Atom Indonesia Vol. 36 No. 2 (2010) 59 - 62

The Importance of Magnetic Reflection Condition and Polarization Factor: Case Study of MnF_2

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ARTICLE INFO

Article history:
Received 19 May 2009
Received in revised form 30 August 2010
Accepted 31 August 2010

Keywords:
Magnetic
Neutron
Diffraction
Manganese
Collinear
Antiferromagnetic

ABSTRACT

Neutron diffraction has been widely accepted as a versatile tool to investigate magnetic structure of crystalline materials, which contribute significantly to the scientific and technological advances. Starting from a general formulation of the magnetic structure factor, one can often simplify the formulation depending on the crystallographic structure and the magnetic wave propagation vector of the sample. The simplification allows magnetic moment coupling and polarization deduction without the need of the refinement process. This paper elaborates such simplification for MnF_2 to provide the determination of the magnetic moment coupling and polarization direction simply based on the reflection condition and polarization factor. The determination of the magnetic structure excluding its magnitude by the reflection condition and polarization factor is much more conclusive than by any magnetic structure refinement. Furthermore, MnF_2 illustrates a rare compound that has antiferromagnetic structure with zero magnetic wave propagation vector, i.e.; it has the same antiferromagnetic and crystallographic unit cell.

INTRODUCTION

Neutron diffraction has been widely accepted [1,2] as a versatile tool to investigate magnetic structure of crystalline materials. The structure, governed by the magnetic moment vectors belonging to the magnetic ions, ranges from simple collinear commensurate to complicated noncollinear incommensurate. For some materials in which the single crystal forms are not easily accessible, the diffraction measurement can also be conducted in the powder form. Furthermore, the powder diffractometer, suitable for such measurement, is available in Indonesia as a user facility with the aim mainly for scientific collaborations [3].

Apart from the importance mentioned above, it is widely understood that the analysis of the diffraction measurement is tedious as there are various steps to follow due to intrinsic microscopic nature of the measurements. Various measurement artifacts, such as noise and convolution-deconvolution [4] steps also complicate the data analysis. To avoid such problem, one usually restricts the analysis based on possible models that are generated before conducting the analysis. For crystalline materials, the models can be obtained by group theory, which deals with the crystallographic [5,6] and/or magnetic [7-11] symmetry of the model systematically.

This paper elaborates the reflection condition and polarization factor to deduce the magnetic structures in a simplest case in which the magnetic wave propagation vector **k** is 0, and yet provide an illustration on the antiferromagnetic structure with the same unit cell as the crystallographic unit cell. Note that most antiferromagnetic compounds do not have a magnetic unit cell of the same dimension as the crystallographic unit cell. The complication that requires the symmetry consideration based on the magnetic Shubnikov analysis [7], the representation theory [8] and the corepresentation (coset representation) analysis [9-11] do not appear.

EXPERIMENTAL

The crystallographic structure and the magnetic reflections of MnF_2 were obtained from elsewhere [12-14]. From the crystallographic structure, the atomic positions within a unit cell were obtained. The analysis was conducted starting from a general form of the structure factor of the magnetically ordered unit cell. As there are only 2 magnetic atoms located in the mirror plane symmetry, several simplifications were performed.

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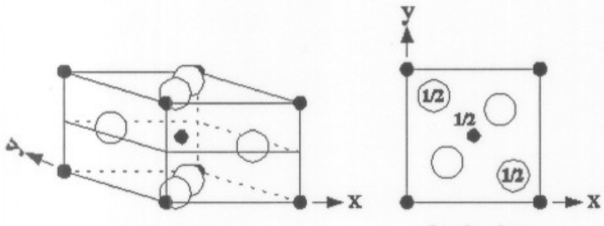
A conclusive deduction of the magnetic moment coupling and the magnetic polarization direction were obtained analytically by using the magnetic reflection condition and the polarization factor.

Crystallographic Structure

MnF_2 crystallizes in the tetragonal rutile structure which belongs to the the $P4_2/mnm$ tetragonal nonsymmorphic space group. Two manganese (Mn) atoms are at (0,0,0) and (1/2,1/2,1/2) and four fluorine (F) atoms at $(u,u,0)$, $(-u,-u,0)$, $(-u+1/2,u+1/2,1/2)$ and $(u+1/2,-u+1/2,1/2)$, where u has a value of 0.3053 and is the only internal coordinates that is not fixed by symmetry [12]. The tetragonal lattice parameters are a=4.8734Å and c=3.3099Å.



(a) schematic (b) ab-plane

Fig. 1. An (a) schematic and (b) *ab*-plane projection of the MnF_2 crystallographic structure. The atomic positions within a unit cell and the atom size ratio between Mn (smaller balls) and F (bigger balls) are drawn to scale. In (b), the 1/2 notation indicates the z-positions within the tetragonal unit cell.

Magnetic Structure

Below the Neel temperature, T_N of approximately 70K, superlattice magnetic peaks are observed and can be indexed in the parent tetragonal symmetry as (100), (111), (210), and (201) [12-14]. As the magnetic contribution can be indexed in the crystallographic symmetry, the magnetic unit cell has the same dimensions as the chemical unit cell.

Magnetic Structure Factor Formulation

One could start from a general magnetic elastic scattering cross section for unpolarized neutrons suitable for representation analysis in the following form (taken from elsewhere [15]):

$$\left(\frac{d\sigma}{d\omega}\right)=\left(\frac{\gamma r_0}{2}\right)^2 N\frac{(2\pi)^3}{v}\exp(-2W)\sum_{\alpha\beta}\{\delta_{\alpha\beta}-(\hat{\tau}_\alpha+\hat{q}_\alpha)(\hat{\tau}_\beta+\hat{q}_\beta)\} \quad (1)$$
$$\sum_{dd'} f_d(\mathbf{\tau}+\mathbf{q})f_{d'}(\mathbf{\tau}+\mathbf{q})\mu_{d,\beta}\exp(i\mathbf{q}\bullet\mathbf{d})\exp(i\mathbf{q}\bullet\mathbf{d'})\exp\{i(\mathbf{d}-\mathbf{d'})\}$$

where the classical radius of the electron is

$$r_0=\frac{\mu_0}{4\pi}\frac{e^2}{m_e}=2.818\times10^{-15}\,\text{m}, \qquad (2)$$

N is the number of unit cells in the crystal, γ is the neutron magnetic moment expressed in nuclear magnetons (equal to 1.913) and $f_d(\tau+\mathbf{q})$ is the (magnetic) form-factor of atom d which is related to the Fourier transform of the electronic magnetization density. The exp($-2W$) term is the Debye-Waller factor, or the thermal (temperature) factor in crystallographic language. It arises from the vibration of the atoms about their equilibrium positions. The factor $\boldsymbol{\mu}_{d,\beta}$ is the βth Cartesian component of the moment belonging to atom d.

For the commensurate structure, one can still use Eq.(1) by substituting $\mathbf{q}$=0. Significant simplification is obtained if the magnetic structure is commensurate and collinear. In the collinear model, the magnetic moment directions are either parallel or antiparallel with respect to only one particular direction α. First, $\Sigma_{dd'}$ can be turned into Σ_d by using the relation:

$$\left|\sum_d \mu_{d,\alpha}\exp(i\mathbf{\tau}\bullet\mathbf{d})\right|^2=\sum_d \mu_{d,\alpha}\exp(i\mathbf{\tau}\bullet\mathbf{d})\sum_{d'}\mu_{d',\alpha}\exp(-i\mathbf{\tau}\bullet\mathbf{d'}) \quad (3)$$
$$=\sum_{dd'}\mu_{d,\alpha}\mu_{d',\alpha}\exp\{i\mathbf{\tau}\bullet(\mathbf{d}-\mathbf{d'})\}.$$

Second, as there is only one moment direction to be considered, $\Sigma_{\alpha\beta}$ is irrelevant and the surviving terms only depend on one particular moment direction, which simplifies the polarization factor

$$\sum_{\alpha\beta}\left(\delta_{\alpha\beta}-\hat{\tau}_\alpha\hat{\tau}_\beta\right)\hat{\mu}_\alpha\hat{\mu}_\beta=1-\hat{\mathbf{\tau}}\bullet\hat{\boldsymbol{\mu}}=\sin^2\eta \qquad (4)$$

where η is the angle between the reciprocal vector τ and the moment μ. Note, that the polarization factor in Eq.(4) has nothing to do with the polarized or unpolarized neutron. One can then write Eq.(1) in a much simpler form as

$$\left(\frac{d\sigma}{d\omega}\right)=\left(\frac{\gamma r_0}{2}\right)^2 N\frac{(2\pi)^3}{v}\exp(-2W)\sin^2\eta\left|F(\mathbf{\tau})\right|^2 \quad (5)$$

where the magnetic structure factor F as a function of τ is

$$F(\mathbf{\tau})=\sum_d f_d(\mathbf{\tau})\mu_d\exp(i\mathbf{\tau}\bullet\mathbf{d}) \qquad (6)$$

It is always useful to do a simple check for the magnetic refinement based on systematic absences for the magnetic reflections. The systematic absences are governed by 3 factors:

1. Zero net moment on the plane in the direct lattice corresponding to the reflection of interest.

2. Destructive interference due to a 180^0 phase difference between the adjacent planes containing nonzero net moments.
3. Zero polarization factor; i.e.; the polarization vector $\sin^2\eta=0$, if the net moment μ points parallel or antiparallel to the reciprocal vector τ.

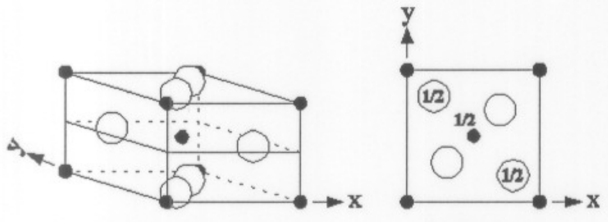
This method is valid for both collinear and noncollinear cases, though it is not always easy to apply in the latter case. Furthermore, for powder diffraction, there is an added complication of reflection multiplicities. For example, one observes no (00*l*) peak for compounds with ferromagnetic or antiferromagnetic order along the *c*-axis in tetragonal, hexagonal and orthorhombic symmetries, irrespective of whether the compound is a powder or single crystal. However, one would see it in the powder data of a compound with cubic symmetry. This is because (00*l*) is equivalent to (*h*00) and (0*k*0) and the polarization factor is nonzero for the last two reflections.

RESULTS AND DISCUSSION

Based on the magnetic atoms at (0,0,0) and (1/2,1/2,1/2) in the unit cell, one can further simplify Eq. (5) and (6):

$$F(\boldsymbol{\tau}) = f_{\mathrm{Mn}}\mu_{\mathrm{Mn}}(\boldsymbol{\tau})\left\{1 \pm (-1)^{h+k+l}\right\} \qquad (7)$$

where the (+) and (-) signs belong to the ferromagnetic and antiferromagnetic alignments, respectively. The first and second terms belong to atoms at (0,0,0) and (1/2,1/2,1/2), respectively.



(a) schematic

(b) ab-plane

Fig. 2. A (a) schematic and (b) *ab*-plane projection of the MnF_2 magnetic structure. The atomic positions within a unit cell and the atom size ratio between Mn and F are drawn to scale. In (b), the 1/2 notation indicates the *z*-positions within the tetragonal unit cell. Black circles and a cross denote atoms with moments pointing into and from the reader, respectively.

For this simple structure, one can draw 2 important results based on the systematic absences, without any refinement:

1. In order to have nonzero magnetic structure factor shown in Eq.(7) for the nonzero observed (100) magnetic reflection, one has to choose the antiferromagnetic coupling between the two magnetic atoms. This important result can be obtained even before any refinement, as there are only 2 magnetic atoms and they are located in the special position fixed by symmetry.
2. One more important result is to deduce the direction of the moments, based on the polarization factor shown in Eq.(4). The fact that no (00*l*) magnetic reflections are seen implies that the moments must be parallel to the *c*-axis (see Eq.(4)).

To determine the magnitude of the magnetic moments, one needs the refinement, which can be done by using various magnetic structure analysis software packages [16,17]. Other magnetic reflections (i.e.; (111), (210), and (201)) are certainly useful at this stage.

CONCLUSIONS

The simplest account on the magnetic structure determination excluding the magnetic moment magnitude based on the reflection condition and polarization factor of the magnetic neutron powder diffraction has been elaborated in the case of MnF_2. It has been shown that the general formulation of the magnetic cross section collapses into much simpler form for the commensurate collinear magnetic structure. It is even simpler for the case of MnF_2, which contains only two magnetic atoms per-unit cell with locations fixed by symmetry. The moment coupling between the two atoms (i.e.; antiferromagnetic) and the moment directions (i.e.; along the tetragonal *c*-axis) are conclusively determined by the existence of only one magnetic reflection (i.e.; (100)) and the absence of another (i.e.; (001)), respectively. It is important to note that the MnF_2 antiferromagnetic configuration can be obtained although the magnetic wave propagation vector is $\mathbf{k}=0$, i.e.; the antiferromagnetic and crystallographic unit cells are the same.

ACKNOWLEDGEMENT

This work was supported by Daftar Isian Pelaksanaan Anggaran (DIPA) 2007-2008: *the empowerment of the neutron beam facility for materials characterization*.

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