ABSTRACT

Recently, we have developed the experimental setup for high pressure neutron diffraction experiment with using Hybrid-Anvil-Cell in combination with high flux cold neutron time of flight (TOF) diffractometer WISH at ISIS. By using this unique setup, we have succeeded in measuring pressure induced magnetic Bragg reflections for the multiferroic compounds CuFeO$_2$ and TbMnO$_3$. The former shows pressure induced polar magnetic phases up to 7.9 GPa. For the latter compound, we have determined the magnetic structures under not only high pressure (5 GPa) but also high magnetic field (8 T) condition. In this article, I would like to show utilization of the combination, and encourage researchers in other fields as well as multiferroics to use the unique combination.

Keywords: Multiferroics, Neutron diffraction, Hybrid-Anvil-Cell

1. Introduction

One of the most powerful experimental techniques for investigation of magnetic orderings is neutron diffraction. However, there is a serious drawback for high pressure experiments which limit the sample size down to a small volume. Experiments with combination of pressure and magnetic field bring a further challenge owing to low-temperature and high-magnetic field equipment as well as pressure cell. Recently, in order to overcome this difficulty, we have developed powerful combination of hybrid-anvil-type pressure cell[1, 2] and the cold neutron time of flight neutron instrument WISH at ISIS neutron facility[3]. The cell is potentially capable of generating pressures up to 10 GPa and can be used at low temperatures and high magnetic fields. In this article, I present overview of the experimental setup, and application examples of two multiferroics, CuFeO$_2$[4] and TbMnO$_3$[5].

2. Combination of Hybrid-Anvil-Cell and WISH diffractometer

The Hybrid-Anvil-Cell has been originally developed by Dr. Osakabe in JRR-3 Tokai for diffraction with monochromatic beam [1,2] . We use two anvils (WC and SiC or sapphire) made of different materials to generate hydrostatic pressure up to 10 GPa. Typical sample size is 0.6 x 0.6 x 0.2 mm$^3$. The SiC (or sapphire) anvil is transparent to make visible laser transmit for measuring pressure with ruby fluorescence method. The detail description can be read in the other literature [1,2].

The cell has large opening windows 87 degrees for horizontal direction and -35 to 45 degrees for vertical direction (Fig. 1(a)). Therefore, it is more effective to use large coverage detector and TOF technique with white beam such as WISH [3] (Fig. 1 (c)) . Typical diffraction data measured with one side of detectors were shown in Fig. 1(d). We can observe several magnetic and nuclear reflections with low background at the same time. Reduction of background (mainly caused by the anvils) is realized by using BN mask (Fig. 1(b)) to avoid incident beam hit the anvils and oscillating collimator (originally equipped on WISH) to cut scattered beam from off-center position.

3. Application for Multiferroics

In spin-driven multiferroics, a ferroelectric polarization is induced by a magnetic ordering with polar
magnetic point group. Assuming that such a ordering is realized by competing exchange interaction, external pressure can modify the competition by changing lattice parameter, leading to different magnetic ordering. I introduce two examples that show drastic change in magnetic ordering and ferroelectric properties by pressure.

3.1. Pressure-induced polar phases in delafossite CuFeO$_2$[4]

CuFeO$_2$ is known as typical triangular lattice antiferromagnet. For the last two decades, the compound has been studied as a frustrated system due to novel magnetic properties such as the complex magnetic phase diagram, and strong spin-lattice coupling [6]. Since discovery of magnetic field induced ferroelectric polarization in CuFeO$_2$, it has been studied for understanding the mechanism regarding onset of ferroelectricity [7]. Application of magnetic field along the hexagonal c axis at low temperature gives rise to ferroelectricity for $7 \, \text{T} < H_c < 13.5 \, \text{T}$, and noncollinear proper screw ordering is concomitantly realized. It can be induced by chemical doping as well [8,9]. Since the doping should disturb the balance of frustrated exchange interactions, we can anticipate that external pressure also affects the magnetic ordering. In this study, we investigated and determined the pressure versus temperature magnetic phase diagram (Fig. 2) by the neutron diffraction experiment.

The neutron diffraction pattern at ambient pressure is drastically changed by pressure above 3 GPa (Fig. 3). The low pressure ground state of collinear commensurate uudd configuration (CM1) with $k=(0,1/2,1/2)$ is stable up to 3 GPa, while the k-vector becomes incommensurate $k=(0,q,1/2; q-0.2)$ for 3 ~ 4 GPa (ICM2). Above 4 GPa, the k-vector changes from line of symmetry to general point, $k=(q_x,q_y,q_z; q_x\sim0$, $q_y\sim0.34$, $q_z\sim0.43$) in ICM3 phase. With further increasing pressure, the intermediate temperature phase with collinear sinusoidal spin modulation (ICM1) is survived as short range order down to the lowest temperature 3 K.

In the pressure induced phase, ICM2, we could determined the magnetic structure to be a proper screw one with the polar 21’ magnetic point group. The polar order is also seen in magnetic field or chemical doping induced phase. Magnetic structure refinement for ICM3 could not be carried out due to a small number of measured reflections. However, considering the general k-vector, giving either polar 11’ or nonpolar -11’ magnetic point group and phase stability at low temperature, we can expect the polar 11’ point group
induced phase. Magnetic structure refinement for ICM3 could not be carried out due to a small number of measured reflections. However, considering the general $k$-vector, giving either polar $11'$ or nonpolar $-11'$ magnetic point group and phase stability at low temperature, we can expect the polar $11'$ point group for ICM3 phase. Because, collinear spin density wave with $-11'$ is not generally stable at low temperature for localized spin system.

3.2. Magnetic orderings in high-pressure phases with giant ferroelectric polarization in perovskite TbMnO$_3$[5]

Recently, Aoyama et al. have discovered pressure induced ferroelectric polarization flop phenomenon with drastic enhancement of the polarization value in multiferroic perovskite TbMnO$_3$ [10]. The determined magnetic phase diagram is illustrated in Fig. 4(a). The pressure induced polarization value is further increased by application of magnetic field, leading to the maximum polarization of 1.8 $\mu$C/cm$^2$. Magnetic structures in the high pressure phases have not been experimentally investigated, apart from powder neutron diffraction for limited pressure range [11]. In this work, we performed the neutron diffraction experiment with Hybrid-Anvil-Cell and WISH combination in TbMnO$_3$.

At ambient pressure, the magnetic propagation vector (associated with the cycloid order) for Mn spin order is $k=(0, 0.28, 0)$, while the $k$-vector for Tb moments is $k=(0, 0.42, 0)$ (Fig. 5). When we applied pressure, the incommensurate order is stable with slight change in the incommensurability up to 4.2 GPa. Above the critical pressure 4.5 GPa reported in the polarization measurement, the peak position is significantly changed to the commensurate $(0, 3/2, 0)$, indicating $k=(0, 0.5, 0)$. Since the $E$-type spin configuration for Mn spins gives reflections on $(0,1/2+-m, n)$ with only $n$-odd due to antiferromagnetic stacking along the c axis, the reflection with $n$-even originates from Tb ordering. Application of magnetic field along the a-axis gives rise to disappearance of $n$-even (Tb order) above the critical field 2 T, and instead, reflections associated with $k=(0, 0, 0)$ are induced by the field. In contrast, the $E$-type Mn order is kept even above 2 T (Fig. 6).

As the results of magnetic structure refinements for high pressure and low field (HP-LF) phase, and HP and high field (HP-HF) phase, we determined the magnetic structures including Tb as well as Mn orderings (Fig. 4(b,c)). The magnetic order for Mn spins was determined to be the $E$-type structure with polar magnetic point group 2mm, in both two phases. For Tb moments, the noncollinear polar ordering (Fig. 4(b)) gives the best result in this refinement for the data measured at 7.5 K, 0 T and 5.0 GPa in HP-LF phase. On the other hand, for HP-HF phase (1.5 K, 8 T and 5.0 GPa), the Tb ordering was determined to be nonpolar $k=(0, 0, 0)$ structure (Fig. 4(c)).

We thus have understood nature of the phase transitions observed in the previous polarization measurements. The giant ferroelectric polarization with magnitude of order 1.0 $\mu$C/cm$^2$ is induced by the E-type magnetic ordering for Mn spins. Moreover, determining the additional Tb spin orderings, we can propose that the magnetic field induced polarization enhancement occurs via a mechanism in which the polarization, reduced by polar ordering of the Tb moments in a zero field, is recovered through the field-induced transition from polar to nonpolar Tb orderings at 2 T.
Fig.6 (a,b) Magnetic field dependence of neutron diffraction profile along at 1.5 K and 5.0 GPa [5].

4. Conclusions and Remarks
We have developed the experimental setup for neutron diffraction experiment under multi-extreme conditions, low temperature, high magnetic field and high pressure, by employing Hybrid-Anvil-Cell and the cold neutron TOF diffractometer WISH. As described in this article and original literatures[4,5], we have understood the nature of pressure induced magnetic/dielectric phase transitions in the multiferroics, by measuring high quality data, which is attributed to the well designed pressure cell and high flux and low background diffractometer. Now, we plan to perform experiments on not only multiferroic but also other fields.

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