Helical Ordering of Spin Trimers in $Gd_3Ru_4Al_{12}$ with a Distorted Kagome Lattice

We have found a novel ordering phenomenon of S_T=21/2 spin trimers in a distorted kagome lattice of S=7/2 4*f*-spins of Gd ions in $Gd_3Ru_4Al_{12}$ by resonant X-ray diffraction with polarization analysis. The successive magnetic phase transitions at 18.5 K and 17.5 K were found to be paramagnetic to sinusoidal ordering in the hexagonal c-plane and to helical ordering with both the c-plane and the c-axis components. It is very rare that quantum mechanical multimerization is realized in localized and metallic *f*-electron systems. It is also significant that a spontaneous chiral symmetry breaking was found in the process of sinusoidal to helical successive phase transitions.

In magnetic materials with geometrically frustrated interactions in triangular, kagome, or pyrochlore lattice systems, various kinds of nontrivial orderings are observed: non-collinear and incommensurate spin structures, as well as successive transitions through partially disordered states. Most of them are difficult to predict because a large number of spin structures are generally degenerate. If the magnetic ions are located on a triangular or kagome lattice, and if the exchange interaction is antiferromagnetic, one cannot find a simple structure to satisfy the interactions consistently. In such cases, the system usually ends up with a so-called 120° structure as a result of compromise. In the crystal structure of $Gd_3Ru_4Al_{12}$ shown in Fig. 1, with a distorted kagome, or breathing kagome lattice, one may simply assume that the 120° spin structure should be realized.

However, in $Gd_3Ru_4Al_{12}$, it was recently pointed out by Nakamura that the Gd^{3+} spins of S=7/2 on the nearest neighbor triangle form a ferromagnetic “spin trimer” state with S_T=21/2 [1]. They showed that the anomalous temperature dependence of the magnetic susceptibility and specific heat can be well explained by a spin trimer model $H = -J(S_1 \bullet S_2 + S_2 \bullet S_3 + S_3 \bullet S_1)$ with a ferromagnetic exchange constant of $J = 13.5$ K, where $\boldsymbol{S}_i$ (i = 1–3) represents the S=7/2 spin on the nearest neighbor triangle. Although such quantum spin states are frequently observed in insulating *d*-electron systems with small spin moments, they are rarely observed in mostly metallic *f*-electron systems with relatively large angular moments. The only exception is a spin dimer formation in $YbAl_3C_3$ [2]. The spin trimer formation in $Gd_3Ru_4Al_{12}$ may be the first case in *f*-electron systems.

Another interesting property found in $Gd_3Ru_4Al_{12}$ is the antiferromagnetic phase transitions at 18.5 K and 17.5 K. Since the binding energy of the spin trimer is higher than 100 K, these antiferromagnetic transitions at low temperatures are considered as the orderings among the well-developed ferromagnetic spin trimers. To investigate the ordered spin structure, we have utilized resonant X-ray diffraction at beamline 3A. Compared with neutron diffraction, which is a typical method used to investigate magnetic structures, resonant X-ray diffraction offers the advantages of element and orbital selectivity by using X-ray energies near the absorption edge of the target element, effective usage of a polarized incident beam and polarization analysis, high *Q*-resolution, and applicability for tiny samples. In addition, it has been remarked that the present observation performed for a Gd compound with extremely high neutron absorption is almost impossible by neutron diffraction.

From careful measurements and data analysis, especially from the result of polarization analysis, we concluded that the transition at 18.5 K is an ordering of spin trimers from paramagnetic to sinusoidal structure, and that at 17.5 K is a transition from sinusoidal to helical structure, as shown in Fig. 1 [3].

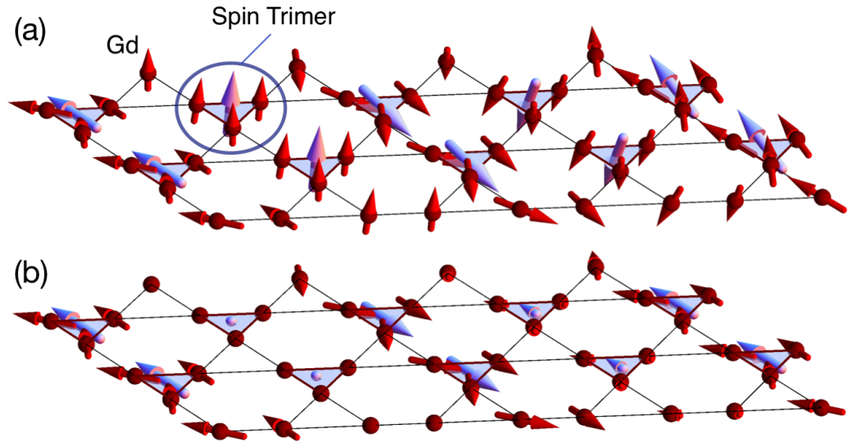

Figure 1: (a) Helical trimer spin structure below 17.5 K, propagating along the a*-axis. The total spins of each trimer are represented by the bigger arrows at the center of the colored triangles. **(b)** Sinusoidal trimer spin structure between 17.5 K and 18.5 K.

An important problem of this sinusoidal structure is that there remain magnetic sites with small, or even vanishing, ordered moments. This means that there remains unreleased magnetic entropy, or degeneracy, which must be lifted at lower temperatures. The sinusoidal structure with $\boldsymbol{q}$ = (0.27, 0, 0) just below the Néel order reflects weak anisotropy in the c-plane and an intrinsic magnetic exchange interaction via the conduction electrons. However, it is not preferable to maintain this collinear structure down to lower temperatures because of the thermodynamic reason of magnetic entropy.

The spin system of $Gd_3Ru_4Al_{12}$ chooses to become helical below 17.5 K by inducing the c-axis spin component, i.e., by transforming the structure into a non-collinear form. In other words, the chiral degeneracy in the sinusoidal structure is lifted spontaneously by the transition to the helical structure, which allows all the Gd spins to fully develop.

Chirality plays important roles in a wide range of fields in nature from biology and chemistry to particle physics and materials science. In magnetic materials with chiral crystal structure, the emergence of nontrivial chiral objects such as skyrmions and chiral soliton lattices have recently been attracting widespread interest both for applications and basic science. Although the crystal structure of $Gd_3Ru_4Al_{12}$ is not chiral, the present discovery of spontaneous breaking of chiral symmetry is expected to stimulate further research and a deeper understanding of chiral magnets [4].

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