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NEUTRON SCATTERING STUDY OF MnX_2 ($X = Br, I$)

Taku SATO and Hiroaki KADOWAKI*

Department of Physics, Tokyo Institute of Technology
Oh-okayama, Meguro-ku, Tokyo 152, Japan

*The Institute for Solid State Physics, The University of Tokyo
Roppongi, Minato-ku, Tokyo 106, Japan

Abstract

Successive magnetic phase transitions in MnX_2 ($X = Br, I$), found by bulk measurements, are studied by neutron scattering experiments. There occur two ($T_{N1} = 2.32K$, $T_{N2} = 2.17K$) and three ($T_{N1} = 3.95K$, $T_{N2} = 3.8K$, $T_{N3} = 3.45K$) phase transitions in $MnBr_2$ and MnI_2 , respectively. We have found that magnetic structures of the both compounds in the intermediate temperature phases ($MnBr_2$: $T_{N1} > T > T_{N2}$; MnI_2 : $T_{N1} > T > T_{N3}$) are transverse sinusoidally-modulated structures with incommensurate wave-vectors which vary as a function of temperature. As the temperature is lowered into the lowest temperature phases, the magnetic structures change via first order transition into $\uparrow\uparrow\downarrow\downarrow$ and a helical structure for $MnBr_2$ and MnI_2 , respectively, which were determined by previous experiments. The successive phase transitions in $MnBr_2$ are accounted for quantitatively using a mean field approximation of a Hamiltonian consisting of exchange interactions up to third inter- and third intra-layer neighbor sites and the dipolar interaction.

INTRODUCTION

Magnetic properties of transition metal dihalides which crystallize in CdI_2 or $CdCl_2$ hexagonal layer structure have been investigated for decades. A spin structure which is most commonly seen in these magnets are the antiferromagnetic stacking of the layers of ferromagnetically aligned spins, which is observed in most of Fe, Co and Ni chlorides and bromides. Among those compounds, MnX_2 ($X = Br, I$) exhibit complicated structures^{1,2}). In $MnBr_2$ magnetic moments order in up-up-down-down sequence with modulation vector $\vec{q} = (1/4, 0, 1/4)$, where the spin direction is parallel to the b-axis. On the other hand in MnI_2 , a proper helical structure with a modulation vector $\vec{q} = (3/16, 0, 7/16)$ is realized. The complicated structures in MnX_2 are attributed to competing exchange interactions. Recently, two successive phase transitions were found by magnetic circular dichroism³) and optical birefringence⁴) measurements for $MnBr_2$ and MnI_2 , respectively. They showed that the higher and lower temperature phase transitions are a second and first-order transitions, respectively. On a theoretical basis these first-order phase transition is puzzling and cannot be accounted for by a simple Heisenberg model. Since magnetic ions form a Bravais lattice and have Heisenberg spins, the ground state

magnetic structure is a helical structure with a wave vector at which $J(\vec{q})$ has the maximum. If the anisotropy is a pure Heisenberg or an XY type, there occurs only one second-order phase transition in finite temperatures. On the other hand, if the anisotropy is a weak Ising type, two second-order phase transitions take place, where the easy and hard axis components order at a higher and lower temperatures, respectively. Therefore a certain reason other than the weak Ising anisotropy is required for explaining the first-order phase transitions. In this work we have determined magnetic structures in the intermediate phases of MnX_2 by neutron scattering experiments. Using the observed structures we discuss the successive phase transitions on the basis of a mean field approximation.

EXPERIMENTAL RESULTS

The single crystals were grown in silica ampoules by the Bridgeman method. Neutron scattering measurements were performed on ISSP-ND1 (JRR-2), 4G-TAS and PONTA (JRR-3M) triple axis spectrometers at JAERI (Tokai). Single crystals of $MnBr_2$ (0.23cc) and MnI_2 (0.51cc) were mounted in a 3He cryostat. The temperature of the sample was monitored by a Ge sensor and controlled within $\pm 0.01K$.

$MnBr_2$

We confirmed that two successive phase transitions occur at $T_{N1} = 2.32K$ and $T_{N2} = 2.17K$. Magnetic reflections in the low temperature phase ($T < T_{N1}$) appear at $\vec{Q} = \vec{G} \pm \vec{q}$, where \vec{G} and $\vec{q} = (1/4, 0, 1/4)$ denote reciprocal lattice and modulation vectors, respectively. In the intermediate temperature phase ($T_{N1} > T > T_{N2}$), we found that the modulation vector $\vec{q} = \vec{q}_{INC} = (q_a, 0, q_c)$ becomes incommensurate and depends slightly on temperature. In Fig. 1 we show the magnetic Bragg positions in the reciprocal lattice space and the temperature dependence of the modulation vector \vec{q} . It should be remarked that modulation vector exhibits hysteresis effect in the intermediate temperature phase. In Fig. 2 scattering intensities of the magnetic reflections are plotted as a function of temperature. One can see from this figure that T_{N2} is a first order phase transition temperature. Magnetic structures of the low and intermediate temperature phases were determined by observing integrated intensities of the magnetic reflections. We confirmed the previous result that in the low temperature phase, moments order in up-up-down-down sequence with modulation vector $\vec{q} = (1/4, 0, 1/4)$, which is shown in Fig. 3.

In the intermediate temperature phase, we found that the transverse sinusoidally-modulated structure is realized. The moments on the ac -plane are depicted in Fig. 4.

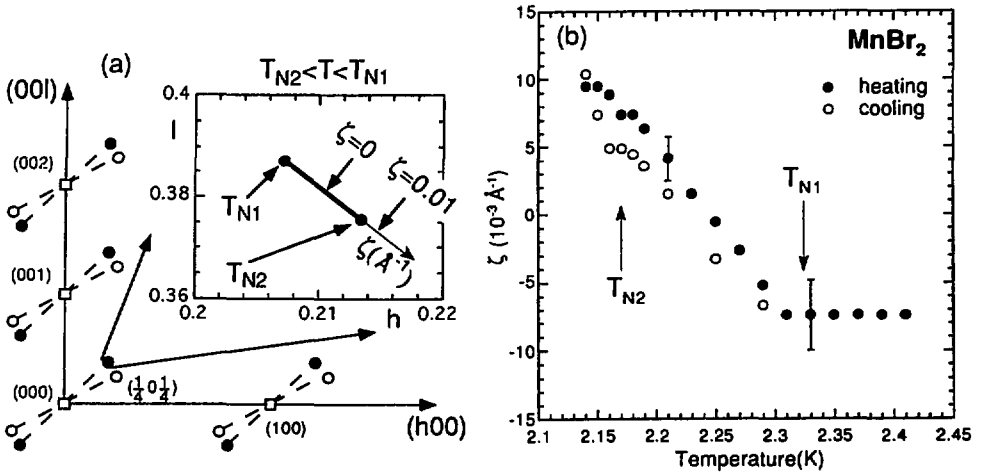


Figure 1: (a) Nuclear and magnetic Bragg positions in the $(h0l)$ zone of MnBr_2 . Square denotes nuclear Bragg position. Open and filled circles stand for magnetic Bragg positions at $T_{N1} > T > T_{N2}$ and $T < T_{N2}$, respectively. Inset shows locus of magnetic reflection $\vec{Q} \sim (0.38, 0, 0.21)$ which varies as a function of temperature at $T_{N1} > T > T_{N2}$. (b) Temperature variation of modulation vector along the locus. Parameter ζ is defined in the inset of (a).

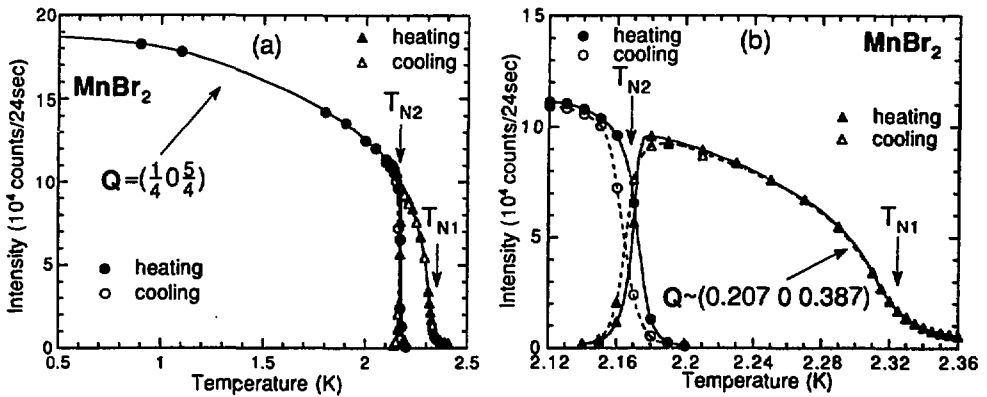


Figure 2: (a) Temperature dependence of peak intensity of magnetic reflection in wide (a) and small (b) temperature range. Solid and dashed lines are guides to the eye.

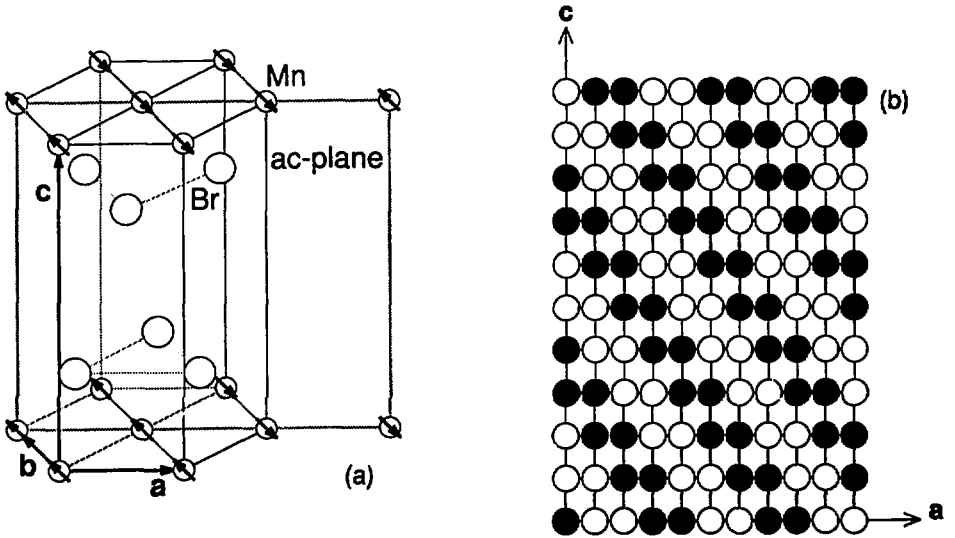


Figure 3: Spin arrangement in the low temperature phase of MnBr_2 . (a) moments are depicted on the CdI_2 structure. (b) moments in the *ac*-plane. Open and filled circles denote up and down spins, respectively.

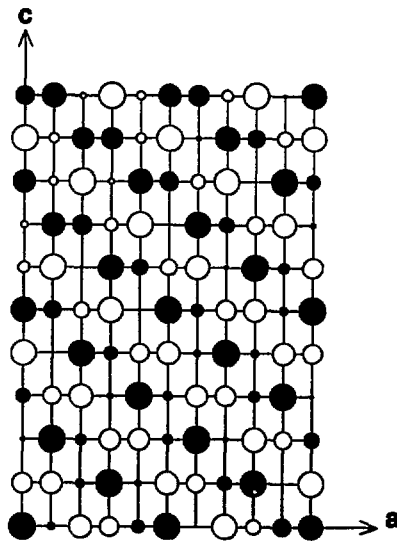


Figure 4: Spin arrangement in the intermediate temperature phase of MnBr_2 . The same manner as in Fig. 3 (b) is used to show the moments in the *ac*-plane. Radius of each circle represents magnitude of moment parallel to the *b*-axis.

MnI₂

A new phase transition was found at $T_{N2} = 3.8\text{K}$ in addition to the two previously observed transitions at $T_{N1} = 3.95\text{K}$ and $T_{N3} = 3.45\text{K}$. As temperature is decreased from the paramagnetic phase, magnetic reflections with wave vector $\vec{Q} = \vec{G} \pm \vec{q}$, where $\vec{q} = (0.1025, 0.1025, 1/2)$ appear at T_{N1} . The second phase transition temperature T_{N2} is characterized as a temperature below which the modulation vector \vec{q} starts to vary as a function of temperature. The locus of modulation vector is schematically shown in Fig. 5 (a) and (b). At the third phase transition T_{N3} the modulation vector \vec{q} jumps into the $(h\ 0\ l)$ plane at $\vec{q} \simeq (0.181, 0, 0.439)$, which is close to the previously reported $\vec{q} = (3/16, 0, 7/16)$, but is definitely incommensurate and exhibits slight temperature dependence. Temperature dependence of the magnetic scattering intensities are shown in Fig.6.

Magnetic structures were determined by observing integrated intensities of magnetic reflections. The helical structure reported in the previous work was confirmed in the low temperature phase ($T_{N3} > T$). In the intermediate temperature phase ($T_{N1} > T > T_{N3}$), the transverse sinusoidally-modulated structure was found. It can be written as $\langle \vec{S}_i \rangle = \vec{S} \sin(\vec{q} \cdot \vec{r}_i + \phi)$, where the polarization \vec{S} is in the c -plane and perpendicular to the modulation vector \vec{q} .

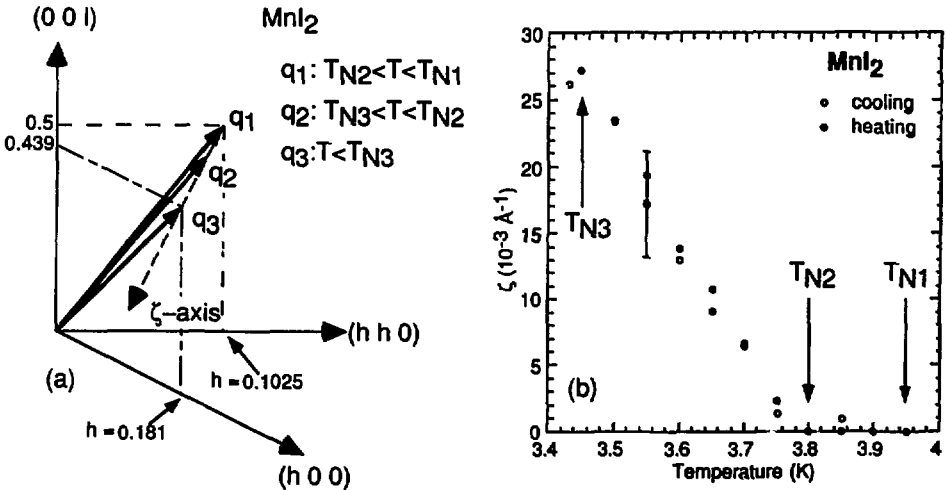


Figure 5: (a) Schematic locus of modulation vector \vec{q} . \vec{q}_1 and \vec{q}_3 are confined in $(h\ h\ l)$ and $(h\ 0\ l)$ planes, respectively. (b) Temperature dependence of $\vec{q} = \vec{q}_2$ is plotted using ζ -axis defined in (a). $\zeta = 0$ corresponds to $\vec{q} = \vec{q}_1$.

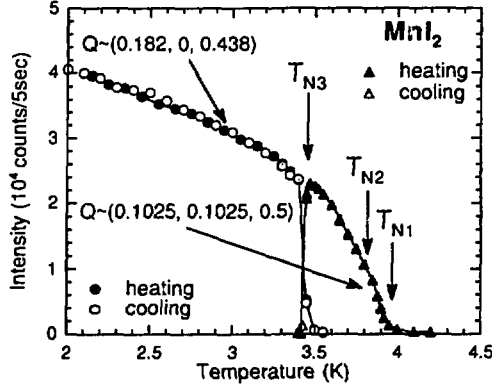


Figure 6: Temperature dependence of the peak intensity of magnetic reflection. The solid lines are guides to the eye.

DISCUSSION

Present neutron scattering experiment shows that the first order phase transitions in both MnBr_2 and MnI_2 are characterized by the jumps of the modulation vectors, and that in the intermediate temperature phase the magnetic structures are transverse sinusoidally modulated structures. One can easily attribute the sinusoidally modulated structure to Ising type anisotropies. However the first order phase transitions are puzzling as discussed in the introduction. We attempted to interpret the first order transitions in terms of a model Hamiltonian consisting of the exchange and the dipolar interaction within a mean field approximation.

The model Hamiltonian is given by

$$H = -2 \sum_{\langle ij \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j + \sum_{\langle ij \rangle} D_{ij}^{\alpha\beta} \vec{S}_i^\alpha \vec{S}_j^\beta = \sum_{\vec{q}\alpha\beta} \vec{S}_{\vec{q}}^\alpha \vec{S}_{-\vec{q}}^\beta H^{\alpha\beta}(\vec{q}), \quad (1)$$

$$H^{\alpha\beta}(\vec{q}) = [-J(\vec{q})\delta^{\alpha\beta} + D^{\alpha\beta}(\vec{q})] \quad (\alpha, \beta = x, y, z), \quad (2)$$

where $D_{ij}^{\alpha\beta}$ and $D^{\alpha\beta}(\vec{q})$ represent the dipolar interaction and its Fourier transform, respectively. Within a mean field approximation, the phase that has the highest ordering temperature corresponds to the lowest eigenvalue of the matrix of $H^{\alpha\beta}(\vec{q})$. To reproduce the sinusoidally modulated structure of MnBr_2 , we solved the eigenvalue problem including a lot of adjustable exchange constants and found that three intra- and three inter-layer interactions are indispensable for maximizing $J(\vec{q})$ at observed \vec{q}_{INC} . The dipolar interaction gives the correct polarization parallel to the b -axis.

At lower temperatures, either the helical with $\vec{q} = \vec{q}_{INC}$ or the up-up-down-down structure is more favorable, since these structures allow greater average moments. Using the parameters which is determined to reproduce the sinusoidally modulated phase, we calculated the free energies of the three structures:(1) incommensurate sinusoidally modulated structure (F_{ICS});(2) commensurate sinusoidally modulated (up-up-down-down)

structure (F_{CS}); (3) incommensurate helical structure (F_{IH}). They are plotted in Fig. 7. One can see from this figure that the up-up-down-down structure is most stable below T_{N2} and that the transition is first order.

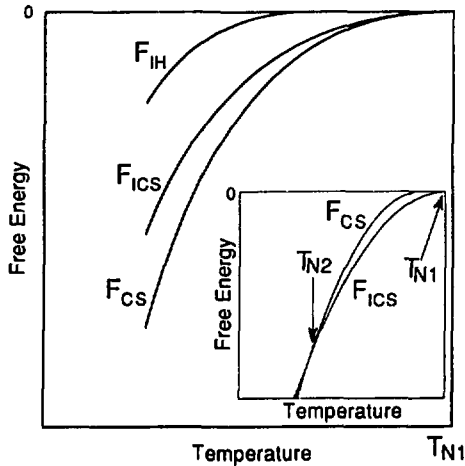


Figure 7: Free energies of incommensurate sinusoidal (F_{ICS}), commensurate sinusoidal (F_{CS}) and incommensurate helical (F_{IH}) structures.

Temperature dependence of the modulation vector in the intermediate temperature phase of $MnBr_2$ were studied. We found that it can be understood quantitatively by using the Landau like expansion of free energy up to 4th order terms. This mechanism is essentially the same as that in the ANNNI model⁷⁾.

Although the phase transitions in $MnBr_2$ can be understood quantitatively, these in MnI_2 are more complex and left for a further study.

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