MÖSSBAUER SPECTROSCOPY OF MAGNETIC PHASES IN $FeCl_2 \cdot 2H_2O$

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Mössbauer spectroscopy of the three magnetic phases of single crystal $FeCl_2 \cdot 2H_2O$ in external magnetic fields at 4.2 K is reported.

Monoclinic $FeCl_2 \cdot 2H_2O$ orders antiferromagnetically at $T_N = 23$ K [1] and the magnetic structure consists of two sublattices of $FeCl_2$ chains lying along the *c*-axis. The coupling along the chains is ferromagnetic with weak antiferromagnetic coupling between chains. Application of an external magnetic field along the easy axis *a* at 4.2 K induces phase transitions at $H_1 = 39$ kOe and $H_2 = 46$ kOe [1–3]. In this letter we report the use of Mössbauer spectroscopy in external magnetic fields to study the magnetic structure of each of the three phases.

Previous Mössbauer work in $FeCl_2 \cdot 2H_2O$ includes a power study by Chandra and Hoy [4] and a single crystal study by Johnson [5]. They found a magnetic hyperfine field of 250 kOe at 4.2 K and an electric quadrupole interaction of 2.30 mm/sec with asymmetry parameter $\eta = 0.3$. The principle component of the *efg* is at right angles to the magnetic hyperfine field. Johnson [5] also determined that the spins lay in the ac plane at an angle of 66.2° from *a* axis, in agreement with results obtained by Narath [1] from susceptibility and proton magnetic resonance measurements.

In the present work, a large single crystal was grown by slow evaporation at 85°C. A slice was cut parallel to the bc plan and placed at 32° to the γ-ray beam and external magnetic field H_0, so that H_0 was parallel to the easy axis *a*. The direction of the positive *c* axis was determined by orienting the sample in a small magnetic field at room temperature. The $H_0 = 0$, 4.2 K spectrum is shown in fig. 1a. There is a small

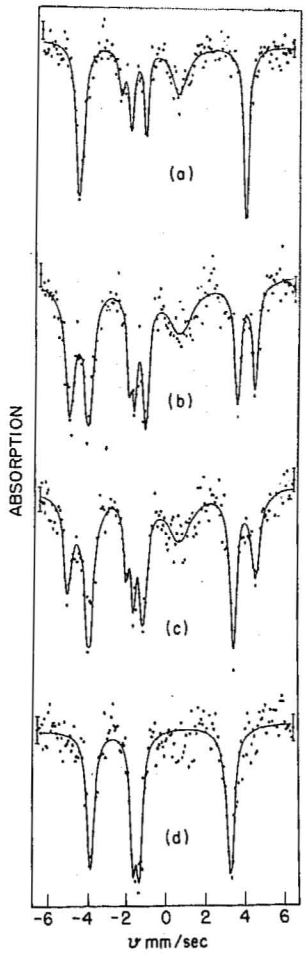

Fig. 1. Mössbauer spectra of $FeCl_2 \cdot 2H_2O$: a) $H = 0$, $T = 4.2$ K; b) $H = 35$ kOe, $T = 4.2$ K; c) $H = 42$ kOe, 4.2 K; d) $H = 50$ kOe, $T = 4.2$ K. See text for sample orientation.

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residual absorption at +2.5 mm/sec and 0.07 mm/sec due to paramagnetic $FeCl_2 \cdot 4H_2O$. Analysis of the spectra were made using some of the parameters given by Chandra and Hoy [4] and by Johnson [5]. Using the nomenclature in fig. 3 of Narath's paper, $H_{hf} \| a$ and $V_{zz} \| b$. In addition, we find the best fit with the principle axes V_{xx} and V_{yy} of the *efg* tensor oriented along the c and a^* direction in the *ac* plane.

The spectra in various external magnetic fields are shown in figs. 1b, 1c and 1d. For $H_0 < H_1$, the spectrum (fig. 1b) consists of two superposed spectra of equal intensity corresponding to the external field H_0 adding and subtracting respectively from the hyperfine fields for the ions in the spin down and spin up sublattice, respectively. For $H_1 < H_0 < H_2$, the spectrum (fig. 1c) consists of two superposed spectra corresponding to the spin up and spin down sublattices, but now with relative intensities approximately 2:1. Since the majority spins have a smaller splitting than the minority spins, the sign of the hyperfine field is negative. For $H_2 < H_0$, we observe a single spectrum (fig. 1d). For all three phases, the sign, magnitude and orientation of the *efg* is the same as in zero magnetic field, showing that the spins remain collinear in all three phases and that there is no spin canting. Moreover, the magnetic hyperfine interaction (exclusive of the applied field) is the same for all three phases indicating that the moment per ion is unchanged by the increasing magnetic field or phase transitions. For all H_0 then the net field at the nucleus is given by $H_n = H_{hf} \pm H_0$. The demagnetization correction is without the limit of error of the hyperfine field measurements.

Narath [1] has introduced a six sublattice model and has proposed that the three phases consist (in order of increasing applied field) of (1) antiferromagnetic with 3 spins up, 3 spins down, (2) ferromagnetic with 4 spins up, 2 spins down, and (3) paramagnetic with 6 spins up. The measured moment of the ferrimagnetic phase is 1/3 that of the paramagnetic phase [1], indicating 2 ions on the spin up lattice to 1 ion on the spin down lattice as in the model. Oguchi and Takano [6] had earlier proposed a four sublattice model to account for the transitions in the magnetically similar material $C_oCl_2 \cdot 2H_2O$. In this model the first transition consists of one of the down spins turning over, making three up spins to one down spin, in the ferrimagnetic phase. Our experimental results (fig. 1) are close to 2:1 for the ferrimagnetic phase and thus provide direct confirmation for the 6 sublattice model proposed by Narath.

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