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LETTER TO THE EDITOR

Observation of field-induced magnetic and structural transitions in an antiferromagnet by means of synchrotron x-rays

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Abstract

In the first experiment of its kind, we have used x-ray diffraction to study magnetic and charge properties of an antiferromagnet as a function of an applied magnetic field $\boldsymbol{H}$. The intensity of hard x-rays diffracted at the space-group-forbidden reflection (3, 0, 0) of MnF_2 with $\boldsymbol{H}$ parallel to the easy axis at $H = H_c/\sqrt{2}$ shows evidence of a spin-flop transition associated with the surface magnetization, and at $H_c = 9.3$ T a spin-flop transition in the bulk. Above H_c we found intensity much larger than that predicted for purely magnetic scattering. We attribute the unexpected intensity to charge scattering created by a field-induced structural phase transition.

Historically, neutron diffraction has been the preferred experimental technique by which to establish magnetic structures and the configuration of moments in magnetically ordered materials. X-rays interact with the magnetic moments and so we can get information on the magnetic structure by means of x-ray diffraction. The contribution to the amplitude of x-rays diffracted by a magnetic material coming from spin and orbital moments is depressed relative to the charge contribution (Thomson scattering) by two factors. First, an explicit factor τ equal to the x-ray energy relative to the rest mass energy of an electron: 511 keV. Secondly, mean values of magnetic moments arise from the few unpaired electrons in the valence shell whereas

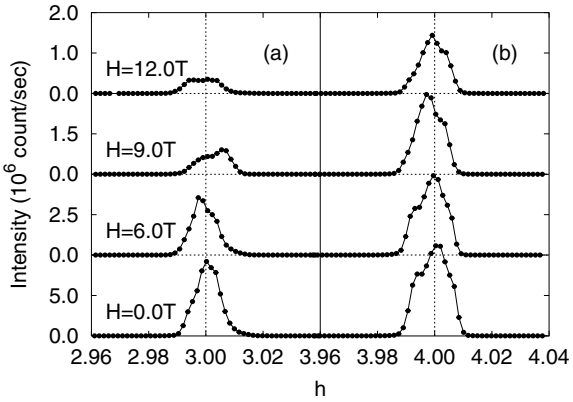

Figure 1. The measured scan profiles of the (a) (3, 0, 0) and (b) (4, 0, 0) reflections for some selected fields at 5 K. The intensity at (4, 0, 0) is decreased by $\sim 10^4$ using an attenuator.

Thomson scattering engages all electrons in the ion. In consequence, full realization of the potential benefits of magnetic x-ray diffraction demands the use of instruments operating at synchrotron facilities.

Let the Cartesian coordinates x, y lie in the plane of scattering, which contains the π-component of polarization. The applied magnetic field $\boldsymbol{H}$ and σ-component of polarization are along the z-axis normal to the plane. With this geometry and notation, the unit-cell intensity of primary π-polarized x-rays deflected through an angle θ is [1]

$$I = \{\cos^2\theta |F_c(\boldsymbol{k})|^2 + \tau \sin 2\theta \,\mathrm{Im}[(F_s^z(\boldsymbol{k})^* F_c(\boldsymbol{k})] + \tau^2 \sin^2\theta |F_s^z(\boldsymbol{k})|^2 + \tau^2(1-\cos\theta)^2 |F_s^x(\boldsymbol{k})\sin(\theta/2) + F_s^y(\boldsymbol{k})\cos(\theta/2)|^2\}, \quad (1)$$

where $F_c(\boldsymbol{k})$ is the charge structure factor, and $F_s^\alpha(\boldsymbol{k})$ ($\alpha = x, y, z$) is the spin structure factor. We omit the structure factor due to the orbital moment because it is expected to be very small for Mn^{2+} ($3d^5$). In addition, structure factors are here purely real and the second term in equation (1) is zero.

The x-ray diffraction experiment was performed at the beamline BL19LXU [2] on the third-generation synchrotron SPring-8. This beamline is equipped with a 25 m undulator [3], so the intensity of the x-rays is five times stronger than for any other beamline at SPring-8. We used x-rays with energy = 30 keV. An avalanche photo-diode (APD) was used as a detector. Magnetic fields up to 13 T (15 T at 2 K) were generated by a superconducting magnet manufactured by Oxford Instruments, UK. A variable-temperature insert generates temperatures down to 1.5 K at the sample position. The material MnF_2 chosen for this study has a rutile structure, and below 67.3 K Mn spin moments adopt a simple antiferromagnetic configuration with moments aligned with the tetragonal c-axis. In our experiment on a single crystal, $\boldsymbol{H}$ is applied along the easy axis.

Figure 1 shows profiles of diffraction in the magnetic (3, 0, 0) and charge (4, 0, 0) reflections for the designated magnetic fields. For (4, 0, 0), copper plates attenuated the x-ray beam by a factor $\sim 10^4$. We report a diffracted (3, 0, 0) intensity up on previous work by about four orders of magnitude [4, 5].

We show the magnetic field dependence of the integrated intensities in the (3, 0, 0) and (4, 0, 0) reflections in figure 2. The intensity at (4, 0, 0) first decreases with H up to about 1.5 T and does not depend much on H afterwards. We believe that this change in the (4, 0, 0) intensity is caused by a slight movement of the crystal in an applied field. Although changes in

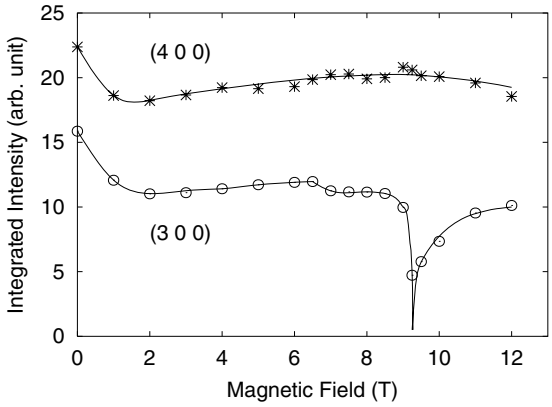

Figure 2. The integrated intensity of the (3, 0, 0) and (4, 0, 0) reflections as a function of applied magnetic field measured at 5 K. The integration was made on the data shown in figure 1 with each intensity normalized by 50 000 monitor counts. The uncertainty of the data is within the size of the circles. The solid curves are drawn as guides to eye.

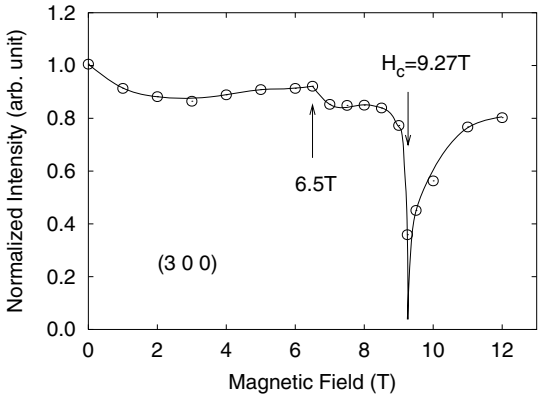

Figure 3. The magnetic field dependence of the (3, 0, 0) intensity at 5 K after being normalized with respect to that of the (4, 0, 0) one. The uncertainty of the data is within the size of the circles. The solid curve is drawn as a guide to the eye.

the intensity at the magnetic superlattice reflection (3, 0, 0) with H are visible in the raw data shown in figure 2, we plot in figure 3 the H-dependence of the (3, 0, 0) intensity normalized with respect to the (4, 0, 0) intensity, for clarity. With increasing field, one sees a small step at about 6.5 T followed by a steep decrease in intensity at about 9.3 T. Above 9.3 T the intensity begins to increase and recovers about the same intensity as observed in zero field.

In the remaining part of this letter we focus on the interpretation of the data displayed in figure 3. We will argue that the sudden change of intensity around 9.3 T reflects the spin-flop transition. First, this field coincides with the known value $H_c = 9.27$ T for the spin-flop transition obtained from a bulk measurement [6]. Secondly, a sudden change in the intensity is anticipated from equation (1). In the range $H < H_c$ spins point parallel or antiparallel to the c-axis. In this case, the intensity at the purely magnetic (3, 0, 0) reflection is

$$I = 4\tau^2 \sin^2\theta \langle S\rangle^2 \{f_s(\boldsymbol{k})\}^2, \tag{2}$$

where $\langle S\rangle$ is the sublattice moment, which does not change much with H at low temperatures, and $f_s(\boldsymbol{k})$ is the magnetic form factor. Above H_c, spins lie in the xy-plane, keeping an

antiferromagnetic arrangement. The field-induced ferromagnetism is proportional to $\sin\beta$ where β is the spin canting angle relative to the xy-plane. The intensity at (3, 0, 0) is then

$$I = 2\tau^2\langle S\rangle^2\{f_s(\boldsymbol{k})\}^2(1-\cos\theta)^2\cos^2\beta. \tag{3}$$

Here, we have averaged over all possible orientations of spins in the c-plane. From equations (2) and (3) the ratio of the (3, 0, 0) intensity immediately above and below H_c for the x-rays of 30 keV is 0.008. This explains the steep decrease of the (3, 0, 0) intensity on passing through 9.27 T.

Since β increases from 0 to $\pi/2$ with increasing $H > H_c$, equation (3) tells us that the (3, 0, 0) intensity gradually *decreases* with H, in contradiction with our data. A model consistent with our data involves a distortion of the rutile structure driven by magnetostriction. The distortion should break the extinction rule that forbids charge scattering at (3, 0, 0) in space group $P4_2/mnm$ (No 136 [7]). In looking for minimal models of the crystal distortion, we leave unchanged the body-centre relation of Mn ions, and break the tetragonal symmetry of rutile by allowing position parameters, u and u', different from the original $u_0 = 0.31$, for F ions in planes normal to the c-axis that pass through [0, 0, 0] and [0, 0, $\frac{1}{2}$]. The distorted structure belongs to space group $Cmmm$ (No 65 [7]). The structural phase transition that we invoke is ferroelastic and it is allowed to be continuous in Landau and renormalization-group theories. The charge structure factor for the (3, 0, 0) reflection from the distorted lattice is

$$F_c(\boldsymbol{k}) = -4f_c(\boldsymbol{k})\sin\{3\pi(u+u')\}\sin\{3\pi(u-u')\}. \tag{4}$$

We propose that this structure factor describes the intensity that continuously increases with H beyond H_c. In order to get an orientation to the magnitude achieved by $u-u'$ we equate the intensity of Thomson scattering from the distorted rutile structure to the magnetic scattering that occurs below H_c, which is roughly what is seen in our data in figure 3. We take $(u+u')/2 = 0.31$, $f_s(0) = 1$, $f_c(0) = 10$ and $\langle S\rangle = \frac{5}{2}$, and find $(u-u')/u_0 = 0.0015$. Hence, the intensity observed above H_c is described by our model of a field-driven structural phase transition when a quite realistic value of the distortion is invoked.

Finally we discuss the small step in intensity observed around 6.5 T. We note that this value is close to $H_c/\sqrt{2} = 6.55$ T. It was predicted theoretically [8] that a surface spin-flop transition takes place at $H_c^{(B)}/\sqrt{2}$, where $H_c^{(B)}$ is the critical field for the spin flop in the bulk, equal to $(2H_EH_A)^{1/2}$, where H_E is the exchange field and H_A the anisotropy field. Because half of the exchange paths are missing at the surfaces, the critical field, $H_c^{(S)}$, for the surface spin flop becomes $1/\sqrt{2}$ smaller than that of the bulk. Using the known values [6] of $H_E = 53$ T and $H_A = 0.82$ T for MnF_2, we get $H_c^{(S)} = 6.59$ T in good agreement with the observation. Although the penetration depth of 30 keV x-rays in MnF_2 is about 1 mm, the intensity of the x-rays inside of the crystal decreases exponentially with the distance from the surfaces. Consequently, the scattering at the surfaces is enhanced compared with that in the bulk. Because we did not polish the surfaces nor anneal the sample after cutting it, there are possibly many defects near the surfaces. These defects act as a nucleation centre for the spin reorientation at $H_c^{(S)}$ and thus enhance the intensity change. These are the reasons that we were able to observe the spin-flop transition at the surfaces as well as that in the bulk. We believe that high-energy x-ray magnetic scattering is a unique method for probing simultaneously the magnetic structures at the surfaces and in the bulk of magnetic materials.

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References

[1] Lovesey S W and Collins S P 1996 *X-Ray Scattering and Absorption by Magnetic Materials* (Oxford: Clarendon)
[2] Yabashi M, Mochizuki T, Yamazaki H, Goto S, Ohashi H, Takeshita K, Ohata T, Matsushita T, Tamasaku K, Tanaka Y and Ishikawa T 2001 *Nucl. Instrum. Methods* A **467–468** 678
[3] Hara T, Yabashi M, Tanaka T, Bizen T, Goto S, Maréchal X M, Seike T, Tamasaku K, Ishikawa T and Kitamura H 2002 *Rev. Sci. Instrum.* **73** 1125
[4] Goldman A I, Mohanty K, Shirane G, Horn P M, Greene R L, Peters C J, Thurston T R and Birgeneau R J 1987 *Phys. Rev.* B **36** 5609
[5] Brückel T, Lippert M, Bouchard R, Schmidt T, Schneider J R and Jauch W 1993 *Acta Crystallogr.* A **49** 679
[6] Hagiwara M, Katsumata K, Yamada I and Suzuki H 1996 *J. Phys.: Condens. Matter* **8** 7349
[7] Hahn T (ed) 1983 *International Tables for Crystallography* (Dordrecht: Reidel)
[8] Mills D L 1968 *Phys. Rev. Lett.* **20** 18