Journal of the Physical Society of Japan
Vol. 70, No. 1, January, 2001, pp. 37-40

Magnetic Structure of β-MnO_2: X-ray Magnetic Scattering Study

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(Received October 6, 2000)

An X-ray scattering experiment using synchrotron radiation has been performed on rutile-type β-MnO_2 single crystal. Below T_N, satellites due to magnetic scattering appear, which provides direct evidence of a helical magnetic structure. The wave number of the magnetic helix is approximately $0.297c^*$, incommensurate to the lattice and shows very weak temperature dependence. The extinction rule of the satellites is consistent with the magnetic structure proposed by Yoshimori [J. Phys. Soc. Jpn. **14** (1959) 807] in which the nearest helix chains are coupled in an antiferromagnetic way. The temperature dependence of the scattering intensity indicates that the critical exponent β is anomalously small for an ordinary three dimensional antiferromagnet; this strongly suggests a large chiral degeneracy effect of helical magnetism.

KEYWORDS: helical magnet, X-ray magnetic scattering, manganese oxides, phase transition, synchrotron radiation, critical phenomena

Rutile-type manganese dioxide, β-MnO_2, is one of the most popular magnetic materials owing to its helical magnetic structure. Since Yoshimori theoretically demostrated the stability of the magnetic helix for the first time,[1)] most textbooks on magnetism have described β-MnO_2 as a prototypical material for helical magnetism. However, it is very surprising that, thus far, there has been no publication of the neutron diffraction data, which is the only experimental evidence for the helical magnetic structure in β-MnO_2, even though the theory is well established. The neutron diffraction data which Yoshimori based his calculation on has been provided by Erickson, but he has not yet published the detailed data on β-MnO_2 with the exception of a few comments.[2,3)] According to private communication between Yoshimori and Erickson, the magnetic helix is commensurate to the lattice with the period of $7c/2$, where c is one of the lattice constants along the tetragonal axis.[1)] However, it is not clear how accurately the magnetic helix is commensurate to the crystal lattice, or whether the pitch of the helix is dependent on temperature or not. Detailed information regarding the extinction rule of the magnetic scattering is also lacking. We can expect a singular critical phenomenon on β-MnO_2, since its helical magnetic structure has a topology very different from that of ordinary collinear antiferromagnets. However, there has been no information reported about the temperature dependence of the order parameter.

In order to clarify these remaining issues, detailed analysis of the magnetic structure is necessary. Therefore, we carried out an X-ray magnetic scattering experiment using synchrotron radiation (SR).[4)] We chose this method rather than neutron diffraction based on the following two points. The first relates to its high resolution in q-space because SR can generate an extremely straight beam. This advantage has been utilized for very precise analysis of the magnetic structure of holmium.[5)] Another advantage is SR's applicability to a small single crystal of sub-millimeter size. This is indispensable for our material, β-MnO_2, because the growth of a large crystal is very difficult. Generally speaking, X-ray scattering caused by a magnetic moment is far weaker than that caused by an electric charge. Their ratio is given by $(\hbar\omega/mc^2)^2(N_m^2/N^2)\langle S\rangle$,[4)] which is around 10^{-6} for a typical experimental condition, where ω, N_m, N and S are the angular frequency of the X-ray, the number of magnetic electrons, the number of total electrons and the spin of the magnetic atoms, respectively.

Single crystals of β-MnO_2 were synthesized by a hydrothermal technique whose details have been given elsewhere.[6)] The X-ray magnetic scattering measurements on a single crystal of β-MnO_2 ($0.5\times0.5\times1\,mm^3$ in size) were carried out at the experimental station BL-4C in KEK-PF, Tsukuba. The incident beam was monochromatized by a Si(111) double crystal and focused by a bent cylindrical mirror. The energy of the X-ray was fixed at 17.46 keV, which corresponds to the energy of a conventional X-ray source with a Mo target. The single crystal was mounted on a diffractometer with six movable axes (four axes for the sample and the detector+two axes for the analyzer). In order to reduce the background signals, the scattered X-ray was passed through an analyzer utilizing (004) diffraction of pyrolitic graphite and three slits. In this way, we reduced the background to less than 0.8 cps.

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For the X-ray with the energy of 17.46 keV, the linear absorption coefficient is calculated as $109\,\mathrm{cm}^{-1}$. Since the measured crystal was as thick as 0.5 mm, it was not transparent for the X-ray and only the diffractions from the surface of the sample were detectable. The peak profiles of fundamental diffractions exhibited asymmmetric shapes because the crystal had an asymmetric outline and was smaller than the beam size. On the other hand, the ω-scan profiles had a very sharp peak with the full width at half maximum of 0.02°. This indicates that the mosaicity was extremely small in our crystal.

First, we carried out a search for magnetic scatterings at 10 K on the $(0, 0, l)$ line in the reciprocal space, but they were absent within the range of sensitivity of our instruments. Thus, we performed a peak search on the $(1, 0, l)$ line and identified a weak peak around $l = 2.297$, as shown in Fig. 1. Its intensity is almost 10^{-6} smaller than that of the $(1, 0, 3)$ diffraction. The scans around $(1, 0, 2.297)$ along the $\boldsymbol{a}^*$, $\boldsymbol{b}^*$ and $\boldsymbol{c}^*$ axes revealed that the linewidth was almost the same as that of the fundamental diffractions. This indicates that this peak is the diffraction caused by a well-developed long-range order. The asymmetric shape occurs for the same reason as the fundamental peaks. We call this peak $(1, 0, 2+q)$ and interpret it as a satellite diffraction, with a wave vector $q\boldsymbol{c}^*$, accompanied by the $(1, 0, 2)$ fundamental diffraction.

Figure 2 shows the temperature dependence of the intensity of the $(1, 0, 2+q)$ diffraction with $q \approx 0.297$. The intensity becomes weaker as the temperature increases and the satellite disappears entirely at the antiferromagnetic transition temperature, $T_N \approx 93$ K. This unambiguously demonstrates that the satellite comes from the magnetic order. Strictly speaking, polarization analysis is desired in order to confirm that this diffraction is a purely magnetic scattering. We have not carried it out yet because the intensity of the $(1, 0, 2+q)$ diffraction through the polarization analyzer was too weak for the present X-ray source. However, the intensity, which is almost 10^{-6} weaker than that of the fundamental diffraction and the behavior of the temperature dependence of the intensity, brings to mind an order parameter of a second-order phase transition and strongly suggests that the satellite at $(1, 0, 2+q)$ is a magnetic scattering.

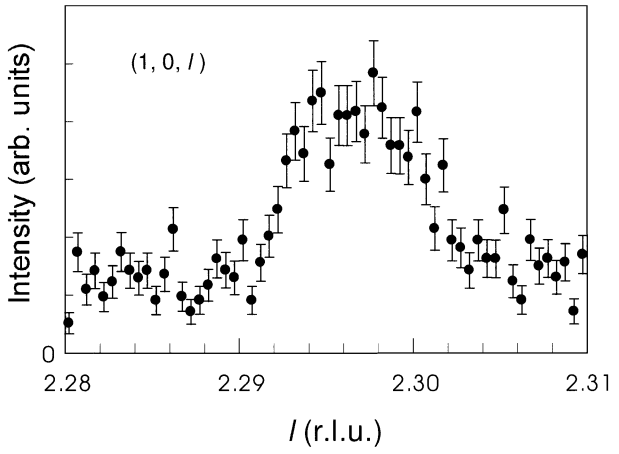

Fig. 1. Satellite scattering around $(1, 0, 2.297)$ detected at $T = 10$ K. The unit r.l.u. means reciprocal-lattice unit.

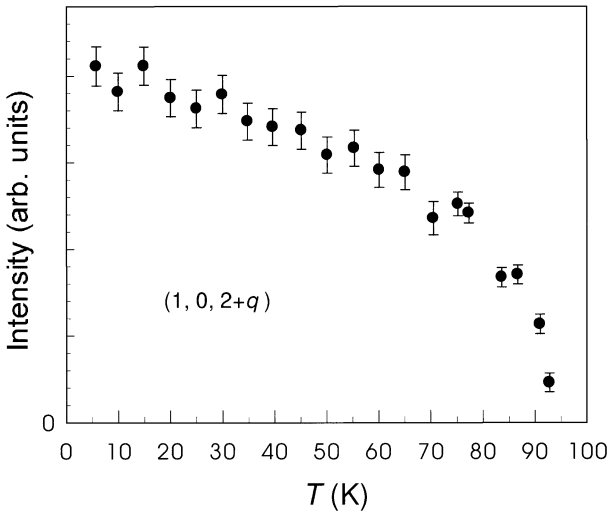

Fig. 2. Temperature dependence of the integral intensity of the satellite at $(1, 0, 2.297)$.

According to the unpublished neutron diffraction results by Erickson, the wave number of the magnetic helix is considered to be $(2/7)c^* \approx 0.2857c^*$. This value is not far from our value, $0.297c^*$, but there is a significant difference between them. We argue that our value is more exact and that the magnetic helix is basically incommensurate to the crystal lattice, because the error in the measurement of q is only about 0.001 in our method. This resolution is far higher than that of Erickson's neutron powder diffraction experiment.[3] Yoshimori constructed a magnetic helix model with a wave number of $(2/7)c^*$.[1] However, such a commensurate structure is not necessarily a consequence of his model because the wave number of the magnetic helix can have an arbitrary value which depends only on the ratio between the exchange interactions up to the third-nearest neighbors.

Figure 3 shows the temperature dependence of the wave number of the magnetic helix, q. It is very weakly dependent on temperature and the variation is smooth, without any jumps. This indicates that the magnetic helix is incommensurate and that there are no indications of '*lock-in*' (incommensurate-commensurate) phase transitions, unlike holmium metal. The absence of commensuration indicates that the spin-lattice coupling is very weak. This is not strange because Mn^{4+} $(S = 3/2)$ has three t_{2g} electrons and the shape of the d orbital is almost isotropic.

With further peak search, we succeeded in identifying satellites at $(1, 0, 2-q)$, $(1, 1, 3-q)$ and $(2, 0, 1+q)$. All of the intensities of these satellites are about 10^{-6} weaker than those of typical fundamental diffractions. The absence of satellites at other points suggests that the extinction rule is that the satellites around points $(h\,k\,l)$ are absent in the case of $h + k + l = 2n$, where n is an arbitrary integer. Below, we discuss the magnetic model based on this extinction rule. For consideration of the magnetic structure, we can only take into account

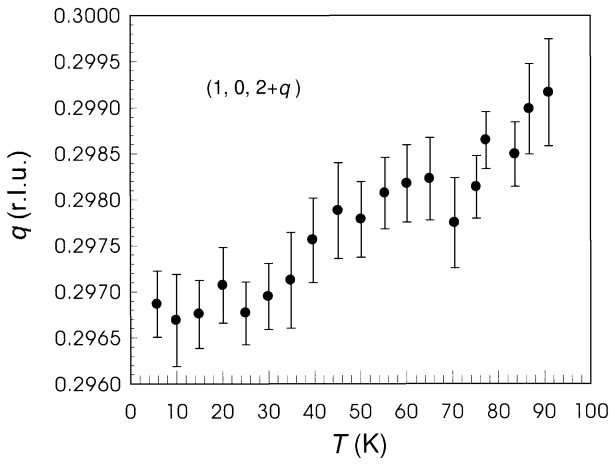

Fig. 3. Temperature dependence of the wave number of the magnetic helix estimated from the peak center of the $(1, 0, 2 + q)$ satellite.

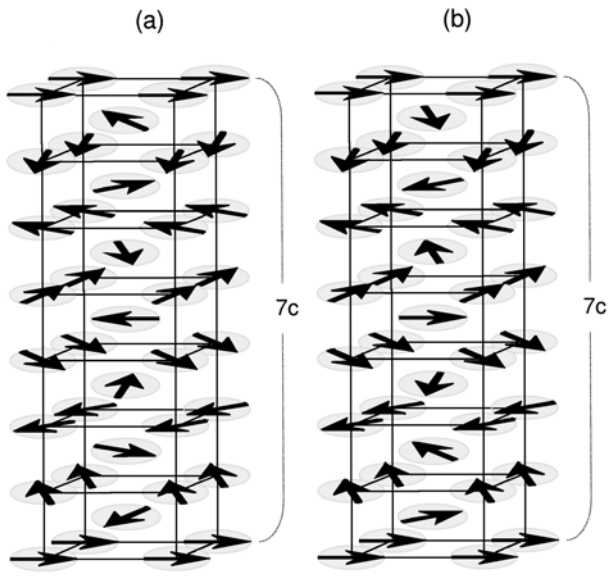

Fig. 4. Models of the magnetic structure of β-MnO_2 given by (a) Yoshimori and (b) Osmond. The interchain coupling between the nearest screws are antiferromagnetic (in Yosimori's model) and ferromagnetic (in Osmond's model).

the Mn atoms that form a body-centered lattice. Yoshimori proposed a model of magnetic structure, shown in Fig. 4(a), in which the magnetic moments on the corner Mn sites and those on the body-center Mn sites are antiparallel to each other.[1)] On the other hand, considering the sign of superexchange interaction, Osmond claimed that the model shown in Fig. 4(b) is more realistic.[7)] As explained below, we can conclude that Yoshimori's model is correct. The structure factor can be divided into that from fundamental diffraction and that from magnetic scattering as[4)]

$$F = F_{\rm fund} + F_{\rm mag}, \tag{1}$$

and

$$F_{\rm mag}(\boldsymbol{K}) = \left(\frac{e^2}{mc^2}\right)\left(\frac{\hbar\omega}{mc^2}\right) f_D \left[\frac{1}{2}\boldsymbol{L}(\boldsymbol{K})\cdot\boldsymbol{A} + \boldsymbol{S}(\boldsymbol{K})\cdot\boldsymbol{B}\right], \tag{2}$$

where $\boldsymbol{K}, f_D, \boldsymbol{L}(\boldsymbol{K})$ and $\boldsymbol{S}(\boldsymbol{K})$ are the scattering wave vector, the Debye-Waller factor, and the Fourier transforms of the atomic orbital magnetization density and of the spin magnetization density, respectively. The vectors $\boldsymbol{A}$ and $\boldsymbol{B}$ are defined as

$$\boldsymbol{A} = 2(1-\boldsymbol{k}\cdot\boldsymbol{k}')(\boldsymbol{\epsilon}'\times\boldsymbol{\epsilon}) - (\boldsymbol{k}\times\boldsymbol{\epsilon})(\boldsymbol{k}\cdot\boldsymbol{\epsilon}') + (\boldsymbol{k}'\times\boldsymbol{\epsilon}')(\boldsymbol{k}'\cdot\boldsymbol{\epsilon}) \tag{3}$$

$$\boldsymbol{B} = \boldsymbol{\epsilon}'\times\boldsymbol{\epsilon} + (\boldsymbol{k}'\times\boldsymbol{\epsilon}')(\boldsymbol{k}'\cdot\boldsymbol{\epsilon}) - (\boldsymbol{k}\times\boldsymbol{\epsilon})(\boldsymbol{k}\cdot\boldsymbol{\epsilon}') - (\boldsymbol{k}'\times\boldsymbol{\epsilon}')\times(\boldsymbol{k}\times\boldsymbol{\epsilon}), \tag{4}$$

where $\boldsymbol{k}, \boldsymbol{k}', \boldsymbol{\epsilon}$, and $\boldsymbol{\epsilon}'$ are the incident and scattered wave vectors, and the polarization vectors of the incident and scattered waves, respectively. Since the orbital angular momentum is quenched in the case of Mn^{4+} because of the t_{2g}^3 electron configuration, the term $\boldsymbol{L}(\boldsymbol{K})$ disappears.

Taking into account the body-centered structure of Mn atoms, the magnetic structure factor for β-MnO_2 is easily calculated as

$$F_{\rm mag}(h\,k\,l) \propto \sum_{n_c}\left[\cos(2\pi q n_c)\mathrm{e}^{2\pi i l n_c} \pm (-1)^{h+k}\cos\{2\pi q(n_c+1/2)\}\mathrm{e}^{2\pi i l(n_c+1/2)}\right], \tag{5}$$

where n_c is an integer indexing the position of the unit cell along the c axis, and $\pm$ should be $-$ for Yoshimori's model and $+$ for Osmond's model. Therefore, the magnetic structure factor becomes nonzero in the case of

$$l = l' + q, \tag{6}$$

where l' is an integer and

$$\begin{cases} h+k+l' = 2n & \text{(for Osmond's model)} \\ h+k+l' = 2n+1 & \text{(for Yoshimori's model)} \end{cases}, \tag{7}$$

should be satisfied. The observation that satellites appear only around the fundamental diffraction (h, k, l) with $h + k + l = 2n + 1$ is clearly consistent with Yoshimori's model.

From a fundamental point of view of phase transition, β-MnO_2 is a very important material. Kawamura pointed out that helical magnets such as β-MnO_2, $MnAu_2$, Ho, Dy and Tb belong to a new universality class because of *chiral degeneracy*, that is, the degeneracy between left-handed and right-handed helices.[8-10)] The anisotropy of the magnetic susceptibility[6, 11)] shows that the spins have XY-type anisotropy thus they are aligned perpendicular to the c axis. Therefore, the universality class to which β-MnO_2 belongs is considered to be the same as that of triangular XY antiferromag-

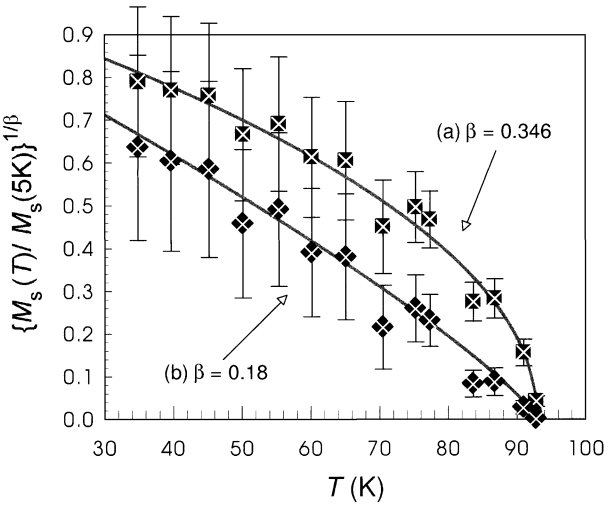

Fig. 5. Plots of the $1/\beta$-th power of the sublattice magnetization as a function of temperature for (a) $\beta = 0.346$ (S_1 model) and for (b) $\beta = 0.18$. The thin curves are visual guides. The $Z_2 \times S_1$ model ($\beta = 0.253$) gives a intermediate behavior between (a) and (b).

nets, $V = Z_2 \times S_1$ =O(2), which is thoroughly different from $V = S_1$ =SO(2) of the XY ferromagnet. The difference in universality class should appear most significantly in the critical phenomena. From a Monte Calro simulation, the critical exponent β, which is defined as $\langle M_s \rangle \propto (T_N - T)^\beta$ where $\langle M_s \rangle$ is the sublattice magnetization, of an XY helical magnet is estimated at 0.253 ± 0.01, very different from the value 0.346 for an XY ferromagnet.[9] Therefore, it is very interesting to obtain the critical exponent β experimentally. Because the intensity of the magnetic scattering is the square of the scattering factor (eq. (2)), it is proportional to $\langle M_s \rangle^2$. Therefore, we can estimate the critical exponent β. Because of the limited data points in the vicinity of T_N, a qualitative determination of β is difficult at present, but we can qualitatively determine which model, $Z_2 \times S_1$ or S_1, is more suitable for our system. In Fig. 5, we plot $\langle M_s \rangle^{1/\beta}$ as a function of temperature. The correct value of β should give a straight line. From the figure, we can say, at least, that the $Z_2 \times S_1$ model with $\beta = 0.253$ gives a straighter line for a wider temperature range than the S_1 model with $\beta = 0.346$. For obtaining a straight line only, $\beta = 0.18$ is the best value, as shown Fig. 5(b). This clearly proves that β of β-MnO_2 is anomalously small compared with the ordinary three-dimensional collinear antiferromagnet because of its chiral degeneracy.

In conclusion, we have carried out an X-ray magnetic scattering study on β-MnO_2, which is a prototypical material for helical magnetism. High-resolution analysis in the reciprocal space clarified that the magnetic helix is incommensurate to the crystal lattice and that the temperature dependence of its wave number is very weak and smooth, exhibiting no lock-in transitions. The critical exponent β is far smaller than the value 0.346 expected in three-dimensional XY ferromagnets, indicating the large effect of the chiral degeneracy. For a quantitative analysis of the critical exponent, experiments with a stronger X-ray source will be carried out in the future.

We would like to thank Professor Hikaru Kawamura for useful discussion and encouragement. This work is partly supported by a Grant-in-Aid for Scientific Research Nos. 10740318 and 10149101 from the Ministry of Education, Science, Sports and Culture, Japan.

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