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## LETTER TO THE EDITOR

# The coexistence of magnetic phases at the first-order phase transition of a metamagnet FeCl$_2$·2H$_2$O studied by x-ray diffraction

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**Abstract**
The results of non-resonant magnetic x-ray diffraction measurements of the metamagnet FeCl$_2$·2H$_2$O subjected to an applied magnetic field, $H$, are reported. The material shows two successive first-order phase transitions: at $H_{c1} = 3.62$ T from the antiferromagnetic (AF) to intermediate (I) phases, and at $H_{c2} = 4.67$ T from phase I to a ferromagnetic phase at low temperatures. We find that the AF and I phases coexist over a wide range of $H$ below $H_{c1}$, when $H$ is decreased from the I phase. We were able to follow the evolution of the AF and I domains with the change of $H$. The coexistence appears not to come from demagnetizing effects, and instead reflects the intrinsic nature of the material.

The study of first-order phase transitions is a central subject in condensed matter research. A first-order phase transition in solids is characterized by the coexistence of two homogeneous phases. A metastable state appears when the canonical external parameter is changed rapidly. Examples of first-order phase transitions in magnetic systems can be found in several antiferromagnets with strong uniaxial anisotropy, named metamagnets [1]. When an external magnetic field, $H$, is applied along the anisotropy axis, the bulk magnetization, $M$, at low temperatures, shows a jump at a critical field denoted here by $H_c$. In some metamagnets, such as MCl$_2$·2H$_2$O (M = Fe, Co, and Ni), two successive first-order phase transitions occur as a function of the applied magnetic field [2].

A standard method to observe the coexistence of the magnetic phases is the use of an optical microscope [3]. This technique gives a direct image of domain distributions in the sample with a spatial resolution of $\sim\mu$m. A more sophisticated technique using a micro superconducting quantum interference device, or a micro Hall probe, would give better resolution. To the best

of our knowledge, such a high resolution measurement has not been done yet in the study of the first-order phase transition in magnetic systems. Only diffraction measurements, either with neutrons or x-rays, can give information on the magnetic structures of the coexisting phases. In this letter, we report the results of magnetic x-ray diffraction studies of a coexistence and metastability at the first-order transition in a metamagnet. In some metamagnets, such as anhydrous $FeCl_2$, a coexistence of antiferromagnetic (AF) and ferromagnetic (F) phases has been observed near $H_c$, due to the demagnetizing field [1]. In this case, the magnetization change becomes broad at around $H_c$, the width of which is determined by the shape of the sample. As will be shown, coexistence and metastability do not appear to come from demagnetization effects. We were able to observe a coexistence of two magnetic phases and their evolution over a wide range of magnetic field.

The material chosen for this study is $FeCl_2 \cdot 2H_2O$ (abbreviated to FC2 hereafter), which shows anomalous hysteretic behaviour in applied magnetic fields [4]. This compound has a monoclinic structure, with the lattice constants $a = 7.355$ Å, $b = 8.548$ Å, $c = 3.637$ Å and $\beta = 98.18°$ [5]. The crystal consists of $FeCl_2$ chains, running along the $c$ axis, which are linked together by hydrogen bonds. From susceptibility measurements, FC2 is antiferromagnetic below 23 K with the easy axis parallel to the $\alpha$ axis, which lies in the $ac$-plane and makes an angle of $32°$ with the $c$ axis [6]. When $H$ is applied parallel to the easy axis at low temperatures, a jump in $M$ occurs at $H_{c1} = 3.62$ T, followed by a second jump in $M$ at $H_{c2} = 4.67$ T [4]. A large hysteresis is observed at $H_{c1}$ even under a slowly varying field. The magnetic structures in zero and non-zero applied fields have been determined by neutron diffraction [7, 8]. Along the $c$ axis all the moments are aligned parallel, and so the magnetic structures in the respective phases may be described by an arrangement of the magnetic moments in the $ab$-plane. The arrangement of the moments projected onto the $ab$-plane is shown in figure 1 for the AF phase below $H_{c1}$ and the intermediate (I) phase at $H_{c1} < H < H_{c2}$. Phase I has a magnetization with one-third of the saturation magnetization. Above $H_{c2}$ the sample is in a saturated phase F.

Large single crystals of FC2 (about 5 mm $\times$ 5 mm $\times$ 20 mm) were grown from a solution. We measured the heat capacity of a single crystal of FC2 using a Quantum Design Physical Property Measurement System. The heat capacity shows a peak at 21.5 K in zero field associated with the magnetic ordering. This value of antiferromagnetic ordering temperature, $T_N$, is somewhat lower than that reported before [6]. As discussed by Fisher [9], the magnetic heat capacity, $C_m$, of an antiferromagnet with short-range interaction is related to the magnetic susceptibility, $\chi$, as $C_m \cong A\partial(\chi \times T)/\partial T$, where, $A$ is a constant and $T$ is the temperature. $T_N$ defined as the peak position in $\chi(T)$ is higher than that obtained from $C_m(T)$.

Non-resonant magnetic x-ray Bragg diffraction measurements were performed on the same crystal at the beam line BL19LXU [10] on the third-generation synchrotron SPring-8. This beam line is equipped with a 27 m undulator [11] so that the intensity of the x-rays is five times stronger than any other beam line at SPring-8. Primary x-rays had an energy $= 30$ keV. An avalanche photo diode (APD) was used as a detector. The slit aperture was limited to 1.0 mm $\times$ 0.5 mm in size. This setup gives a resolution of $\sim 0.017$ reciprocal lattice units (rlu). Magnetic fields at the sample position up to 8 T were generated by a superconducting magnet manufactured by Oxford Instruments, UK. A variable temperature insert generates temperatures down to 1.7 K at the sample position. A needle-shaped single crystal of FC2 with of size about 0.3 mm $\times$ 1 mm $\times$ 10 mm was mounted with the $c$ axis vertical and $H$ parallel to $c$. In this configuration, the critical fields are a factor 1.18 ($= 1/\cos 32°$) larger than those along the easy axis $\alpha$.

Figure 2 shows profiles of diffraction at the charge $(2, 0, 0)$ and antiferromagnetic $(3, 0, 0)$ Bragg reflections measured at 5 K and in zero magnetic field. The mosaic spread of the crystal was about $0.02°$ at full width at half maximum (FWHM) measured at the $(2, 0, 0)$ reflection.
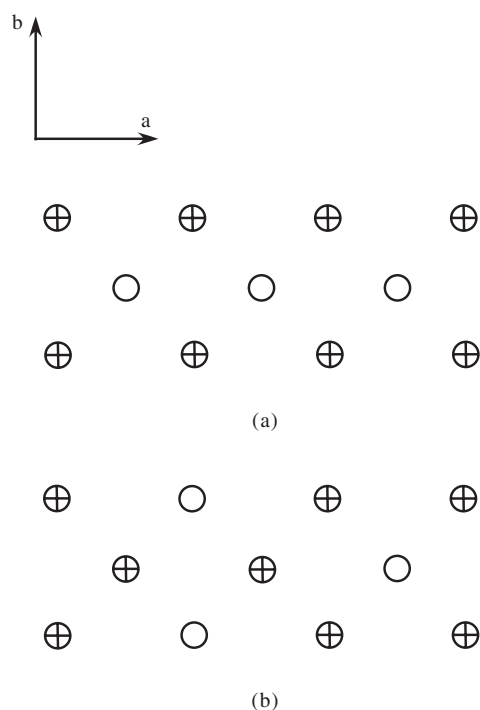
Figure 1. The arrangement of the magnetic moments projected onto the $ab$-plane of $FeCl_2 \cdot 2H_2O$ in the (a) antiferromagnetic and (b) intermediate phases. Here $\oplus$ and $\bigcirc$ mean magnetic moments point parallel and antiparallel to the $\alpha$ axis, respectively. The external magnetic field is assumed to be parallel to the $\alpha$ axis.
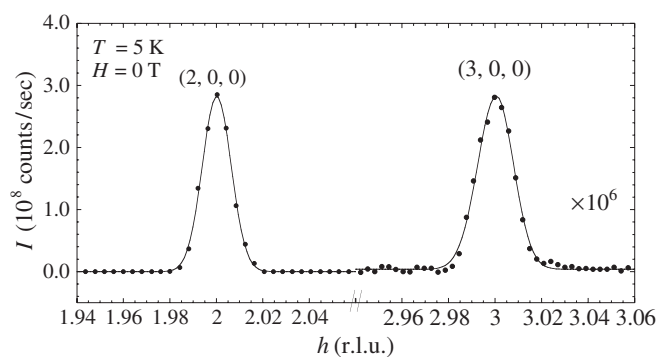


Figure 2. The measured scan profiles of the (2, 0, 0) and (3, 0, 0) reflections in zero field at 5 K. The intensity at (2, 0, 0) is decreased by a factor $\sim 400$ using an attenuator.

We measured the temperature dependence of the (3, 0, 0) intensity and found that it became zero at $21 \pm 0.5$ K, in agreement with heat capacity measurements.

Figure 3 shows the magnetic field dependence of the integrated intensity at the (3, 0, 0) reflection. When $H$ is increased from zero, the intensity remains constant until $H_{c1}$ is approached. A sudden drop of the (3, 0, 0) intensity is observed at $H_{c1}$, signalling that the metamagnetic transition from the AF to I phase has occurred. A sudden drop in intensity
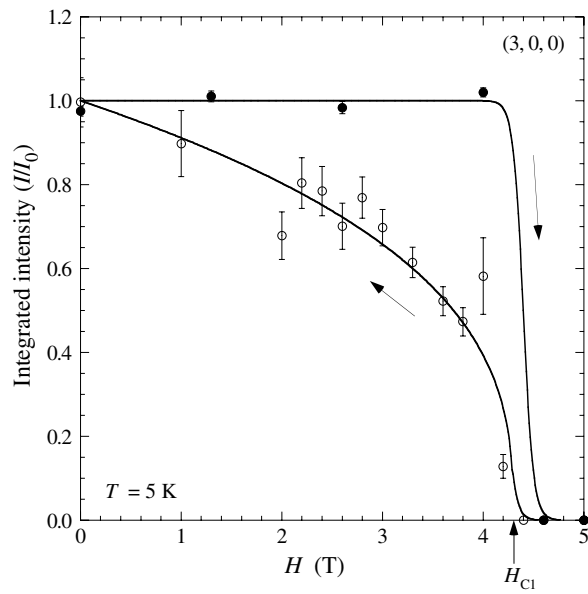
**Figure 3.** The magnetic field dependence of the integrated intensity at the (3, 0, 0) reflection at 5 K for increasing and decreasing field scans. The curves are drawn as guides to the eye.
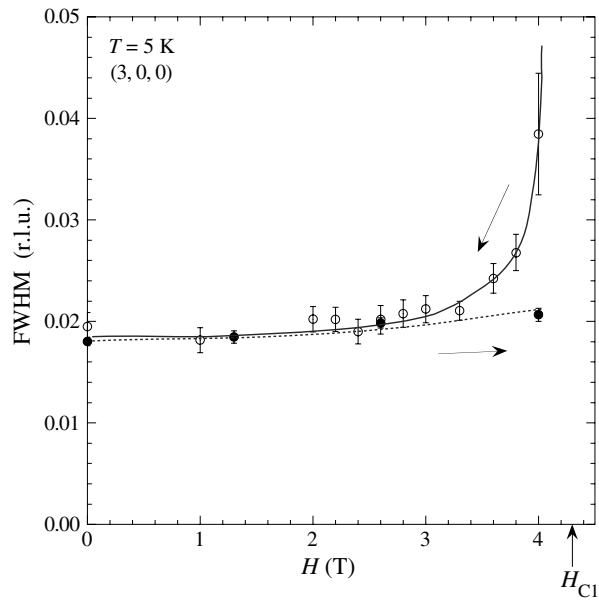


**Figure 4.** The magnetic field dependence of the full width at half maximum of the (3, 0, 0) reflection at 5 K for increasing and decreasing field scans. The curves are drawn as guides to the eye.

found at the spin-flop transition in $MnF_2$ has been analysed theoretically [12]. Since the orbital moment in FC2 is quenched [4], the analysis given in [12] applies to the present case as well. When $H$ is decreased from phase I, the (3, 0, 0) intensity increases gradually from $H_{c1}$ and continues to increase down to zero field. Figure 4 shows the FWHM of the (3, 0, 0) reflection.
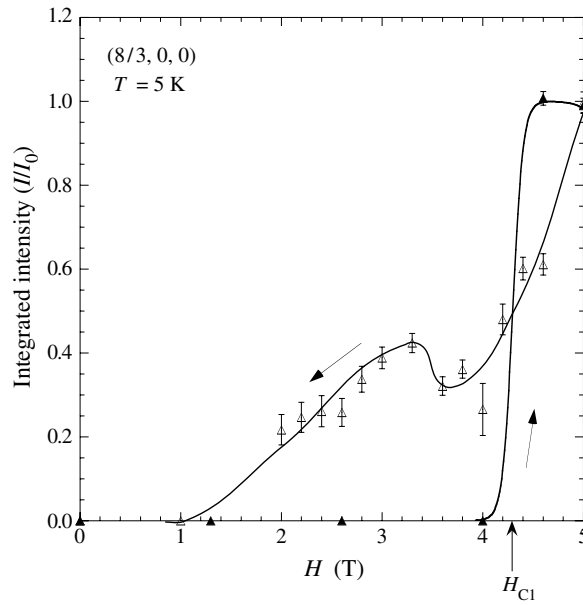
**Figure 5.** The magnetic field dependence of the integrated intensity at the $(\frac{8}{3}, 0, 0)$ reflection at 5 K for increasing and decreasing field scans. The curves are drawn as guides to the eye.

For an increasing field the AF correlation length is longer than the instrumental resolution up to $H_{c1}$, i.e. antiferromagnetic long-range order is established below $H_{c1}$. On the other hand, in a decreasing field from phase I, the correlation length of the AF state is $\sim$20 lattice spacings just below $H_{c1}$. Thereafter, the correlation length grows with decreasing $H$ until it becomes resolution limited.

Figure 5 shows the magnetic field dependence of the integrated intensity of the $(\frac{8}{3}, 0, 0)$ reflection, which represents phase I. On increasing the magnetic field from zero, the $(\frac{8}{3}, 0, 0)$ intensity stays zero until $H_{c1}$ is reached, where it increases abruptly. In a decreasing field and starting from phase I, the intensity decreases at a field above $H_{c1}$ and shows a peak at about 3.2 T. Figure 6 shows the FWHM of the $(\frac{8}{3}, 0, 0)$ reflection observed in a decreasing field from phase I. The FWHM has a minimum at about 4 T and a peak at about 3 T. Below 2.5 T the FWHM increases rapidly with decreasing $H$, indicating that the correlation length of the I domain becomes progressively shorter.

Our results presented in figures 3–6 give important information on the coexistence and metastability of magnetic phases at the first-order phase transition. We note that the phenomena we observed are intrinsic, and not from a demagnetizing effect, because the magnetization jump at $H_{c1}$ of FC2 is sharp above 2.5 K [4]. This is partly due to the orientation of the easy axis which is near the long axis (the $c$ axis) of the crystal. The origin of the anomalously large hysteresis in FC2 comes from a large single-ion anisotropy $D$ ($DS_z^2$; $D \simeq 10$ cm$^{-1}$ and $S = 2$) [4]. Tinkham studied the dynamics of the metamagnetic transition in a similar compound CoCl$_2 \cdot$2H$_2$O (CC2) theoretically [13]. The magnetic properties of CC2 are well described by an Ising model with $S = 1/2$. In this case, once a reversal of a Co$^{2+}$ spin in a chain occurs by a thermal activation, there is no cost in energy for the rest of the spins to flip at the critical fields. FC2 is fundamentally different from CC2 in that a reversal of every Fe$^{2+}$ spin needs to overcome the energy barrier due to the $D$ term. Note that there is no $D$ term for
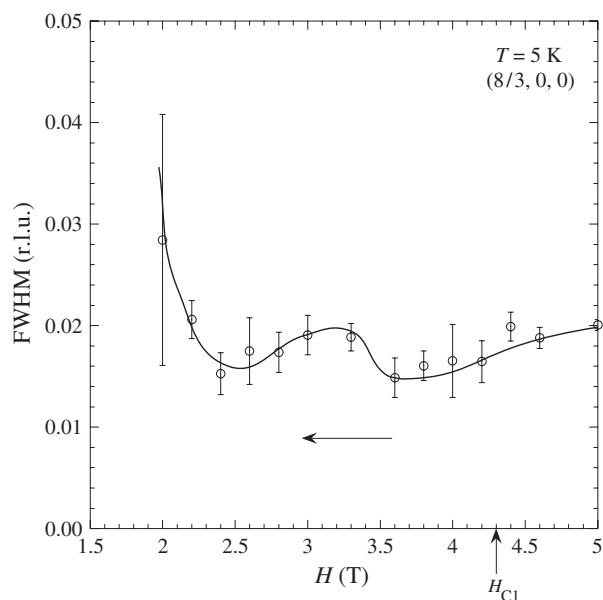
**Figure 6.** The magnetic field dependence of the full width at half maximum of the $(\frac{8}{3}, 0, 0)$ reflection at 5 K for a decreasing field scan. The curve is drawn as a guide to the eye.

the $S = 1/2$ system. It would be easy to imagine that the rearrangements of spins needed for the transition between the AF and I phases takes a long time (of the order of minutes). This is the reason why we were able to observe a coexistence of the I and AF phases over a large field range below $H_{c1}$ (figures 3 and 5). Concomitantly, the size of the AF region (more precisely the correlation length) grows with decreasing $H$ from phase I (figure 4) while that of the I region shrinks (figure 6).

As is seen from figures 3 and 5, the transition from AF to I phases in an increasing field is conventional; the $(3, 0, 0)$ intensity drops suddenly at $H_{c1}$ and conversely the $(\frac{8}{3}, 0, 0)$ intensity grows abruptly with a small coexistence region. In contrast, the transition from the I to AF phases in a decreasing field is anomalous; the $(\frac{8}{3}, 0, 0)$ intensity starts to decrease at a field above $H_{c1}$ and the I and AF phases coexist over a wide range of magnetic field. As reported in [4], a metastable (Met) state with a half of the saturation magnetization appears at the critical field denoted by $H_c'$ ($H_{c1} < H_c' < H_{c2}$) in an increasing field from the AF phase. The origin of the appearance of the Met state has been explained as follows. Since the rearrangement of the spins needed for the transition from the AF to I phases takes time, the AF phase remains as a metastable state above $H_{c1}$, even under a slowly varying field. At $H_c'$ the local field acting on the down spins in the AF phase is equal in magnitude and oppositely directed to the external field, and thus the resultant field at the down spins becomes zero, making the flip of the down spins easy. We have tried to observe the Met state by x-ray diffraction, but were not successful. This implies that the Met state is not long-range ordered. It might be that the size of the Met state is small and/or the number of domains is small. In a decreasing field from phase I, we expect that the Met state will remain in the sample. In a decreasing field, the up spins in the Met state can flip easily at $H_c'$ for the reason described above. This process transforms the Met domains into AF domains. Our data in figure 3 show that the intensity of the $(3, 0, 0)$ antiferromagnetic reflection begins to increase at $H_{c1}$, suggesting that the sizes of AF domains are so small that the $(3, 0, 0)$ reflection is not observed even in a high resolution measurement.

Nevertheless, the change of the Met domains to AF ones at $H'_c$ promotes rearrangements of spins at the boundaries between the Met and I domains. As a result, the total number of spins participating in phase I decreases, as figure 5 shows. With a further decrease in $H$, AF domains grow in size by eroding the I domains. Occasionally, the AF domains will come into contact and there will be rearrangements of spins at the boundaries. The peak observed in the magnetic field dependence of the $(\frac{8}{3}, 0, 0)$ intensity (figure 5) and the FWHM (figure 6) could be explained by this mechanism.

In summary, we have made non-resonant magnetic x-ray diffraction measurements on the metamagnet $FeCl_2 \cdot 2H_2O$ under applied magnetic field. We find that the AF and I phases coexist over a wide range of $H$ below $H_{c1}$, when $H$ is decreased from phase I. We were able to follow the evolution of AF and I domains with the change of $H$. This coexistence does not come from demagnetizing effects, but instead from the intrinsic nature of the material; namely, from the single-ion anisotropy which hampers the flipping of magnetic moments at the critical fields.

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