Quadrupole Orders in the Spin–Orbit-Coupled 5*d* Mott Insulator Ba_2MgReO_6

The crystal structure of the double perovskite Ba_2MgReO_6 having spin–orbit-entangled 5*d* electrons was investigated by X-ray diffraction measurements using high-quality single crystals. The high-intensity and high-resolution synchrotron X-ray source at BL-8A and AR-NE1A enabled us to detect extremely small structural changes through the quadrupole order transition at T_q = 33 K. We observed a slight elongation and a rhomboid distortion of the ReO_6 octahedron, which reveal that the quadrupolar order is composed of antiferroic Q_{x2-y2} and ferroic Q_{3z2-r2} quadrupole moments. These findings demonstrate a unique symmetry-breaking of the multipolar degree of freedom in 5*d* electron systems.

Recently, 5*d* transition metal (TM) compounds have been attracting attention because of the combined effect of electron correlations and spin–orbit interactions (SOIs). For example, strong SOIs in Sr_2IrO_4 effectively enhance electron correlations, and a spin–orbit-entangled Mott insulating state is realized [1]. The 5*d* electrons with strong spin–orbit entanglement may experience various symmetry-breaking transitions, called multipolar orders [2]. Indeed, multipolar orders are predicted to be realized in 5*d* compounds with the d^1 electronic configuration [3]. However, the multipolar order in 5d electron systems has not yet been experimentally well established. The higher-order multipolar order is generally subtle and hard to observe by conventional experimental probes. In addition, 5*d* compounds that show the characteristic features of multipolar orders are lacking thus far.

We focus on a double perovskite (DP) compound, Ba_2MgReO_6 (Fig. 1a). The DP structure is an ordered perovskite structure where the B site in the perovskite ABO_3 is occupied by two kinds of cations in a rock salt manner. In Ba_2MgReO_6, nonmagnetic Mg^{2+} ion and Re^{6+} ion with $5d^1$ electronic configuration occupy B and B′ sites, respectively. Ba_2MgReO_6 is a Mott insulator with a magnetic transition at T_m = 18 K. Another transition was observed at T_q = 33 K in heat capacity, where the slope of the inverse of magnetic susceptibility changes. A spin–orbit-entangled electronic state of Re^{6+} ion is inferred from the reduced effective magnetic moment of ~0.68μ_B and the total electronic entropy close to *R*ln4 [4]. These observations strongly suggest a quadrupolar order in the intermediate phase between T_m and T_q. However, the nature of the phase transition at T_q remains unclear. To reveal the characteristics of the phase transitions at T_q, we performed detailed X-ray diffraction measurements. To reveal the characteristics of the phase transitions at Tq, we performed detailed X-ray diffraction measurements [5].

XRD experiments were conducted on the beamlines BL-8A and AR-NE1A. An incident X-ray with a wavelength λ of 0.690 Å was used at BL-8A and high-flux and short-wavelength X-ray beams with λ = 0.418 Å were used at AR-NE1A in order to detect weak superlattice reflections.

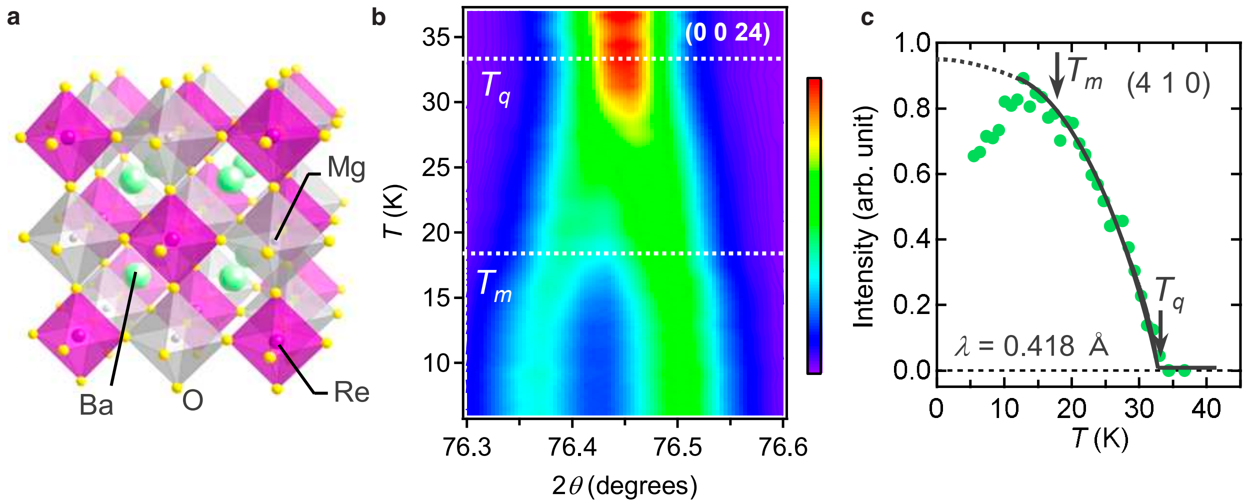

Figure 1: **a** Double perovskite structure of Ba_2MgReO_6. **b** The peak splitting of the (0 0 24) reflection at T_q. **c** Temperature dependence of the intensity of a superlattice reflection (4 1 0) of the tetragonal cell.

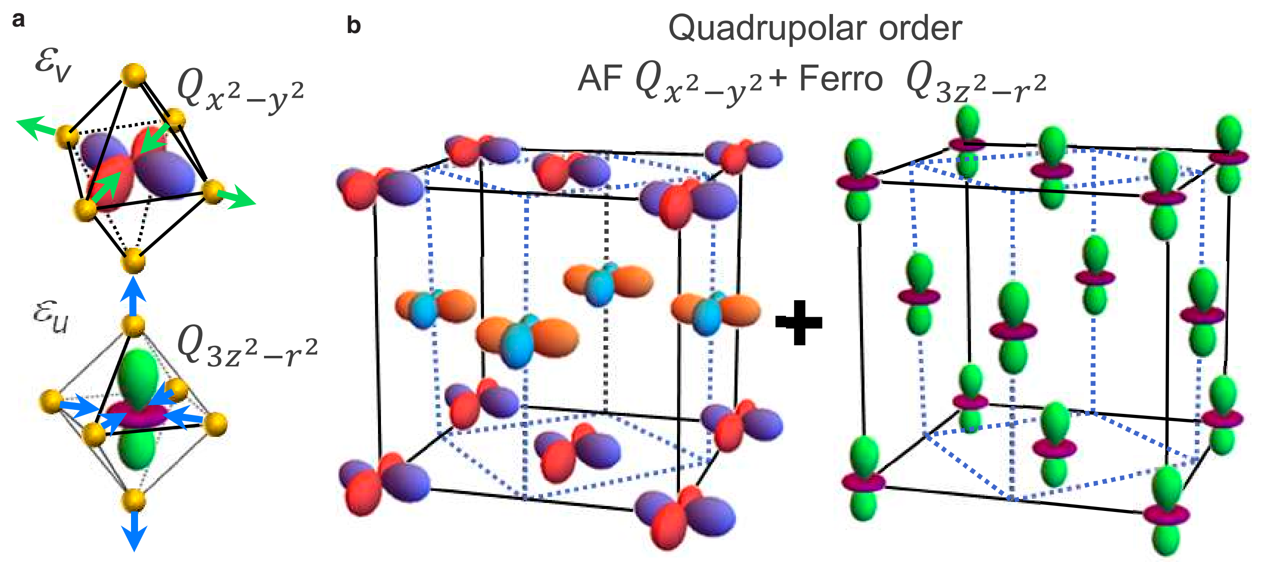

Figure 2: **a** The quadrupolar moments Q_{x2-y2} and Q_{3z2-r2}, which couple with the ε_v and ε_u displacement modes represented by the green and blue arrows, respectively. **b** Observed quadrupolar order patterns in Ba_2MgReO_6.

Extremely small structural changes through the transition at T_q = 33 K were successfully observed thanks to the high-intensity and high-resolution synchrotron X-ray. As shown in Fig. 1b, a splitting of the (0 0 24) Bragg peak is observed, which indicates a cubic-to-tetragonal structural transition. The tetragonal distortion gradually grows below T_q on cooling, resulting in a very small distortion of ~0.09% at 25 K. In addition to such peak splittings, 141 superlattice reflections, which are extremely weak (less than 0.005% of the strongest fundamental reflection), are observed below T_q. For example, the intensity of (4 1 0) superlattice reflection based on the low-temperature tetragonal structure appears at T_q and increases gradually with decreasing temperature, as shown in Fig. 1c. Based on the reflection conditions observed for the superlattice reflections, we conclude that the low-temperature structure is a tetragonal structure with the space group $P4_2/mnm$ (136).

The structural model with the tetragonal $P4_2/mnm$ space group nicely reproduces the intensities of all the observed 141 superlattice reflections as well as those of the fundamental reflections. In this model, the single oxygen site in the high-temperature cubic structure splits into three types of oxygen sites, which leads to a slight elongation of the ReO_6 octahedron in the *c* direction and a rhomboid distortion on the (0 0 1) plane. This distortion can be decomposed into two normal modes of an octahedron ε_u and ε_v (Fig. 2a). A quadrupolar moment, which is an anisotropic distribution of electronic charge, can induce a lattice distortion through electron–phonon interactions. The Q_{x2-y2} and Q_{3z2-r2} quadrupolar moments can linearly couple with ε_u and ε_v modes, respectively. Note that the ε_v distortion is uniform in a layer and stacks in a staggered manner along the c axis, whereas the ε_u distortion is common for all the ReO_6 octahedra. This result indicates an antiferroic Q_{x2-y2} and a ferroic Q_{3z2-r2} quadrupolar order, as depicted in Fig. 2b. Note that the actual quadrupole order is a linear combination of the Q_{x2-y2} and Q_{3z2-r2} orders. Our diffraction study establishes the existence of quadrupolar order for the correlated spin–orbit-entangled *d* electrons in the DP Ba_2MgReO_6. This compound provides an opportunity to experimentally investigate the symmetry-breaking of the multipolar degree of freedom in 5*d* electron systems.

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BEAMLINES

BL-8A and AR-NE1A

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