Orbital Order in Half-Filled Gadolinium Compounds

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The hunt for new functional materials that can be used as 'post-silicon' devices is one of the most important topics in materials research. With this view, strongly correlated electronic systems have been heavily studied because multiple degrees of freedom can be realized from various external triggers and interactions among them generate fascinating exotic properties. For example, spin-orbit coupling interaction can induce multiferroic characteristics in many transition metal oxides. Moreover, the spin Hall effect and topological insulators also come from spin-orbit interactions.

However, in half-filled systems with d^5 or f^7-electron configurations, no orbital moment is expected, which is generally known as 'Hunds' rule'. As a result, in spite of maximized spin moment, there is no spin-orbit coupling and these kinds of half-filled systems have been relatively less studied than other strongly correlated electronic systems. As an exception, anisotropic orbital characteristics have been reported in multiferroic $GaFeO_3$ and its driving force was proposed as the lattice distortion with off-centering site movement. Writing in *Physical Review Letters* [1], scientists from SLAC National Accelerator Laboratory (USA), GIST (South Korea), and Western Michigan University (USA) have discussed an observation of orbital order that was induced by spin orbit coupling in half-filled gadolinium compounds. According to the report, orbital ordering was detected via resonant soft X-ray scattering in GdB_4, and opened a way of studying half-filled Gd compounds as strongly correlated electronic systems.

There have been many studies on rare-earth borides (RB_x, x=2, 4, 6, 12, …). Depending on boron's bonding character, various kinds of orbital and spin orders are formed and exotic properties are realized. For example, superconductivity, heavy fermions, and a signature of a Kondo insulator have been observed in RB_6 series. As another example, RB_4 systems, which have geometrically frustrated Shastry-Sutherland lattice structures among rare-earth sites, show antiferromagnetic phase transition in low temperatures. Interestingly, with the substitution of a small portion of magnetic rare-earth elements by non-magnetic rare-earth elements like Y or Lu, a weak ferromagnetic phase becomes coexistent [2].

In RB_4 systems, orbital order has been reported in DyB_4 and HoB_4 [3]. However, an emergence of orbital order in GdB_4 has been never expected because Gd^{3+} has no orbital moment due to Hunds' rule, although a previous ESR / EPR study proposed the existence of orbital moment [4]. But a recent study of anisotropic tensor susceptibility (ATS) in GdB_4, which was studied by resonant X-ray scattering at the Gd *L*-edge, raised the possibility of the occurrence of orbital moment [5]. Furthermore, in this study [1], ATS was also observed at the Gd *M*-edge, which directly observes a 3d → 4f transition, and this result indicates the existence of orbital moment in the Gd f-band.

It is very surprising that the orbital moment becomes ordered with spin arrangement. GdB_4 becomes antiferromagnetic at 42 K while cooling and its spin structure has been studied by neutron scattering [6]. It is noteworthy that the spin structure has been clarified recently due to a large cross section of neutrons with Gd^{3+}. In this study, for the first time, the spin structure has been studied by resonant X-ray scattering at the Gd *M*-edge. One of the most powerful aspects of resonant X-ray scattering is polarization dependence. Using a linearly polarized X-ray and the exact selection of a scattering plane with respect to the crystalline axis, in addition to an antiferromagnetic signal that is consistent with neutron scattering studies, an unknown signal that cannot be explained by known spin structure was observed in this study. Two distinct features with spin order are photon energy de-

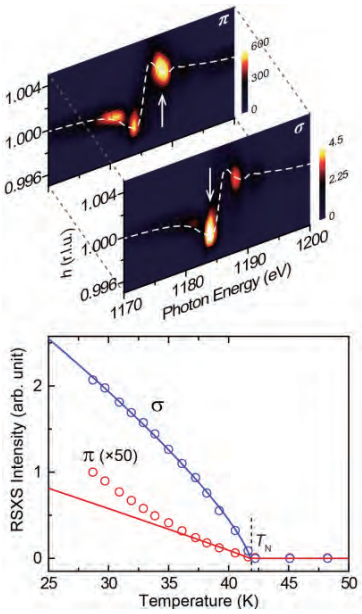

Fig. 1: (Upper panel): Gd M_5-edge photon energy dependence of resonant X-ray scattering signals using different photon polarization. Stronger π-polarization signals represent antiferromagnetic order. Weaker σ-polarization signals represents orbital order. Two energy profiles show different shapes and maximized intensity points show 4 eV differences (1184 and 1188 eV). (Lower panel): π- and σ-polarization signals show different temperature dependence.

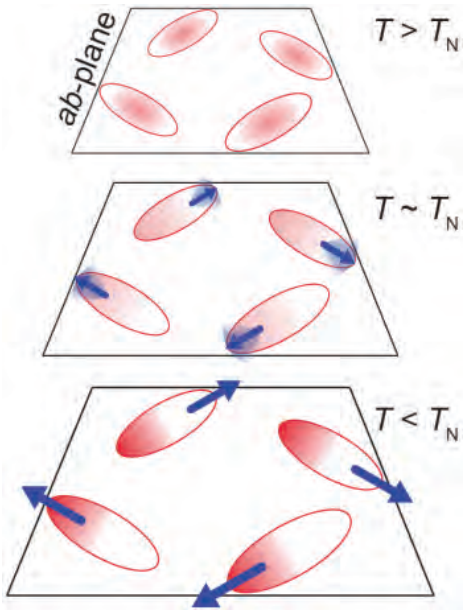

Fig. 2: Temperature dependent spin and orbital order structure changes. (Top panel): Above T_N (=42 K), only anisotropic tensor susceptibility is formed. (Middle panel): At T_N, spin and orbital orders start forming but still with fluctuation. (Bottom panel): Well below T_N, both orders become reinforced and clearly show spin and orbital order.

pendence and temperature dependences (Fig. 1). Note that the signal was much weaker than the antiferromagnetic spin order signal but it could be clearly observed by the resonant effect, which is sensitive to the f-band. In comparison to DyB_4 [5], which shows spin order related orbital order, the unknown order is suggested to be an antiferroquadrupolar orbital order. The maximized photon energy, which coincides with the charge sensitive dispersion term, confirms it as an orbital order. This is also supported by the analysis in X-ray absorption spectroscopy. As a result, the development of spin and orbital order is described in Fig. 2.

This study surprisingly showed a spin-orbit interaction induced orbital order in Gd^{3+} half-filled system. Furthermore, with confirmation of the combination of various degrees of freedom, this study proposed another way of hunting new functional materials.

References

[1] H. Jang et al., Phys. Rev. Lett 117, 216404 (2016).
[2] B. Y. Kang et al., Phys. Rev. B 91, 024414 (2015).
[3] S. Ji et al., Phys. Rev. Lett. 99, 076401 (2007).
[4] B. G. Wybourne, Phys. Rev. 148, 317 (1966).
[5] S. Ji et al., Phys. Rev. Lett. 91, 257205 (2003).
[6] J. A. Blanco et al., Phys. Rev. B 73, 212411 (2006).

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