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研究課題名（和文）Exploring novel magnetoelastic coupling via polyhedral or molecular rotation in unusual quantum spin systems

研究課題名（英文）Exploring novel magnetoelastic coupling via polyhedral or molecular rotation in unusual quantum spin systems

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研究成果の概要（和文）：多面体および分子の回転に関係された独特な自己-格子結合を研究するため、ペロブスカイトと超酸貨物を研究した。 結晶構造と磁気構造分析は現在進行中だ。
超高分解能中性子回折装置を使用して、CoF3とFeF3の常温磁気構造を確認して、40 K以下でCoF3の約強磁性相転移を発見した。Co反強磁性スピン方向とDM相互作用から、Co反強磁性スピン回転による約強磁性メカニズムが予想される。

研究成果の概要（英文）：Exploring novel magnetoelastic coupling via polyhedral or molecular rotation in unusual quantum spin systems, we studied perovskite-type TF3(T=Sc, Ti, Cr, Mn, Fe, Co), superoxide KO2, and etc. The crystal and magnetic structural analysis is going well.
E. O. Wollan et al.(Phys. Rev. 112 1132) reported magnetic structure of CoF3 and FeF3. However, (101) and (003) hexagonal peaks were not distinguished well due to poor resolution of neutron powder diffractometer. By using high resolution neutron powder diffractometer, we confirm the magnetic structure at room temperature. The Fe antiferromagnetic moment is inside hexagonal plane while Co antiferromagnetic moment is parallel with c-axis. DM interaction induces spin canting in the case of FeF3 that causes weak-ferromagnetism. In addition, we find low-temperature weak-ferromagnetic transition in CoF3. This result suggest the Co spin canting will induces weak-ferromagnetism by DM interaction below 40 K.

研究分野：　Magnetism

キーワード：　Perovskite　Fluoride　Superoxide　Neutron diffraction　Magnetism　Crystallography　Phase transition

１．研究開始当初の背景

When magnetic moment ordered in condensed matter, it interplays with another degree of freedom such as the lattice. It is called magnetoelastic coupling which type is strictly followed by crystal and magnetic symmetry.

MnO, CoO, and NiO are standard antiferromagnetic materials which is extensively studied for last several decades. However, detailed crystal and magnetic structure, phase transition mechanism are so debates. Recently, we found spin-direction-dependent magnetoelastic coupling in transition metal monoxide [1]. The exact spin direction or spin symmetry is hidden mechanism to distinguish different magnetic phase transition. The MnO is gamma1 magnetic structure with discontinuous phase transition. Their spin direction is fixed symmetrically. On the other hand, NiO and CoO are gamma2 magnetic structure with continuous phase transition. The spin direction can be rotated. In addition, Gamma2 magnetic structure show unusual linear-cubic magnetoelastic coupling forbidden by time-reversal symmetry.

These results inspire me to explore unusual magnetoelastic coupling forbidden by time-reversal symmetry. It is related with the issue of general magnetic symmetry beyond typical time-reversal symmetry.

２．研究の目的

The double antisymmetry space group introduces rotation-time reversal symmetry [2]. If both rotational axial vector and magnetic axial vector can be reversed simultaneously by rotation-time reversal symmetry, it can allow unusual linear-cubic magnetoelastic coupling forbidden by time-reversal symmetry alone. Because of the edge sharing octahedral of transition metal monoxide, double antisymmetry space group is difficult to apply the case of MnO, CoO, and NiO directly. Thus, we interest the magnetic system which have polyhedral rotation and magnetic moments. The candidates are transition metal trifluoride, KO_2, and etc.

３．研究の方法

The samples are prepared from company or collaborators. We characterize crystal structure by XRD and magnetic properties by SQUID. We employ time-of-flight neutron powder diffractometer, which is SuperHRPD beamline in MLF, J-PARC, to study detailed crystal and magnetic structure simultaneously. The Rietveld analysis is carried out by Z-Rietveld and Fullprof. For advance crystallography and group theory, we used SARAh, bilbaocrystallographic server and ISOTROPY.

４．研究成果

The several experimental results are still under analysis. Those results will be published as soon as possible after summary. Here, I introduce briefly the recent publication of CoF_3 and FeF_3 study [3].

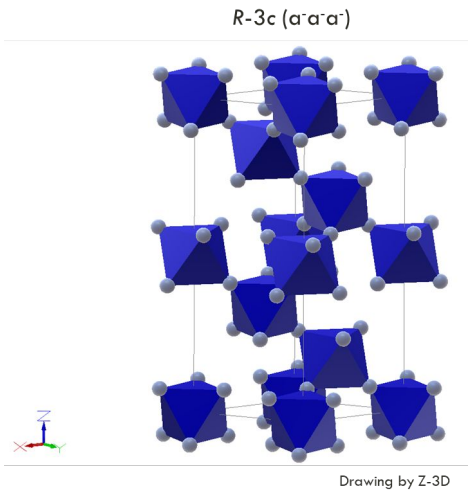

Fig.1 Crystal structure (R-3c, a⁻a⁻a⁻) of CoF_3 and FeF_3.

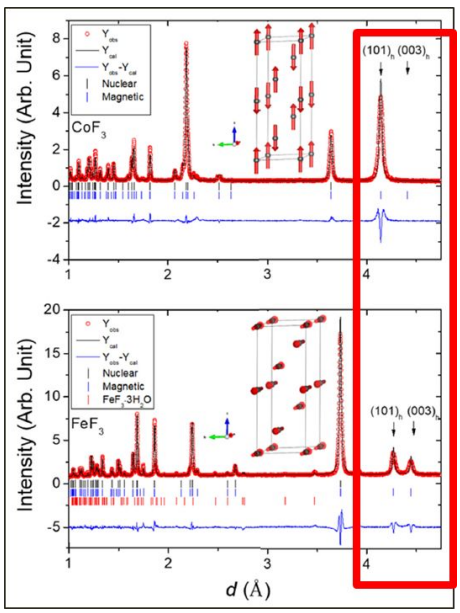

Fig. 2 Time-of-flight neutron diffraction of CoF3 and FeF3 at room temperature.

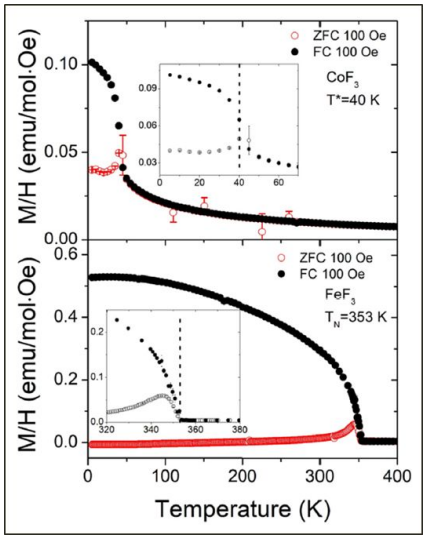

Fig. 3 Magnetic susceptibility measurement of CoF_3 and FeF_3.

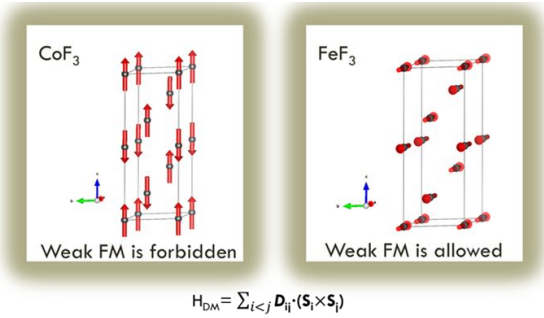

Fig. 4 Weak-ferromagnetism can be induced by DM interaction. At room temperature, weak-ferromagnetism is allowed in FeF_3 magnetic structure.

Cobalt trifluoride CoF_3 and Iron trifluoride FeF_3 have *R*-3*c* space group which is described by Glazer tilting system a-a-a-. From simple cubic perovskite *Pm*-3*m*($a^0a^0a^0$), The octahedral rotates along [100], [010], and [001] pseudocubic direction with antiphase rotation of nearby octahedral. Figure 1 display CoF_3 and FeF_3 crystal structure in hexagonal setting.

These CoF3 and FeF3 crystal and magnetic structure were investigated by early angle-dispersive neutron powder diffractometer[4]. However, it couldn't distinguish 101, 003 magnetic peaks clearly. Thus, proposed magnetic structure are not confirmed completely. As shown in Figure 2, we distinguish 101, 003 magnetic peaks unambiguously that confirm previously proposed magnetic models. At room temperature, Co spins are parallel with hexagonal c-axis while Fe spins are perpendicular to c-axis.

In Fig. 3, magnetic susceptibility measurement shows additional weak-ferrimagnetic transition of CoF_3 at 40 K which is below well-known antiferromagnetic transition 460 K.

Dzyaloshinsky-Moriya(DM) interaction is antisymmetric superexchange interaction which microscopic origin is spin-orbit coupling.DM interaction induces spin canting and cause weak-ferromagnetism. The DM interaction is acting through magnetic atom-ligand-magnetic atom path when there is no inversion symmetry at ligand atomic position. The octahedral rotations shift ligand atoms from inversion symmetry of ideal cubic perovskite. Thus, octahedral rotations are necessary condition for DM interaction.

Since the uncancelled DM vector is parallel with c-axis, DM interaction can induce weak-ferromagnetism such as FeF_3 case. Fe spins are perpendicular to c-axis. Canted Fe spin inside hexagonal plane can reduce total energy through DM interactions while Co spins are parallel with c-axis which has no lower energy via DM interaction. Therefore, only FeF_3 has weak-ferromagnetism at room temperature.

However, as shown in Fig. 3, we find additional weak-ferromagnetism in CoF_3 unexpectedly. The room-temperature CoF_3 magnetic structure can't cause weak-ferromagnetism. In-plan Co spin component is necessary for weak-ferromagnetism. From this antiferromagnetic spin direction and DM interaction, we expect that Co spin will be rotated. After that, in-plan Co spin component will induce weak-ferromagnetism. We carry out further structural study to clarify this weak-ferromagnetism mechanism. It is under analysis.

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② V. Gopalan and D. B. Litvin, Nat. Mater. 10, 376 (2011)

③ S. Lee et al, Physica B: Condensed Matter (2017)
DOI: 10.1016/j.physb.2017.11.082

④ E. O. Wollan *et al.*, Phys. Rev. **112** 1132 (1958)

5．主な発表論文等

〔雑誌論文〕（計　1　件）

① Sanghyun Lee, Shuki Torii, Yoshihisa Ishikawa, Masao Yonemura, Taketo Moyoshi, Takashi Kamiyama, Physica B: Condensed Matter (2017)
DOI: 10.1016/j.physb.2017.11.082

〔学会発表〕(計 8 件)

① 16th Korea-Japan meeting on Neutron Science, Kashiwa in Japan (Jan. 8-10, 2018)
② 24th Congress and General Assembly of the international Union of Crystallography, Hyderabad in India (21-28, August 2017)
③ MRS-Ina C&C 2017, Yogyakarta, Indonesia (8-12, October, 2017)
④ Theme Meeting on Neutron Scattering, Mumbai in India (19, Aug, 2017)
⑤ International Conference on Neutron Scattering, Deajeon in Korea, (July 9-13, 2017)
⑥ 2016 年度量子ビームサイエンスフェスタ, Tsukuba in Japan (March 14-15, 2017)
⑦ 14th Conference of the Asian Crystallographic Association, Hanoi in Vietnam (4-7 December 2016)
⑧ EMN Dalian Meeting, Dalian in China (25-29, July, 2016)

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