Study of spin-dependent *d-p* hybridization mechanism on Multiferroic material

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Shunsuke Hasegawa : His specialized field is measurement of magnetic insulator by using neutron scattering method. In this study, S. Hasegawa is responsible for synthesizing single crystal sample and measuring magnetic susceptibility.

Takahito Takeda : His specialized field is measurement of ferromagnetic semiconductor by using Synchrotron radiation spectroscopy. In this study, T. Takeda is responsible for measurement of XAS, XMCD spectra and cluster-model calculation.

Abstract

Multiferroic material $Ba_2MnGe_2O_7$ with spin-dependent *d-p* hybridization mechanism shows magnetic anisotropy correlated with electric polarization. The orbital state of Mn ions may be important for this anisotropy. However, the detailed mechanism is still unclear. In this study, we measure x-ray absorption spectroscopy and x-ray magnetic circular dichroism spectra and analysis by cluster-model calculation. We found that Mn ions exist as a divalent (Mn^{2+}) and the *d*-orbital of Mn ions hybridized with *p*-orbital of ligand oxygen.

1 Introduction

Multiferroic material indicated material which has magnetic order and electric order simultaneously. It is studied for energy saving device and cross-correlation of non-conjugated physical quantity. One of the origins of electricity derived from spins is spin-dependent *d-p* hybridization mechanism [1]. In this mechanism, *d* orbital of magnetic ion and *p* orbital of ligand which are separated by its spin state owing to spin-orbit interaction hybridized with each other. Remarkable feature of this mechanism is that the electric polarization depends on spin state of hybridized orbital at local cluster. Furthermore, this hybridized orbital may influence magnetic anisotropy through spin-orbit interaction.

Multiferroic material $Ba_2MnGe_2O_7$ with spin-dependent *d-p* hybridization mechanism shows magnetic anisotropy correlated with electric polarization. Figure 1(a) shows a temperature dependence of spin-flop field which corresponds to magnitude of magnetic anisotropy. In ordinal magnet, it is known that the temperature dependence of spin-flop field is scaled to temperature dependence of spin

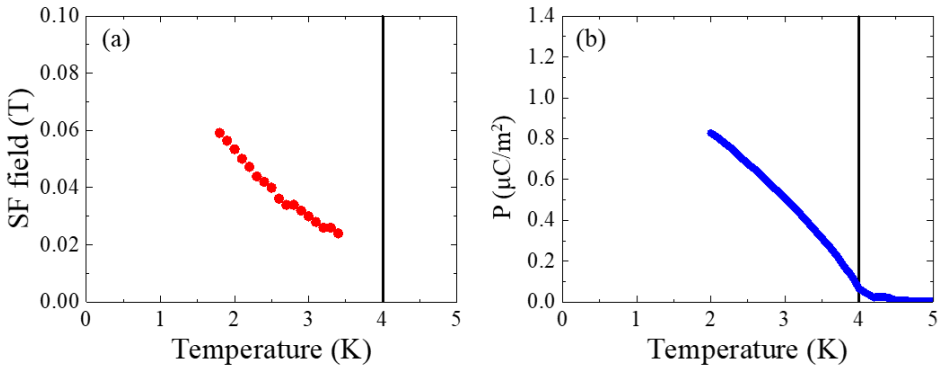

Fig. 1. (a) Temperature dependence of spin-flop field. (b) Temperature dependence of electric polarization[2].

which shows almost no-temperature dependence at low temperature. On the other hand, the spin-flop field is still increasing below 2 K in which spin is saturated in $Ba_2MnGe_2O_7$. Furthermore, spin-flop field monotonically increases from Neel temperature 4 K like an electric polarization as shown in Figure 1(b) [2]. This suggests that hybridized orbital of magnetic Mn ions and ligand O ions in spin-dependent *d-p* hybridized mechanism influenced magnetic anisotropy.

In this study, we focus on orbital of multiferroic material $Ba_2MnGe_2O_7$ which has non-trivial magnetic anisotropy correlated with electric polarization. Since orbital of Mn ions which are combined with O ions is important, we examined electronic structure by elementally selective measurements.

2 Experiment

X-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) measurements were performed to study the electronic structure and magnetic properties of Mn ions in $Ba_2MnGe_2O_7$. XAS and XMCD at the $L_{2,3}$ absorption edge of 3*d* transition metal are the powerful methods to unveil the electronic structure related with the magnetism. The orbital and spin magnetic moments can be estimated individually by the XAS and XMCD spectra using the sum rules [3]. Here, two ways to measure XAS and XMCD signals were used. One was the total electron yield (TEY) mode in which the compensation current was measured. The other was the total fluorescence yield (TFY) mode in which the fluorescent emission was measured. Since the TFY spectra are distorted by self-absorption effects, the effects need correction in the spectra for applying the sum rule. TEY-XAS experiments were conducted at BL23SU at SPring-8 under the condition of $T = 50$ K and $H = 0$ T. TFY-XAS and TFY-XMCD experiments were performed at BL-16 at Photon Factory under the condition of $T = 15$ K and $H = 5$ T. Note that the direction of the magnetic field against the crystal axis is uncertain since the preliminary experiments were not enough due to COVID-19. Since the XAS spectra are not changed by the magnetic-field direction, we mainly discuss the XAS spectra below.

The electronic-structure parameters of the Mn ions were estimated by comparing the cluster-model calculation with the observed XAS spectra. Here, the cluster-model calculation is a computational

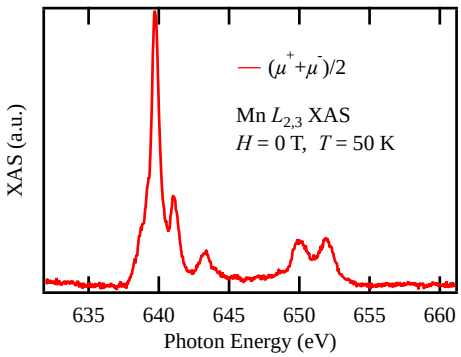

Fig. 2. TEY-XAS spectrum of $Ba_2MnGe_2O_7$ at Mn $L_{2,3}$ absorption edge.

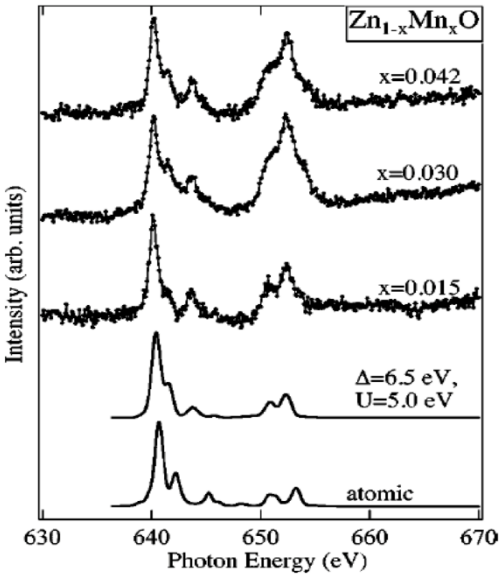

Fig. 3. TEY-XAS spectrum and the results of cluster-model calculation of (Zn,Mn)O at Mn $L_{2,3}$ absorption edge [4] .

method in which the electronic structure of the "cluster", which consists of one ion and the ligands, can be elucidated by calculating the wave function of the linear combination of the charge-transfer states.

3 Result

A) TEY-XAS

The TEY-XAS measurements at T = 5 K, 50 K, and room temperature were conducted. However, the signal was not obtained at T = 5 K since the compensation current did not flow due to the insulating nature of $Ba_2MnGe_2O_7$. Although the TEY-XMCD measurements at T = 50 K were conducted with applying the magnetic field, the TEY signal disappeared under finite magnetic fields as weak as H = 0.1 T. Since this phenomenon does not happen in the case of non-insulators, insulating nature of $Ba_2MnGe_2O_7$ will be related to the disappearance of the TEY signal under magnetic fields. Then, the only TEY-XAS measurements at T = 50 K and H = 0 T were performed. The XAS spectrum at the Mn^{2+} $L_{2,3}$ absorption edge is shown in Figure 2. This spectrum is similar to that of (Zn,Mn)O as shown in Figure 3[4]. This result suggests that the Mn ions in $Ba_2MnGe_2O_7$ are mainly 2+.

B) TFY-XAS and XMCD

The TFY measurements were conducted due to the difficulty of the TEY measurements at low temperatures and under magnetic fields. Figure 4 shows the XAS and XMCD spectra taken in the TFY mode at T = 15 K、H = 5 T. Comparing the TFY-XAS spectrum in Figure 4 with the TEY-XAS spectrum in Figure 2, their line shapes are clearly different from each other. Especially, the ratio of

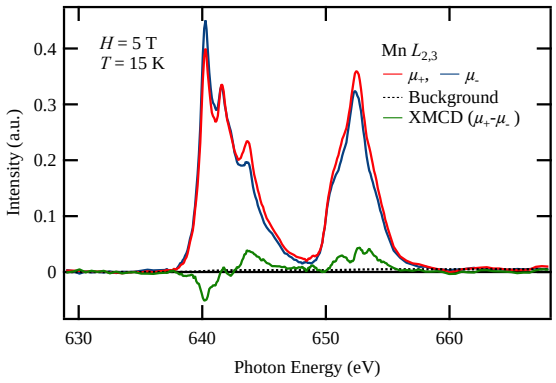

Fig. 4. TFY-XAS and XMCD spectrum of $Ba_2MnGe_2O_7$ at Mn $L_{2,3}$ absorption edge.

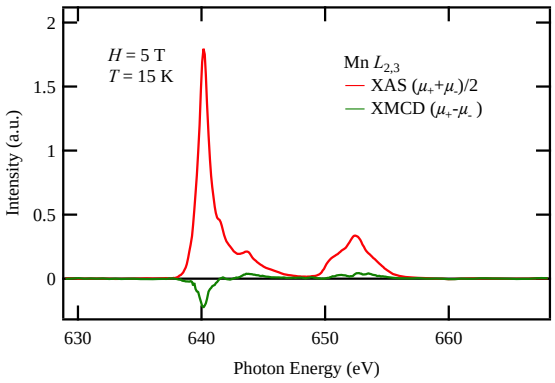

Fig. 5. Corrected TFY-XAS and XMCD spectrum of $Ba_2MnGe_2O_7$ at Mn $L_{2,3}$ absorption edge.

the peaks of L_2 and L_3 absorption edges significantly differs in the two modes. This spectral distortion in the TFY-XAS spectrum originates from self-absorption effects. Figure 5 shows the TFY-XAS and XMCD spectra corrected for the self-absorption effects.

C) Cluster-model calculation

The cluster-model calculation was performed in order to reproduce the XAS spectrum in Figure 5. A Mn ion in $Ba_2MnGe_2O_7$ is surrounded by four O ions with tetrahedral symmetry. That is, the Mn ion is affected by the tetrahedral crystal filed. The results of the cluster-model calculation for Mn^{2+} with varying crystal-filed splitting (10Dq) are shown in Figure 6. The charge-transfer energy (Δ), Slater-Koster parameter ($pd\sigma$), and d-d Coulomb interaction (U_{dd}) are estimated to be 6.5 eV, -1.65 eV, and 6.0 eV, respectively. These parameters are set in reference to those of (Zn,Mn)O [4]. As shown in Figure 6, the result with 10Dq = 0.3 eV well reproduces the experimental spectrum in Figure 5. Under the condition of 10Dq = 0.3 eV, the ratio of the charge-transfer states is $3d^5$:$3d^6\underline{L}$:$3d^7\underline{L}^2$ =

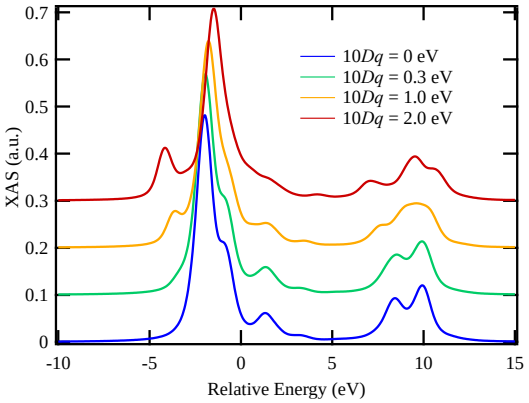

Fig. 6. 10Dq dependence of the XAS spectra by the cluster-model calculation at Mn^{2+} $L_{2,3}$ absorption edge.

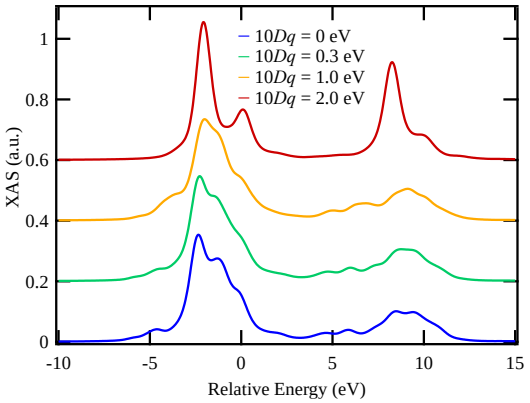

Fig. 7. 10Dq dependence of the XAS spectra by the cluster-model calculation at Mn^{3+} $L_{2,3}$ absorption edge.

85.8%:13.6%:0.5%, where $\underline{L}$ means a hole in the 2*p* orbital of an O ion. For example, $3d^6\underline{L}$ means the state in which an electron in the 2*p* orbital of an O ion transfers to the 3*d* orbital of a neighboring Mn^{2+} ion. As a reference, the results of the cluster-model calculation for Mn^{3+} is shown in Figure 7 with the same electronic structure parameters for the Mn^{2+} in Figure 6. Since the calculated spectrum for Mn^{3+} is clearly different from that for Mn^{2+} shown in Figure 5, Mn ions in $Ba_2MnGe_2O_7$ is expected to be 2+.

4 Discussion

Since any XAS and XMCD studies of $Ba_2MnGe_2O_7$ have never been reported so far, this is the first study of them in this material. Although it is expected that TEY measurements on $Ba_2MnGe_2O_7$ is difficult due to the insulating nature, we tried conducting the measurements. The TEY-XAS measurements without magnetic field are practicable. On the other hand, the measurements applied magnetic fields are impracticable. Then, we have found that TFY measurements are indispensable to measure the XMCD spectra in $Ba_2MnGe_2O_7$. Since the TFY spectra are generally distorted by self-absorption effects, correction for the self-absorption effects is essential in the TFY spectra to apply the sum rules. Since this correction requires the TEY-XAS spectrum irrespective to the self-absorption, the observation of the TEY-XAS spectrum at $H = 0$ T is valuable in the present study.

Comparing the TEY-XAS spectrum in Figure 2 and the corrected TFY-XAS spectrum in Figure 5, there are differences in the spectral line shape at the L_2 absorption edge. This is probably caused by the difference of the probing depth of TEY (~tens nm) and TFY (~hundreds nm). Since the probing depth of TFY is longer than that of TEY, the TEY spectra are more easily affected by the surface contamination, such as the Mn suboxide, than the TFY spectra. Figure 5 also shows the XMCD spectrum. The smallness of the XMCD can be explained by the higher measurement temperature (50 K) than the Neel temperature (4.0 K) and the small susceptibility of $Ba_2MnGe_2O_7$ [5]. In order to study the electronic states in the antiferromagnetic state, the experimental equipment needs improvment to realize the ultra-low temperatures below 4.0 K. This is one of the future challenging work.

The result of the cluster-model calculation suggests that Mn 3*d* states consist of mainly $3d^5$ and partly $3d^6\underline{L}$. This electronic structure indicates that Mn^{2+} is in the high-spin state and the orbital magnetic moment is negligibly small. This is consistent with the magnetic properties that Mn ions have $S = 5/2$ and the magnetic anisotropy is small due to the week spin-orbit interaction. The existence of the $3d^6\underline{L}$ state suggests there is the finite *d*-*p* orbital hybridization in $Ba_2MnGe_2O_7$.

According to the previous studies [5,6], MnO_4 clusters in $Ba_2MnGe_2O_7$ have compressed strain along the *c*-axis direction and two-types of rotation in *ab* plane. However, the effects of them are not contained in the present cluster-model calculation. To reveal the role of the distortion for the magnetic behavior, we will perform the cluster-model calculations taking into account for the distortion and analyze the XAS and XMCD spectra in details.

5 Summary and Future work

In this self-directed joined research, it was found that Mn ions in multiferroic material $Ba_2MnGe_2O_7$ is divalent (Mn^{2+}), and its spin state is high spin state with almost no orbital magnetic moment from comparison of cluster-model calculation with XAS, XMCD spectrum. This is consistent with spin state from the point of view of magnetic susceptibility and neutron scattering. In addition, the orbital of Mn ions is hybridized with orbital of O ions. However, it is difficult to find correlation of this hybridization and non-trivial magnetic anisotropy. $Ba_2CoGe_2O_7$ in which Mn ions are replaced by Co ions shows same magnetic anisotropy of $Ba_2MnGe_2O_7$ [7]. On the other hand, the temperature dependence of spin-flop field shows saturation at low temperature as shown in Figure 8(a). In here, we focus on $Ba_2Mn_xCo_{1-x}Ge_2O_7$. When x = 0.5, the temperature dependence of spin-flop field shows saturation in low temperature as shown in Figure 8 (b). This result implies that the orbital state of Mn ions in $Ba_2Mn_{0.5}Co_{0.5}Ge_2O_7$ is different from $Ba_2MnGe_2O_7$, so that the magnetic anisotropy was changed. By comparing measured XAS and XMCD spectrum and cluster-model calculation of $Ba_2Mn_{0.5}Co_{0.5}Ge_2O_7$, it is expected that further discussion can be held.

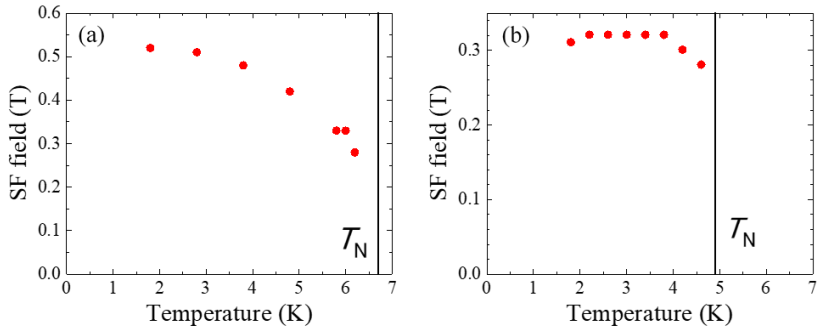

Fig. 8. (a) The temperature dependence of spin-flop field in $Ba_2CoGe_2O_7$. T_N = 6.7 K.
(b) The temperature dependence of spin-flop field in $Ba_2Mn_{0.5}Co_{0.5}Ge_2O_7$. T_N = 4.9 K.

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