

**Magnetoelastic coupling in the incommensurate antiferromagnetic phase of FeOCl**

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The antiferromagnetic phase transition of FeOCl has been studied by temperature-dependent x-ray-diffraction experiments, magnetic susceptibility, heat capacity, and dielectric measurements. The magnetic phase transition is found to be accompanied by a monoclinic lattice distortion, affecting the angle  $\gamma$  between crystallographic axes parallel to the layers comprising the quasi-two-dimensional magnetic system. The temperature-dependent magnitude of  $\gamma$  shows the phase transition to be of second order. Satellite reflections occur in x-ray diffraction with twice the magnetic modulation wave vector. These positions are temperature dependent, providing evidence for an incommensurate character of the magnetic order. The observed Néel temperature is  $T_N = 81.0(2)$  K.

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**I. INTRODUCTION**

Layered compounds MOCl ( $M = \text{Ti, Cr, V, and Fe}$ ) have recently been studied because of their low-dimensional magnetic properties.<sup>1-3</sup> Different magnetic behaviors of these isostructural compounds have their origins in orbital order of the various number of 3d electrons of the  $M^{3+}$  ions.<sup>2,4-7</sup>  $\text{Ti}^{3+}$  possesses a single 3d electron. Orbital order makes TiOCl a quasi-one-dimensional magnetic system, which develops a spin-Peierls state at low temperatures.<sup>1-3</sup> The other compounds have transition-metal ions with two or more 3d electrons. They form two-dimensional magnetic systems and exhibit antiferromagnetic order at low temperatures.<sup>8-10</sup>

Magnetic order is geometrically frustrated on the arrangement of  $M^{3+}$  ions within the orthorhombic crystal structure of MOCl. Accordingly, the low-temperature phases of TiOCl have been found to be monoclinic.<sup>3,4,11</sup> Despite earlier reports of magnetic order with orthorhombic symmetry,<sup>9,10</sup> VOCl has a twofold magnetic superstructure with monoclinic symmetry and strong magnetoelastic coupling as expressed by a monoclinic angle of  $\gamma = 90.211$  deg and  $T_N = 80.3$  K.<sup>12,13</sup> CrOCl has a fourfold magnetic superstructure, which is again monoclinic, but with an apparently less strong magnetoelastic coupling than in VOCl, as expressed by a significantly smaller monoclinic angle of  $\alpha = 90.071$  deg and  $T_N = 13.5$  K.<sup>14</sup>

FeOCl was the first compound to be synthesized among the MOCl compounds.<sup>15</sup> The antiferromagnetic phase transition was discovered in 1971 by Mössbauer spectroscopy and since then has been characterized by several other techniques (Table I). Values between 80 and 92 K have been reported for the Néel temperature. Neutron powder diffraction has shown the appearance of incommensurate superlattice reflections with an incommensurate magnetic modulation wave vector of  $\mathbf{q}_M = (0.5, 0.275, 0.5)$  at  $T = 4.4$  K.<sup>8</sup> More recent work has suggested a commensurate modulation wave vector of  $(0.5, \frac{2}{7}, 0.5)$ .<sup>18</sup> Models for the magnetic superstructure were proposed, that are based on the assumption of orthorhombic symmetry of the crystal structure.<sup>8,18</sup>

Here, we present the results of temperature-dependent single-crystal x-ray diffraction, which show that the magnetic phase transition of FeOCl is accompanied by the development

of a monoclinic lattice distortion at low temperatures. This finding puts the magnetic order in FeOCl on equal footing with that in the other MOCl compounds. We furthermore present the temperature dependencies of the specific heat, the anisotropic magnetic susceptibility, and the dielectric properties. These investigations evidence a second-order phase transition and provide a consistent value of the Néel temperature of 82.0(2) K (Table I).

**II. EXPERIMENTAL****A. Crystal growth**

Thin platelet single crystals of FeOCl were grown by vapor phase transport in evacuated quartz-glass ampoules according to procedures described elsewhere.<sup>20</sup> Starting materials were a stoichiometric mixture of  $\text{Fe}_2\text{O}_3$  (purity 99.999%) and  $\text{FeCl}_3$  (Purity 99.99%). Small single crystals were selected for x-ray-diffraction experiments and larger single crystals were used for the measurements of the magnetic, dielectric, and thermal properties.

**B. Magnetic and thermal measurements**

The magnetic susceptibilities of two crystals of mass 0.510 and 1.3 mg, selected from batch 1 and 2, respectively, were measured in a Quantum Design Magnetic Property Measurement System (MPMS) between 3 and 300 K in magnetic fields between 0.1 and 7 T. The magnetic fields were applied along the  $\mathbf{c}$  direction, which is perpendicular to the surface of the platelike crystals, and in the  $\mathbf{a-b}$  plane, respectively [Figs. 1(a) and 1(b)].

The same crystals were subsequently used for measurements of the heat capacity, using a Quantum Design physical properties measurement system employing the relaxation method. The crystals were attached with a minute amount of Apiezon N grease to the platform. To enable a reliable correction for the heat capacities of the empty sample platform and the Apiezon grease their heat capacities had been determined in preceding empty runs and were subsequently subtracted from the total heat capacities in order to obtain the samples' heat capacities [Fig. 1(c)].

TABLE I. Transition temperature  $T_N$  of FeOCl.

Method	$T_N$ (K)	Reference
Mössbauer spectroscopy	92 (3)	Grant (1971) <sup>16</sup>
Neutron diffraction	89 (4)	Adam and Buisson (1975) <sup>8</sup>
Magnetic susceptibility	84 (1)	Bannwart <i>et al.</i> (1987) <sup>17</sup>
Neutron diffraction	~80	Hwang <i>et al.</i> (2000) <sup>18</sup>
Mössbauer spectroscopy	85 (1)	Dai <i>et al.</i> (2002) <sup>19</sup>
Magnetic susceptibility	~82	This work
Heat capacity	82.1 (2)	This work
X-ray diffraction	77.4 (1.7)	This work

The dielectric capacitances at 1 kHz of the samples were measured as a function of temperature with an Andeen and Hagerling 2500A ultraprecision capacitance bridge with an excitation voltage of 0.75 V [Fig. 1(d)]. Thin (~0.1 mm) optically perfect crystals with large lateral extension (several mm<sup>2</sup>) were selected from batch 1 and electrodes were affixed by using a silver conductive paint to either side of the crystal plates.

Antiferromagnetic ordering below ~82 K with the *c* axis as easy axis is indicated by the magnetic susceptibility and the heat capacity. The latter show small  $\lambda$ -type anomalies at 81.6(2) and 82.6(2) K for the crystals taken from batch 1 and 2, respectively. The entropy contained in the anomaly amounts to ~0.12 J/mol K, which covers only about 1% of  $R \ln(2 \times 5/2 + 1)$  expected for the ordering of a  $S = 5/2$  spin system. The anomaly of the sample taken from the second batch is somewhat smaller and slightly broadened as compared to that of the crystal taken from the first batch. The magnetic susceptibility shows a broad hump with its maximum occurring at ~350 K, indicating pronounced short-range ordering characteristic for a low-dimensional antiferromagnetic system. Antiferromagnetic ordering is not reflected in the dielectric constant, which monotonously drops starting from a room temperature value of about 35. A broad bump centered at about 150 K precedes antiferromagnetic long-range ordering. Slight wiggles are seen in the temperature derivative of  $\epsilon_{rel}$ , but no distinct anomaly is detected.

### C. Single-crystal x-ray diffraction

Single-crystal x-ray diffraction was measured at beamline D3 of HasyLab at Deutsches Elektronen-Synchrotron (Hamburg, Germany), employing synchrotron radiation of a wavelength of 0.5600 Å. Two crystals were selected for diffraction experiments. They were glued to carbon fibers and mounted on a closed-cycle helium cryostat on the Huber four-circle diffractometer at beamline D3. Crystal A was of dimensions 0.25 × 0.13 × 0.005 mm<sup>3</sup>, and crystal B was of dimensions 0.1 × 0.06 × 0.005 mm<sup>3</sup>.

At each selected temperature the setting angles of 18 reflections were determined, from which the lattice parameters were calculated. For crystal A at room temperature, values of  $a = 3.7773(6)$ ,  $b = 3.3046(7)$ , and  $c = 7.9156(16)$  Å were obtained for the orthorhombic lattice parameters, in agreement with the lattice of FeOCl.<sup>15,21</sup> Similar results were obtained for crystal B. In this setting with space group  $Pm\bar{m}n$ , layers FeOCl are stacked along *c* (Fig. 2).

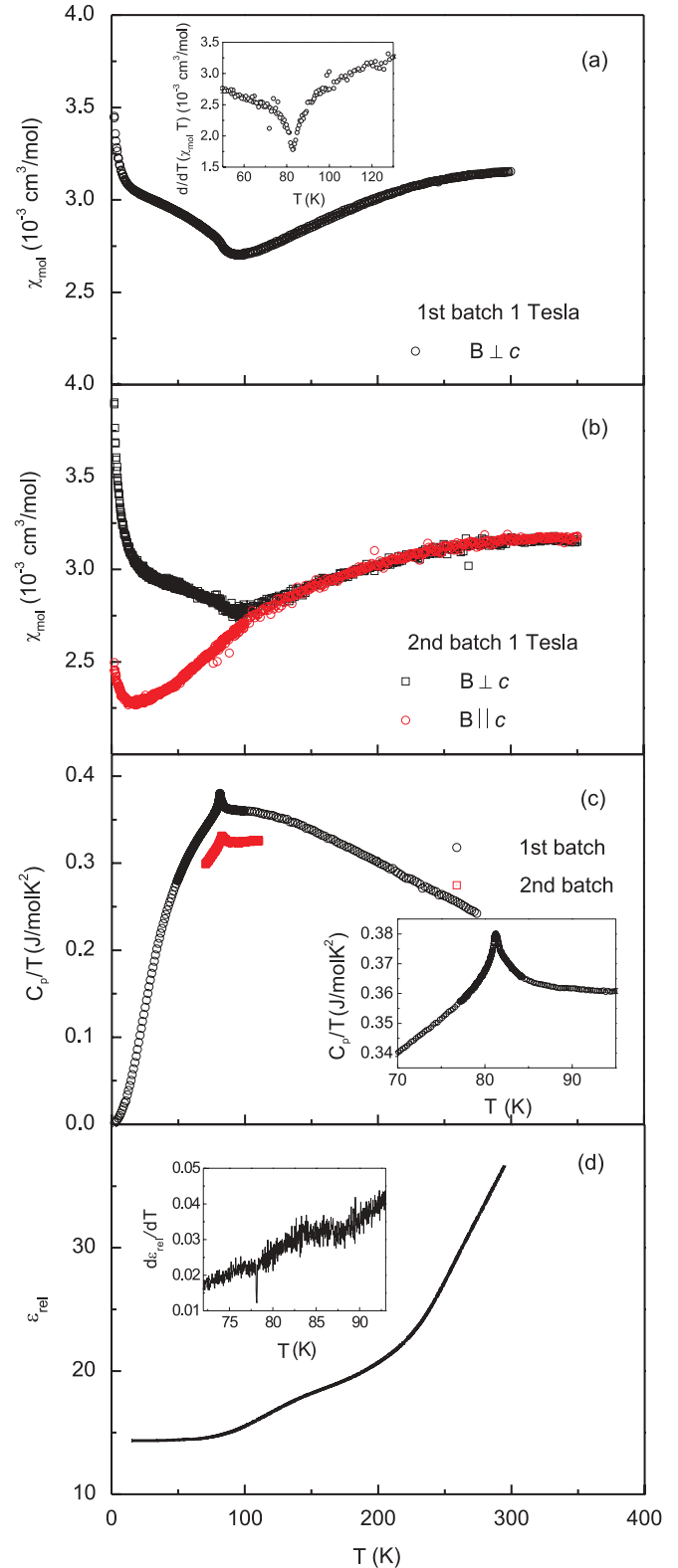


FIG. 1. (Color online) (a) Magnetic susceptibility of a crystal of FeOCl from batch 1. Inset: Derivative with respect to temperature of the quantity  $\chi_{mol} \times T$ . (b) Magnetic susceptibility of a crystal of FeOCl from batch 2. (c) Heat capacities of the same crystals measured in zero external magnetic field. Inset: Enlargement of the temperature range where a  $\lambda$ -type anomaly is seen. (d) Relative dielectric constant of FeOCl at 1 kHz measured perpendicular to the crystal plate.

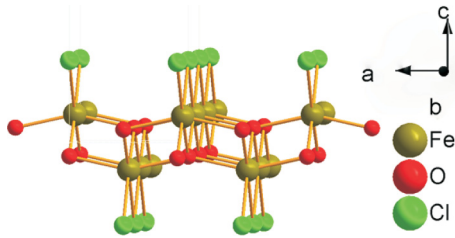


FIG. 2. (Color online) The crystal structure of FeOCl.

Possible lattice distortions can be obtained from peak splittings in the direction of the scattering angle  $2\theta$ . A splitting of  $(h k 0)$  would indicate a deviation from 90 deg of the angle  $\gamma$ . Splittings of  $(h 0 l)$  and  $(0 k l)$  allow the angles  $\beta$  and  $\alpha$ , respectively, to be calculated. Accordingly,  $\omega$ - $2\theta$  maps have been measured on both crystals at selected temperatures for the reflections  $(2 2 0)$ ,  $(2 0 \bar{4})$ , and  $(0 2 \bar{5})$ . Detector slits were set to  $6 \times 0.02 \text{ mm}^2$ , which corresponds to an acceptance angle of 0.0031 deg in the direction of  $2\theta$ . Step sizes of 0.002 deg were chosen for both the directions  $\omega$  and  $2\theta$ .

$\omega$ - $2\theta$  maps of the  $(2 2 0)$  reflection show single peaks at temperatures above  $T_N$ , while they show a double peak for  $T < 75 \text{ K}$  (Fig. 3). The reflections  $(2 0 \bar{4})$  and  $(0 2 \bar{4})$  do not exhibit peak splittings at any temperature, although they do have a broadened appearance into the direction of  $\omega$  at low temperatures [data not shown; compare to Fig. 3(d)]. Broadening into the direction of  $\omega$  may be explained by internal strain due to the phase transition as well as by damage to the crystal originating in external strain due to different thermal expansions of sample and glue. These results show that the lattice of FeOCl is  $c$ -unique monoclinic in the antiferromagnetic phase.

The magnitude of the splitting in  $2\theta$  can be obtained from the  $2\theta$  dependence of the diffracted intensity that is obtained by collecting all intensity measured at a single value of  $2\theta$  (integration over  $\omega$ ). The plot of the diffracted intensity vs  $2\theta$  at  $T = 145 \text{ K}$  reveals that crystal A consists of two domains with orientations differing by a few hundredths of a degree, while crystal B was of much better quality [Figs. 4(a) and

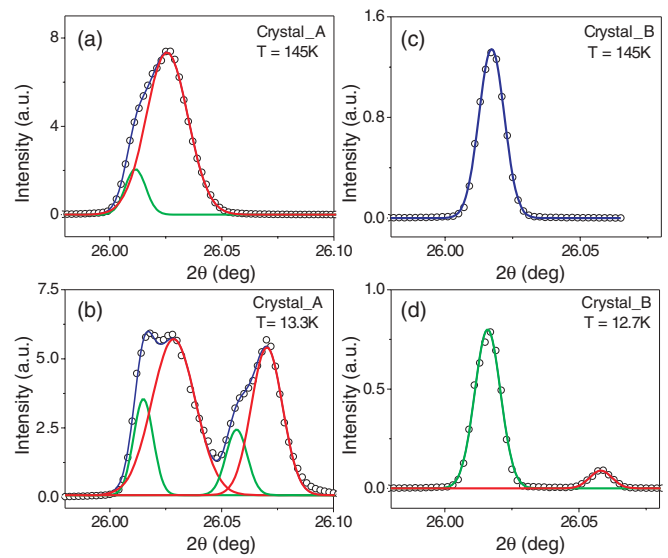


FIG. 4. (Color online) Diffracted intensity as a function of the scattering angle  $2\theta$  for the reflection  $(2 2 0)$  for both crystals at different temperatures. All peaks were fitted by Gauss functions.

4(c)]. The broadened peak of crystal A is well described by two overlapping Gaussian functions, while the peak of crystal B can be fitted with a single Gaussian. At low temperatures, crystal A displays two broadened peaks of similar intensities for  $(2 2 0)$ , while crystal B exhibits two peaks of different intensities [Figs. 4(b) and 4(d)]. These results indicate that crystal A consisted of two monoclinic domains of comparable volumes, while crystal B was almost a single domain crystal.

The peak splitting depends on temperature and it was too small to be determined close to  $T_N$ . The peak splitting in  $2\theta$  of  $(2 2 0)$  directly gives the angle  $\gamma$  of the monoclinic lattice. We have obtained peak splittings at six temperatures for crystal A and at two temperatures for crystal B. Limited beam time at the synchrotron did not allow experiments at more temperatures on crystal B. Nevertheless, the monoclinic angles for crystals A and B match very well (Fig. 5). The deviation from 90 deg of the monoclinic angle can be considered as the order parameter,

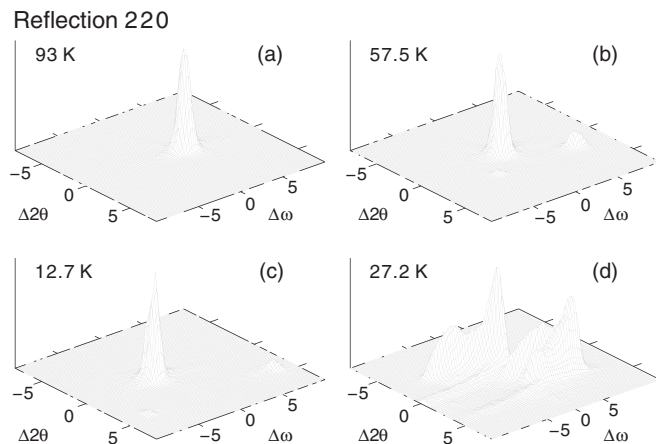


FIG. 3. Diffracted intensity as a function of the scattering angle  $2\theta$  and the crystal orientation  $\omega$  for reflection  $(2 2 0)$  of crystal A (d) and crystal B (a–c) at selected temperatures.  $\Delta 2\theta$  and  $\Delta\omega$  indicate the deviation from the center of the scan in units of 0.01 deg.

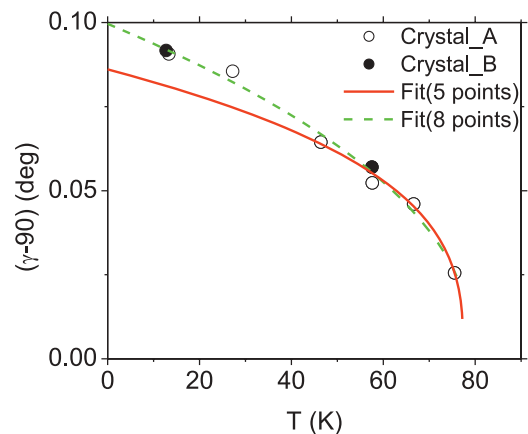


FIG. 5. (Color online) Temperature dependence of the monoclinic angle  $\gamma$ . The (red) solid line represents a fit of Eq. (1) to the five data points at  $T > 40 \text{ K}$ . The (green) dashed line is a fit to all eight data points.

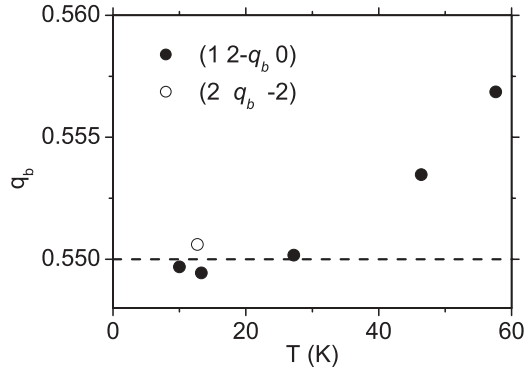


FIG. 6. Incommensurate component  $q_b$  of the modulation wave vector  $\mathbf{q}_X = (0, q_b, 0)$ , as determined by  $\mathbf{q}$  scans along  $\mathbf{b}^*$ . The dashed line indicates value  $0.550 = 2 \times 0.275$ .

and the temperature dependence of its value can be described by the function

$$\gamma - 90 \text{ deg} = \Delta\gamma_0 \left(1 - \frac{T}{T_N(\text{x ray})}\right)^\beta. \quad (1)$$

Critical behavior according to Eq. (1) is only expected close to  $T_N$ . An excellent fit of Eq. (1) to the five data points at  $T > 40$  K has been obtained (Fig. 5), resulting in an estimate for the transition temperature of  $T_N(\text{x ray}) = 77.4(1.7)$  K and a critical exponent of  $\beta = 0.32(9)$ . The latter value is close to the critical exponent of the three-dimensional Ising model, but the large standard uncertainty prevents a meaningful interpretation of this parameter.

The fitted function clearly underestimates the values of  $\gamma$  at low temperatures, thus demonstrating deviations from critical behavior below  $T \approx 40$  K. A fit of reasonable quality has also been obtained for all eight data points (dashed line in Fig. 5). This fit resulted in somewhat different values for the two fit parameters,  $T'_N(\text{x ray}) = 79.8(2.0)$  K and  $\beta' = 0.46(5)$ . The second fit function allows the determination of the extrapolated value of the monoclinic angle at  $T = 0$  K as  $\gamma_0 = 90.100$  deg.

In another experiment superlattice reflections were searched by  $\mathbf{q}$  scans along  $\mathbf{b}^*$  for selected reflection pairs  $(h k l) \rightarrow (h k + 1 l)$ . A total of 43  $\mathbf{q}$  scans were measured on crystal A at temperatures of 10 and 13.3 K. Superlattice reflections were found in two scans, at  $(1 \ 1.45 \ 0)$  (weak) and at  $(2 \ 0.55 \ -2)$  (very weak). The values of the component  $q_b$  as obtained from the two reflections are in agreement with each other (Fig. 6). The strong satellite reflection could be measured at selected temperatures up to 58 K. The results of the  $\mathbf{q}$  scans show that the length of the incommensurate modulation wave vector depends on temperature.

### III. DISCUSSION

The crystals of FeOCl presently studied undergo an antiferromagnetic phase transition as evidenced by the temperature dependence of the magnetic susceptibility (Fig. 1), in agreement with the literature.<sup>17</sup> The ordered magnetic moments possess a component along  $\mathbf{c}$ , but it cannot be excluded that there also is a component along  $\mathbf{b}$ .<sup>8</sup>

Values for the Néel temperature have been reported between 80 and 92 K (Table I). We have obtained a consistent value of  $T_N = 82.0(2)$  K from the temperature dependencies of x-ray diffraction, specific heat, and magnetic susceptibility. This value is in accordance with the more recent values in the literature and thus will be close to the true transition temperature of pure FeOCl.

The major finding of the present experiments is the monoclinic lattice distortion, whose development accompanies the magnetic transition (Fig. 5). The thermal evolution of the monoclinic angle indicates the second-order character of the phase transition, and extrapolation of the measured values allows an accurate estimate of the Néel temperature (Table I). The value of  $\gamma = 90.10$  deg at low temperatures suggests strong magnetoelastic coupling, in agreement with the observations on VOCl and CrOCl.<sup>12–14</sup> Satellite reflections in x-ray diffraction are much weaker for FeOCl than for CrOCl or TiOCl, indicating that relative atomic coordinates deviate from their orthorhombic values by a small amount only, and that the major structural distortion is the monoclinic lattice distortion.

Another point of debate was the precise value of the modulation wave vector of the magnetic superstructure. For a structure with antiferromagnetic order described by modulation wave vector  $\mathbf{q}_M$  one can expect a structural distortion with modulation wave vector  $2\mathbf{q}_M$ , which may give rise to satellite reflections in x-ray diffraction.<sup>22</sup> Since  $2 \times 0.5 = 1$ , we have here employed  $\mathbf{q}_X = 2\mathbf{q}_M - \mathbf{a}^* - \mathbf{c}^* = (0, q_b, 0)$ .

Below  $T \approx 30$  K we have found that the incommensurate component of  $\mathbf{q}_X$  is equal to 0.550 (Fig. 6). This value is exactly two times the value of 0.275 as reported for  $\mathbf{q}_M$  at  $T = 4.2$  K, and the present x-ray-diffraction experiment confirms the observations by neutron diffraction by Adam and Buisson.<sup>8</sup> Above 40 K the modulation wave vector depends on temperature, proving that the modulation is incommensurate. Hwang *et al.*<sup>18</sup> proposed a commensurate magnetic modulation wave vector of  $2/7$ . The value of  $2 \times 2/7 = 0.5714$  is not observed at any temperature.

The present results open the possibility of a lock-in transition with a transition temperature between 30 and 45 K, at which the magnetic modulation wave vector attains the value of  $0.275 = 11/40$ . However, none of the other experiments show evidence for an additional phase transition at these temperatures.

### IV. CONCLUSIONS

X-ray diffraction has shown that the antiferromagnetic phase transition of FeOCl is accompanied by a monoclinic lattice distortion, in agreement with the distortions observed for CrOCl and VOCl. The need for this distortion lies in the perfect frustration for antiferromagnetic order of the arrangement of magnetic  $M^{3+}$  ions on the orthorhombic lattice. The temperature dependence of the magnitude of the monoclinic angle has shown that the phase transition is a second-order phase transition.

The magnetic superstructure has been found to be incommensurate as evidenced by the temperature dependence of the positions of satellite reflections in x-ray diffraction at  $\mathbf{q}_X = 2\mathbf{q}_M$ .



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