

## Magnetic Susceptibility of FeOCl

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Magnetic susceptibility ( $\chi$ ) measurements on FeOCl are reported. The data were obtained on single crystals over the temperature range 7–400 K. A small but distinct singularity at the Neel temperature  $T_N \approx 84$  K was observed; extensive short-range ordering above  $T_N$  was also evident from these data. The present work suggests that the intrinsic  $\chi(T)$  of FeOCl was masked by magnetic impurities in the two previous  $\chi$  studies of this compound. © 1987 Academic Press, Inc.

### Introduction

There has been considerable study of the magnetic properties of the layered compound FeOCl in the literature. Magnetic susceptibility (1, 2), specific heat (3), powder neutron diffraction (4), Mössbauer spectroscopy (5–7), and X-ray diffraction (8) have been employed in order to understand the magnetic behavior of this compound. This has resulted in a very nearly complete understanding of this quasi-two-dimensional antiferromagnetic system, but some fundamental questions still remain.  $T_N$  has never been observed in susceptibility measurements, and this is the question that the present study addresses. Conditions for the preparation of large single crystal samples of FeOCl are described.

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### Sample Preparation and Structure

FeOCl was prepared (9) in a temperature gradient utilizing vapor transport techniques (10). A Mellen Model 5-210-2 two-zone furnace fitted with a 1.5-in. mullite tube was used, and the temperature was maintained within  $\pm 3^\circ\text{C}$  by dual temperature controllers. Anhydrous  $\text{FeCl}_3$  (3.3 g) and 3.0 g  $\text{Fe}_2\text{O}_3$  were transferred to a Pyrex ampoule 20 cm long  $\times$  20 mm o.d. in a  $\text{N}_2$  purged dry box. The ampoule was evacuated on a vacuum line for approximately 2 hr, sealed, and slowly heated in the furnace to a temperature gradient of 405/315°C, which was maintained for 4 days. After cooling, the ampoule was opened in the dry box and the sample was removed and rinsed with dry ethanol. The yield was about 50%. The lattice parameters determined from Debye–Scherrer powder patterns were  $a = 378.5$  pm,  $b = 790.9$  pm, and  $c = 330.6$  pm.

The structure of FeOCl was first determined by Goldsztaub in 1934 (11). A further refinement by Lind in 1970 confirmed this

work (12). FeOCl crystallizes in the orthorhombic space group  $Pmnm$ . Similar to  $\gamma$ -FeOOH, the structure is characterized by layers of distorted and edge-sharing octahedra. The interlayer  $\text{Cl}^-$ - $\text{Cl}^-$  distance of 3.67 Å is about twice the van der Waals radius of chlorine, and thus is consistent with the layered nature of the compound.

### Previous Work

The temperature dependence of the susceptibility of microcrystalline (powder) FeOCl has been reported in two earlier papers (1, 2). In the study by Bizette and Adam (1), the behavior observed was that characteristic of a Curie-Weiss antiferromagnet, with a large anomaly at 22 K. In the more recent investigation by Halbert *et al.* (2), the susceptibility displayed a small cusp at 15 K and a broad maximum at approximately 350 K. The broad maximum in the susceptibility is characteristic of quasi-two-dimensional antiferromagnetism. Further work in this laboratory on microcrystalline powder samples essentially reproduced the latter of the two experiments. Thus, these two papers both reported an anomaly at approximately  $18 \pm 3$  K, but the character of the anomaly was basically different. Furthermore, in both cases, no discontinuity was observed at  $T_N = 91 \pm 2$  K, the Néel temperature consistent with both Mössbauer spectroscopy (5, 7) and neutron diffraction (4) experiments. The two powder experiments also differed in the temperature of  $x_{\text{max}}$ . In the earlier work, the  $x_{\text{max}}$  occurred at  $\approx 21$  K, while in the subsequent paper  $x_{\text{max}}$  was observed at  $\approx 350$  K. There was agreement in the two experiments, however, on the value of the susceptibility at 300 K.

### Experimental

The susceptibility measurements were performed on an S.H.E. SQUID magne-

tometer at the MIT Francis Bitter National Magnet Lab. The two largest crystals which had been synthesized were used, each of them approximately  $12 \times 6 \times 0.1$  mm and together weighing 13.28 mg. The crystals were cut in half and placed on top of each other so that the final size was approximately  $6 \times 6 \times 0.2$  mm. The sample was wrapped in plastic yellow tape and suspended by a thin copper wire from the metal ribbon of the SQUID magnetometer. The field was parallel to the  $c$ -axis of the crystal and the applied field was 10.00 kG.

The field dependence of the magnetization was studied at 300, 100, and 10 K, in order to determine the level of ferromagnetic impurities present in the sample. At each temperature, the zero field magnetization was less than 1% of the magnetization at 10.00 kG. Therefore, it was not necessary to correct the data for the small amount of ferromagnetic impurities present.

### Discussion and Results

In the present work, the range of susceptibility measurements was extended to 400 K, higher than that in any previous experiment. The susceptibility slowly increased to a broad maximum at  $310 \pm 10$  K (see Fig. 1). A discontinuity in the  $d(\chi T)/dT$  curve was observed at  $84 \pm 1$  K (see Fig. 1). Therefore, for the first time magnetic susceptibility measurements have been able to support evidence for a magnetic ordering temperature in FeOCl consistent with the Mössbauer and neutron diffraction experiments.

$T_N$  has been determined previously by powder neutron diffraction by following the intensity of the strongest magnetic reflection as a function of temperature. The value published is  $89 \pm 4$  K (4). The temperature as determined by Mössbauer spectroscopy is  $92 \pm 3$  K (6, 5). The result of the present susceptibility measurements is  $84 \pm 1$  K.

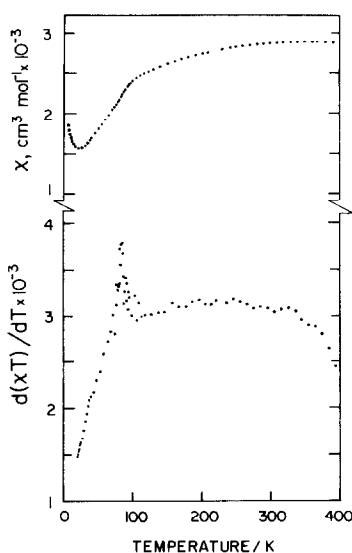


Fig. 1. Magnetic susceptibility of FeOCl (above) and FeOCl  $d(\chi T)/dT$  (below).

Thus, the temperatures determined by the resonance techniques are about  $7^\circ$  higher than the temperature determined by the magnetic susceptibility measurements. This discrepancy is probably due to magnetic relaxation.

No anomaly was observed at temperatures lower than  $84 \pm 1$  K. Thus, in the sample where the transition at 84 K was observed, no anomaly was seen at  $\approx 18$  K. The fact that the anomaly at  $\approx 18$  K is sample dependent is a very strong indication that an impurity is responsible for this behavior. It is likely, then, that the impurity masked the transition at 84 K in the previous susceptibility measurements of FeOCl. In all other respects, this experiment confirms the general character of the suscepti-

bility which was determined previously by Halbert *et al.* (2).

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