MAGNETISM AND FERROELECTRICITY

Magnetic Resonance in a \([\{\text{Cr(CN)}_6\}\{\text{Mn(S)-pnH-(H}_2\text{O})\}] \cdot \text{H}_2\text{O}\) Single-Crystal Molecular Ferrimagnet


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Abstract—The variations in the magnetic resonance spectra accompanying the transition from the paramagnetic to ferrimagnetic state in \([\{\text{Cr(CN)}_6\}\{\text{Mn(S)-pnH-(H}_2\text{O})\}] \cdot \text{H}_2\text{O}\) orthorhombic chiral molecular crystals were studied. The dependence of the EPR linewidth on temperature in the proximity of the transition point \(T_C = 38 \text{ K}\) argues for the two-dimensional character of spin ordering. The spin resonance line was found to undergo exchange narrowing at \(T > T_C\). The ferrimagnetic phase has an easy magnetization axis coinciding with the \(a\) crystallographic axis. © 2005 Pleiades Publishing, Inc.

1. INTRODUCTION

The use of hexacyanometalate complexes \([(M\text{(CN)}_6)_3]^3\), where \(M\) stands for a transition metal] in the synthesis of new molecular magnets has lead to considerable progress in increasing magnetic ordering temperatures and to observation of the photomagnetic effect [1]. The above complexes are molecular precursors capable of being incorporated into various compounds and of controlling the number and efficiency of exchange channels among neighboring spins. This has made it possible to raise the magnetic ordering point to room temperature [2, 3] and prepare monomolecular magnets with spins of up to 27/2 [4, 5]. The high symmetry of the \(M\text{(CN)}_6\) complexes makes their magnetic properties in crystals predictable, and their compatibility with metals of various types makes it possible to vary the symmetry and overlap of electronic shells. Most compounds of this type exhibit three-dimensional (3D) magnetic ordering. However, crystals whose specific structural features are capable of giving rise to magnetism of lower dimensions or helicoidal spin ordering have also attracted attention.

There have been reports [6] on the preparation of a new molecular crystal, \([(\text{Cr(CN)}_6)_3\{\text{Mn(S)-pnH-(H}_2\text{O})\}] \cdot \text{H}_2\text{O}\), which undergoes a magnetic phase transition at \(T_C = 38 \text{ K}\) (orthorhombic crystal structure \(P_{212121}\) with lattice parameters \(a = 7.6280(17)\), \(b = 14.510(3)\), and \(c = 14.935(3)\) Å). Transparent, needle-shaped, greenish crystals have been termed green needles (GNs). The atomic structure of GN crystals is shown in Fig. 1a. Their molecules are coupled to form quasi-two-dimensional wavy layers parallel to the \(ab\) plane. Within a layer, the alternating paramagnetic ions \(\text{Cr}^{3+}\) and \(\text{Mn}^{2+}\) are covalently bonded through \(\text{–CN–}\) groups to form a slightly distorted square lattice (Fig. 1b). The layers are coupled by van der Waals interaction. The local environment of the \(\text{Cr}^{3+}\) ions consists of six carbon atoms occupying the corners of an octahedron. The \(\text{Mn}^{2+}\) ions are also surrounded by six nearest neighbors, five of which are nitrogen atoms and one, an oxygen atom. In addition, as the N5–N6 long axis of the coordination octahedron is displaced along the \(c\) axis, it turns about it. In other words, the structure exhibits chirality with respect to \(\text{Mn}^{2+}\) positions and has no inversion symmetry. The chirality gives rise to circular rotation of the plane of light polarization and to asymmetry in the Faraday rotation, which depends on the strength of an external dc magnetic field [6]. The specific features of magnetic ordering of the GN molecular compound have not yet been adequately studied. In particular, the effect of chirality on the formation of the magnetic structure of this compound remains unclear. It is these features that account for the interest in GN crystals in connection with the progress made in magnetic resonance techniques as applied to chiral ferrites, chiro-FMR (see, e.g., review [7]).

The present study was aimed at determining the type of magnetic ordering and investigating the magnitude and direction of the anisotropy field in a magnetically ordered state, as well as at observing the features in the magnetic properties of GN crystals that originate from the quasi-two-dimensional character of the structure of these crystals.

It is appropriate to note also that \([(\text{Cr(CN)}_6)_3\{\text{Mn(S)-pnH-(H}_2\text{O})\}] \cdot \text{H}_2\text{O}\) can be synthesized (depending on the actual conditions of preparation) in three different orthorhombic modifications hav-
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Fig. 1. Atomic structure of GN crystals as viewed (a) along the $a$ axis and (b) along the $c$ axis.

2. EXPERIMENTAL TECHNIQUE

Crystals were grown as rectangular platelets measuring $0.1 \times 0.3 \times 2$ mm. Experiments were run with $X$-range $(-9.5$ GHz) and $Q$-range $(-32$ GHz) EPR spectrometers (Bruker ESP300E and E500) with $H_{102}$-type rectangular resonators providing modulation frequencies of $1.56-100$ kHz and a dc magnetic field sweeping range $B_0 = 0-1.5$ T. The crystals were fixed in a node of the magnetic component of the applied microwave field. The resonator $Q$ factor was monitored in the course of measurements. The EPR signal was proportional to the first derivative of the imaginary part of the crystal magnetic susceptibility $d\chi/dH$. The temperature was varied in the range $3.1-300$ K. The sample to be

ing the same space group $P2_12_12_1$ to which GNs belong and chirality of the Mn$^{2+}$ positions: GNs themselves; phase I and phase II with the same chemical formula as GNs; and phase III, the dehydrated compound $\left\{ \text{Cr(CN)}_6 \right\} \left\{ \text{Mn(S)}-\text{pnH}-(\text{H}_2\text{O}) \right\} \left[ 6 \right]$. Here, we deal with phase I only.