Microscopic Origin of the Ferroelectricity in Multiferroics $SmMn_2O_5$ Studied by Resonant Soft X-Ray Scattering

We investigated magnetic ordering and electronic state in multiferroic $SmMn_2O_5$. This material has a relatively large electric polarization among members of the RMn_2O_5 (R = rare earth) family and other type-II multiferroic materials. However, the microscopic origin of this large electric polarization was unknown. Our resonant soft X-ray scattering study at the Photon Factory suggested that ionic displacements via a collinear magnetic structure mainly contribute to the large electric polarization, based on measurements of magnetic ordering of the rare-earth, Mn, and also ligand O ions. In addition, the study revealed unique electronic states of Mn and O ions in $SmMn_2O_5$.

So-called type-II multiferroics, where ferroelectricity is driven by magnetic ordering, have attracted intense research interest for several decades. Some of them exhibit a non-linear magnetoelectric (ME) effect, in which the application of an external magnetic (electric) field leads to striking changes of the dielectric (magnetic) properties of the materials. Among them, RMn_2O_5 (R = rare earth) compounds have attracted much attention since they show various ME effects depending on the type of rare-earth ions. Since these ME effects are believed due to the complex magnetic ordering of rare-earth and Mn ions, revealing the magnetic structure is key to understanding the mechanism of multiferroicity in this family. Neutron scattering has been commonly used to observe the magnetic ordering. Resonant soft X-ray scattering (RSXS) is also an effective tool, particularly for materials containing neutron absorber elements, such as Sm or Gd. Furthermore, RSXS makes it possible to detect the electronic state of ions selectively.

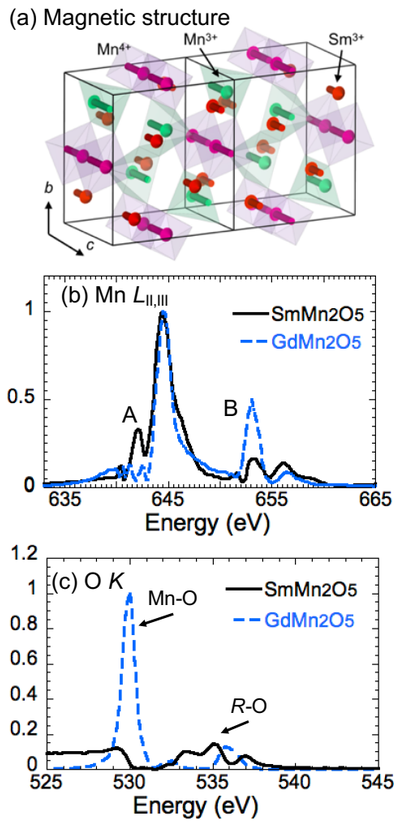

Figure 1: (a) Magnetic structure of Sm and Mn ions. **(b) (c)** Energy spectra around Mn $L_{II,III}$ and O K edges, respectively, in $SmMn_2O_5$ and $GdMn_2O_5$.

$SmMn_2O_5$ has a relatively large electric polarization in the RMn_2O_5 family and multiferroic materials. Our previous resonant hard X-ray scattering study [1] reported a collinear magnetic structure of Sm and Mn ions, where the moments point to the c-axis, as shown in Fig. 1(a), which is responsible for the large electric polarization via exchange interaction. However, a more microscopic origin of the electric polarization, such as magnetic-driven ionic displacements and charge transfer between O and Mn ions, remains elusive. Here we employed RSXS for $SmMn_2O_5$ to observe the magnetic ordering and electronic state of Mn and also O ions, and discuss the mechanism of the ferroelectricity in this material [2].

Figure 1(b) shows RSXS spectra of magnetic reflections around Mn $L_{II,III}$ edges of $SmMn_2O_5$, and also $GdMn_2O_5$ for comparison. The spectrum of $GdMn_2O_5$ is similar to those acquired from other RMn_2O_5 [3]. Meanwhile, somewhat different parts were observed in the spectrum of $SmMn_2O_5$. The intensity increases around E = 642 eV [indicated by A in Fig. 1(b)], while it decreases and another peak appears around E = 652 eV (indicated by B). These differences likely reflect the unique electronic state of Mn ions in $SmMn_2O_5$.

We also observed a magnetic reflection around the O K edge in both $SmMn_2O_5$ and $GdMn_2O_5$ [see Fig. 1(c)]. The spectrum of $GdMn_2O_5$ has a strong peak around E = 530 eV, which indicates the spin polarization of O ions as a result of charge transfer from O to Mn ions. Similar spectra have been also acquired from RMn_2O_5 (R = Tb, Y, Er) [3–5]. A previous RSXS study suggested that this charge transfer makes a primary microscopic contribution to the ferroelectricity in RMn_2O_5 [5]. In sharp contrast, $SmMn_2O_5$ exhibits no evident

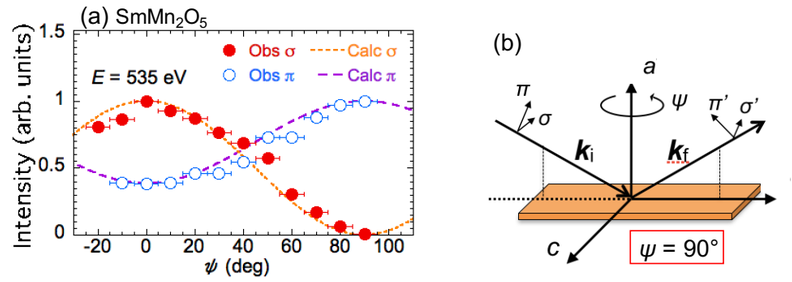

Figure 2: (a) Azimuthal angle dependence of resonant intensities at E = 535 eV and calculation values. **(b)** Experimental geometry at ψ= 90 deg.

peak around E = 530 eV, which suggests that the large electric polarization is mainly caused by not the charge transfer, but ionic displacements due to exchange interaction. Furthermore, this electronic behavior could lead to changes of the effective charge of Mn ions [6], which results in a different spectrum around Mn $L_{II,III}$ edges.

Meanwhile, several peaks were observed around E = 535 eV in $SmMn_2O_5$. This energy range is associated with charge transfer to rare-earth 5d states. Similar rare-earth 5d state contributions have been also observed in $GdMn_2O_5$ [as shown in Fig. 1(c)] and $TbMn_2O_5$ [4]. Hence it can be concluded that spin polarization of O ions is induced by charge transfer between only O and Sm ions. Figure 2(a) presents the azimuthal angle (ψ) dependence of the resonant intensity at E = 535 eV in $SmMn_2O_5$. The experimental geometry is shown in Fig. 2(b), where we defined ψ = 90 deg. when the c-axis is perpendicular to the scattering plane. Figure 2(a) also shows calculation values on the assumption that magnetic moments of O ions point in the direction of the c-axis, which reproduces well the experimental values. This is consistent with our conclusion that magnetic moments of O ions are induced by Sm moments. However, the details of these unique electronic states of O and Mn ions are still unclear; further theoretical and experimental studies are required.

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BEAMLINES

BL-3A, BL-4C, BL-8A, BL-16A and BL-19B

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