_A 424 I, and C 363 S_X 396 S_A 427 I, for **1** and **2**, respectively (the phase transition temperatures are indicated in K; C=crystalline, S_A =smectic A phase, S_X =unknown (X) smectic phase, I=isotropic phase).

A “powder-type” EPR spectrum with the fine structure obliged to the transitions $M=\pm 5/2 \leftrightarrow \pm 3/2 \leftrightarrow \pm 1/2$ of Fe^{3+} (${}^6S_{5/2}$) ion is observed in the isotropic phase. The spectrum is simulated well if one takes: $g=2,1$ and $D=0,04\text{cm}^{-1}$. Slowly cooling the sample to the smectic-A phase in the presence of 0.4T external magnetic field, we observe the orientation of the molecules in the mesophase. The resonance field positions for all the transitions remain the same in the smectic-A phase. The angular dependence of EPR

lines demonstrates an extraordinary orientation of molecules in the mesophase. Different possible reasons for this orientation were considered, but neither of them could explain the orientation observed by EPR. To understand the way of molecular orientation, it was necessary to suppose the existence of an additional paramagnetic molecular susceptibility with the maximum susceptibility axis directed along the Fe-Cl bond. We have supposed that the local electric field existing in the mesophase can induce an additional magnetoelectric susceptibility by means of the magnetoelectric effect. To check it, the temperature dependence of the integrated intensity of Fe³⁺ EPR lines with $g=2.1$ has been measured (see figure 1).

Its behavior shows, as it was supposed, that the paramagnetic susceptibility in the mesophase is really increased as



compared to that predicted by the Curie-Weiss law, and it has an anomaly, which is similar to that of the static dielectric permittivity one. So, iron mesogens investigated may be considered as an example of liquid-crystalline magnetoelectric materials that demonstrate the appearance of the magnetoelectric effect directly in the mesophase [5].

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