

2 Geometrical Correlation Project

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2-1 Introduction

Geometrical frustration in electronic degrees of freedom such as spin, charge, and orbit, which is often realized on stages of highly symmetric crystals, is a major topic in the field of condensed matter physics. In particular, numerous studies of local electronic systems (i.e., insulators) have revealed a wide variety of interesting phenomena associated with geometrical frustration, e.g., incommensurate order with long periodicity, successive unfolding of self-organized structures at different energy scales, nontrivial effects of strong fluctuation originating from the degeneracy of states over a macroscopic scale, weakened critical divergence, and an associated new universality class of criticality.

In contrast, although there has been much speculation, little is actually known about the effect of geometrical “correlation” on *itinerant* electron systems. (Here, we intentionally avoid the term “frustration”, as it is not trivial to define the proper counterpart in itinerant systems.) As one of few such examples, the heavy-fermion (HF) behavior in a cubic vanadium spinel, LiV_2O_4 , has received considerable interest [1,2], where a local electronic correlation specific to the highly symmetric pyrochlore structure (see Fig. 1) may be of direct relevance to the formation of the heavy-quasiparticle (QP) state.

Our research project aims to clarify the microscopic origin of the HF behavior in d -electron metals including LiV_2O_4 and $\text{Y}(\text{Sc})\text{Mn}_2$ [3]. To this end, we are focusing on a class of transition metal oxides having the so-called pyrochlore structure. These compounds have the chemical composition $A_2B_2O_7$, where the crystal structure comprises two interpenetrating networks of corner-shared tetrahedra consisting of A_2O' and B_2O_6 , respectively. Because of the high crystal symmetry in the crystal structure, the presence of antiferromagnetic correlation or charge disproportionation between the metal ions on the pyrochlore lattice induces a geometrical frustration and associated macroscopic degrees of degeneracy for the spin/charge states within their ionic limit. This results in various interesting phenomena such as a “spin-glass” phase and a “spin-ice” phase in insulating pyrochlore oxides.

The pyrochlore structure is also shared by LiV_2O_4 and $\text{Y}(\text{Sc})\text{Mn}_2$, where the t_{2g} orbitals associated with vanadium or manganese ions form a network of intersecting chains. Since these compounds remain mostly paramagnetic, spin fluctuation would be crucially important information for understanding their electronic state. On the other hand, recent

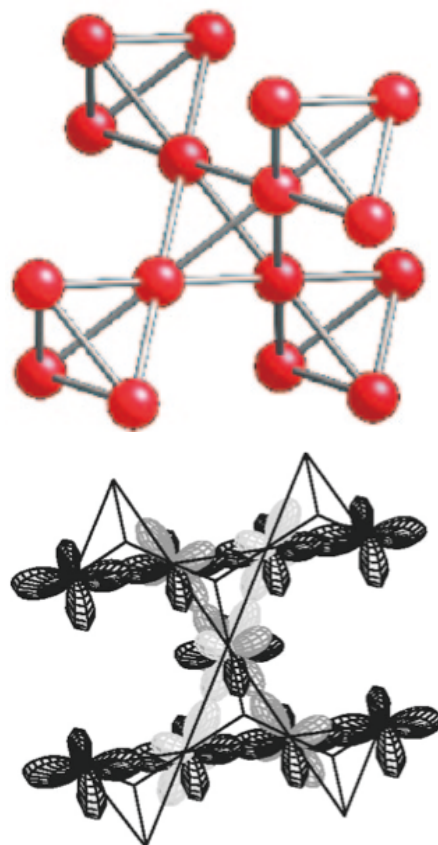


Fig. 1 Pyrochlore lattice consisting of three-dimensional network of corner-shared tetrahedra. (Top: frame of local ions. Bottom: associated t_{2g} orbitals)

developments in high-pressure synthesis have made a new series of pyrochlore metallic oxides available for close scrutiny: although they do not exhibit HF behavior, they seem to provide a new stage for investigating the effect of highly symmetric crystal structure on their electronic properties. With this background, our approach to the issue is twofold:

- i) mapping out the time-space character of spin fluctuation in the d -electron HF compounds, which would be attained by the complementary use of muon spin rotation/relaxation (μSR), inelastic neutron scattering (INS), and synchrotron X-rays (SR), and
- ii) looking into the details of electronic structure and magnetism in newly synthesized non-HF pyrochlore oxides using the abovementioned three microscopic probes.

In FY2010, we summarized our past endeavors on the second approach on ruthenium pyrochlore oxides [4], which is reported below. We also continued our efforts to understand the origin of HF behavior in $\text{Y}(\text{Sc})\text{Mn}_2$. As a result, we found by detailed μSR study that the spin dynamics in $\text{Y}(\text{Sc})\text{Mn}_2$ has a quasi-one-dimensional character at low temperatures, which is common to that in LiV_2O_4 . Further

investigation using inelastic neutron scattering is planned in FY2011.

2-2 Origin of randomness in metallic pyrochlore oxides

In order to gain more insight into the effect of geometrical correlation on *itinerant* electron systems, we studied the magnetism of ruthenium pyrochlore oxides $A_2Ru_2O_7$ ($A = \text{Hg}, \text{Cd}, \text{Ca}$) by muon spin rotation/relaxation (μSR), where the electronic properties of these compounds are characterized by non-degenerate t_{2g} orbitals ($\text{Ru}^{5+}, 4d^3$) within a localized ion picture and thereby subjected to geometrical frustration. The A cation (mostly divalent) was varied to examine the effect of covalency ($\text{Hg} > \text{Cd} > \text{Ca}$) on the electronic properties of the oxides.

In a sample with $A = \text{Hg}$, which exhibits a clear metal-insulator (MI) transition below $T_N \sim 110$ K (associated with a weak structural transition), a nearly commensurate magnetic order is observed to develop in accordance with MI transition (Fig. 2). The absence of enhancement for depolarization expected for critical slowing down of spin fluctuation towards T_N indicates that the magnetic transition is driven by a structural phase transition of the first order.

Meanwhile, in the case of $A = \text{Cd}$ where the MI transition is suppressed to the level of small anomaly in the resistivity, the local field distribution in the ordered phase (below $T_N \sim 100$ K) probed by muons indicates the emergence of a certain magnetic inhomogeneity below $T_{N2} \sim 30$ K (Fig. 3): a similar trend (less obvious) is actually observed in $\text{Hg}_2\text{Ru}_2\text{O}_7$ (see the spectrum at 2 K in which the peak around 30 MHz is broad).

In $\text{Ca}_2\text{Ru}_2\text{O}_7$, which remains metallic, highly inhomogeneous local magnetism is found below $T_g \sim 25$ K (Fig. 4); as inferred from the Gaussian damping of the spectra at their initial part, this magnetism arises from randomly oriented Ru moments and thus is described as a “frozen spin-liquid” state. This is a remarkable feature commonly observed in Zn-substituted LiV_2O_4 that exhibits spin-glass transition at low temperatures, suggesting a kinship between these two systems.

Although the emergence of the spin-glass phase in $\text{Ca}_2\text{Ru}_2\text{O}_7$ is regarded as evidence for the presence of geometrical frustration (presuming that Ru ions bear local moments), the microscopic origin of quasi-static randomness is not clear. Note that the RKKY interaction, which is the primary origin of the spin-glass phase in dilute alloys, cannot be the origin of the quasi-static randomness, because the distance between Ru ions is unique on the pyrochlore lattice. (This would also be true in $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ in which Zn substitution as dilute as $x = 0.05$ leads to the

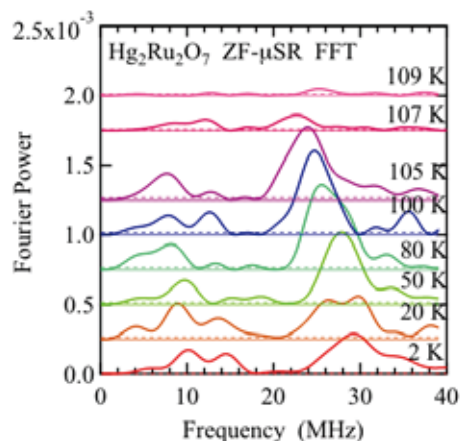


Fig. 2 Fourier transform of time-dependent μ -e decay asymmetry observed in $\text{Hg}_2\text{Ru}_2\text{O}_7$ at various temperatures under zero external field. The development of spontaneous internal magnetic fields is inferred from the peaks around 10 and 25–30 MHz.

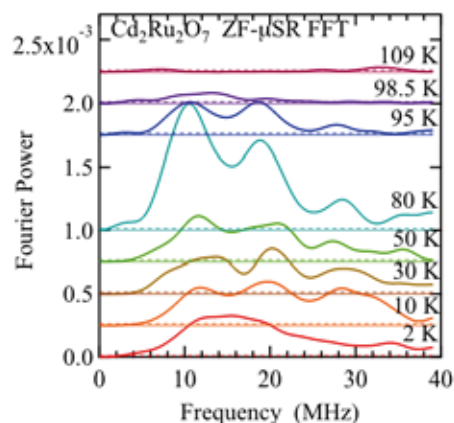


Fig. 3 Fourier transform of time-dependent μ -e decay asymmetry observed in $\text{Cd}_2\text{Ru}_2\text{O}_7$ at various temperatures under zero external field.

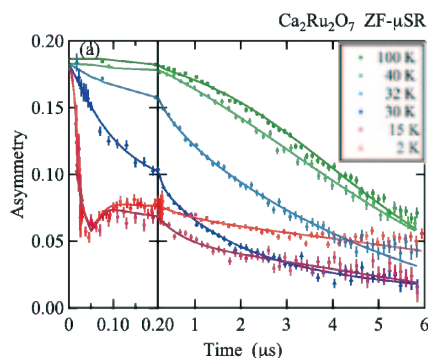


Fig. 4 Time-dependent μ -e decay asymmetry observed in $\text{Ca}_2\text{Ru}_2\text{O}_7$ at various temperatures under zero external field (full asymmetry $A_0 \sim 0.18$). Solid curves are the best fits obtained assuming the Gaussian distribution for the local fields leading to the Kubo-Toyabe relaxation function.

quasi-static spin-glass state). One possibility is that the Dzyaloshinsky-Moriya (DM) interaction may be involved as a competing interaction to the usual exchange interaction: the local exchange path between Ru ions lacks inversion symmetry, leaving room for the DM interaction to be active in these compounds. The common characteristic temperature ($T_{N2} \sim T_g \sim 25\text{--}30$ K) suggests that such interaction exists. In any case, the systematic trend of increasing randomness and itinerant character with decreasing covalency suggests a close relationship between the two characters.

To understand the effect of orbital degeneracy and associated Jahn-Teller instability, we examined a tetravalent ruthenium pyrochlore, $\text{Ti}_2\text{Ru}_2\text{O}_7$ (Ru^{4+} , $4d^4$). The result of μSR indicates a non-magnetic ground state that is consistent with the formation of the Haldane chains suggested by the neutron diffraction experiment.

Acknowledgement

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