2 Geometrical Correlation Project

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2-1 Anomalous spin dynamics in 5*d*-electron pyrochlore $Cd_2Os_2O_7$

Transition metal oxides with the chemical composition $A_2B_2O_7$ crystallize into the so-called cubic pyrochlore structure formed by two interpenetrating networks of corner-shared tetrahedra of A_2O' and B_2O_6. Because of high symmetry in the lattice structure, the presence of antiferroic correlation between local spin and/or charge of the metal ions on the pyrochlore lattice induces geometrical frustration and associated macroscopic degrees of degeneracy to the electronic ground 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.

Recently, particular attention has been paid to 5*d* transition metal oxides such as iridates (A_2IrO_4, A = Sr, Ba) where the strong spin-orbit (SO) coupling comparable with electron correlation might induce an unconventional ground state. This possibility also prompts a reconsideration of the physics of geometrical frustration for the 5*d* pyrochlore oxides.

$Cd_2Os_2O_7$ is one of such compounds with $5d^3$ (Os^{5+}). It is known to exhibit a purely electronic metal-insulator transition (MIT) without structural change, falling into a magnetically ordered state at T_N ~ 227 K [1,2]. Magnetic susceptibility [1,2] and our previous μSR measurements [3] suggested the Néel state below T_N with slight spin density wave (SDW)-like modulation [3], whereas powder neutron diffraction showed no sign of magnetism [4]. Recently, it has been inferred from resonant X-ray scattering (RXS) measurements of high-quality single crystals that the magnetic structure of the Néel state is characterized by a wave vector $\mathbf{q} = 0$, strongly suggesting a noncollinear ("all-in-all-out") spin state [5]. A theory based on the numerical analysis of the LSDA+SO+*U* model (local spin density approximation with appropriate inclusion of SO and on-site Coulomb interaction) suggests that the MIT and associated nontrivial magnetic structure originate from competition between SO and *U*, which are also comparable with the 5*d* bandwidth [6].

While the electronic ground state at $T \sim 0$ has been resolved by RXS analysis, the strong spin fluctuation persisting over a wide range of temperature below T_N inferred by μSR is a remaining issue [3]. Since high-quality single-crystalline (sc) samples are available, we performed detailed μSR measurements at PSI to clarify the spin dynamics in sc-$Cd_2Os_2O_7$ [7]. As shown in Fig. 1a, we confirmed that longitudinal

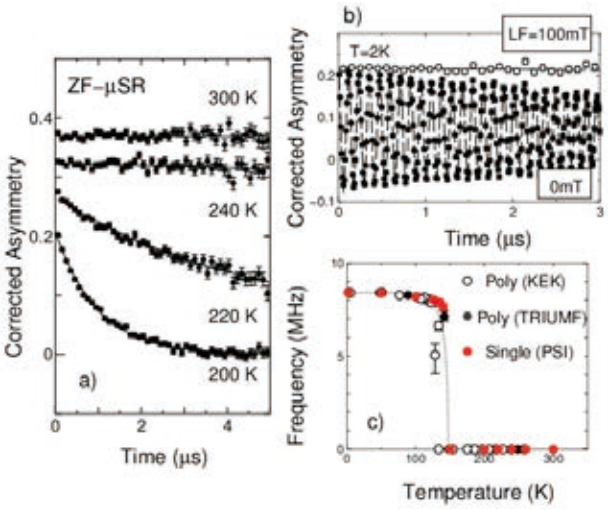

Fig. 1: Typical ZF-μSR time spectra at various temperatures in sc-$Cd_2Os_2O_7$ above a) and below b) 150 K. c) Muon spin precession frequency vs. temperature, where the present data (PSI) are shown together with those from the previous study [3].

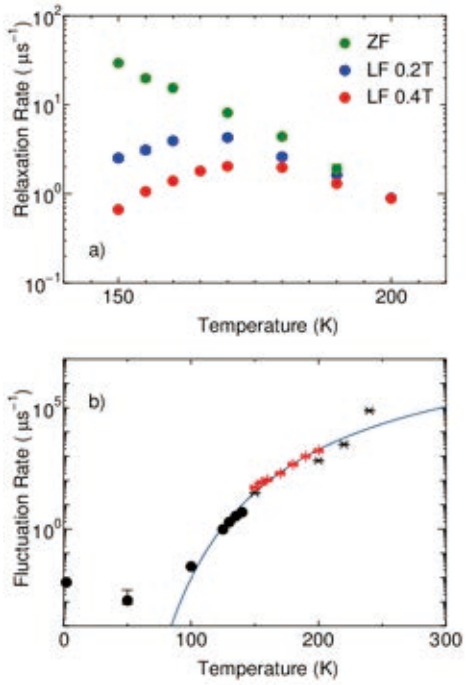

Fig. 2: a) Muon spin relaxation rate as a function of temperature and external field in sc-$Cd_2Os_2O_7$. The peak of relaxation rate corresponds to the "T_1 minimum" where the spin fluctuation rate becomes comparable with muon precession frequency. b) Spin fluctuation rate deduced from the data shown in a) vs. temperature. [Asterisks: from Eq. (3), filled circles: from Eq. (4)]

muon spin relaxation due to Os spin fluctuation persists down to T_m ~ 150 K << T_N, where the depolarization of the asymmetry is described by a simple exponential damping,

$$A(t) = A_0 \exp(-\lambda t), \quad (1)$$

with A_0 being the initial asymmetry. Meanwhile, the spectra below T_m are well represented by a single component of spin precession, indicating that the magnetic structure is mostly uniform over the entire crystal volume. The ZF-μSR time spectra are reproduced by the following simple form for the mosaic crystals,

$$A(t) = A_0[(2/3)\cos(\gamma_\mu H_m t)\, e^{-\sigma t} + (1/3)\exp(-\lambda t)], \quad (2)$$

where H_m is the internal local field felt by muons, γ_μ is the muon gyromagnetic ratio (= 2π × 135.53 MHz/T), and σ is the transverse depolarization rate. This suggests that the SDW-like modulation observed in the earlier data was an artifact due to impurity phases.

The corresponding spin fluctuation rate ν is deduced using the Redfield model for the longitudinal relaxation rate under an external field (H_0),

$$\lambda \approx \frac{2\delta_\mu^2 \nu}{\nu^2 + \gamma_\mu^2 H_0^2}, \quad (3)$$

where δ_μ = 27.8(9) MHz is the muon hyperfine parameter determined by the field dependence of . It is noteworthy in Fig. 2a that the peak of is clearly observed at a temperature T^* where $\nu(T^*) = \gamma_\mu H_0$ as predicted in Eq. (3). The shift of T^* towards lower temperature upon reduced H_0 proves that the fluctuation becomes slower at lower temperatures, thereby allowing us to deduce ν uniquely from Eq. (3) which generally yields two solutions as a quadratic equation of ν. A similar modeling of spin relaxation can be considered for the longitudinal component of the time spectra [i.e., λ in Eq. (2)] below 150 K where a unique internal field H_m sets in,

$$\lambda \approx \frac{2\gamma_\mu^2 H_m^2 \nu}{\nu^2 + \gamma_\mu^2 H_{eff}^2}, \quad H_{eff}^2 = H_0^2 + H_m^2. \quad (4)$$

Figure 2b shows the temperature dependence of the fluctuation rate deduced from the data in Fig. 2a using Eqs. (1) and (2). It exhibits a monotonic decrease with temperature (although a slight glitch is seen at T_m), which may be described by an Arrhenius-type thermal activation. A curve fitting with the relation

$$\nu = \nu_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (5)$$

yields ν_0 = 3.71(4) × 10^{13} s^{-1}, E_a/k_B = 2441(2) K, where the corresponding curve is shown in Fig. 2b.

The relatively smooth change of ν through T_m suggests that T_m is not a point of thermodynamic phase transition but of crossover determined by the condition $\nu \sim \gamma_\mu H_m$ = 53 MHz. Meanwhile, the anomalously expanded temperature range of critical slowing down as well as the characteristic energy scale of the fluctuation inferred by the parameters in Eq. (5) [i.e., $h\nu_0$ = 0.153(2) eV, E_a = 0.2104(2) eV] suggests the presence of frustration originating from competing interactions between 5*d* electrons. In this regard, it is interesting to note that the SO interaction tends to introduce spatially anisotropic intersite interaction strongly correlated with bonding axes. For example, there is a possibility that the effective exchange interaction between J_{eff} = 3/2 moments of Os ions under SO interaction has anisotropy along the {100} or {110} direction (where the observed {111} anisotropy is a result of compromise between the tendency of orientation to three orthogonal directions, which is similar to the situation described by the "compass" model), so the Os moment fluctuates among these three directions.

2-2 Spin-orbital frustration in $CuIr_2S_4$

As mentioned in the previous section, 5*d* transition metal oxides are drawing much interest, because the strong spin-orbit (SO) coupling comparable with electron correlation might induce an unconventional ground state. For example, it has been inferred from resonant X-ray diffraction studies that the crystal field levels of Ir^{4+} ions ($5d^5$) in the insulating phase of an iridium perovskite, Sr_2IrO_4, are reconstructed into a complex spin-orbital state represented by an effective total angular momentum of J_{eff} = 1/2 and 3/2, where the half-filled J_{eff} = 1/2 level serves as a novel stage of the Mott transition due to the on-site Coulomb interaction [8,9]. The strong SO coupling entangles the spin and orbital degrees of freedom, where the magnetic interaction of corner-shared $Ir^{4+}O_6$ octahedra is modeled by the low-energy effective Hamiltonian consisting of terms representing the Heisenberg model, quantum compass model, and Dzyaloshinski-Moriya (DM) interaction [10]. The model has been successful in providing a microscopic account of the canted spin structure in the *xy*-plane in Sr_2IrO_4 observed by resonant X-ray diffraction using *L* edge ($2p \rightarrow 5d$) [9], where interplay between the "compass" and DM interactions is a crucial factor.

Interestingly, the same model predicts a completely different effective Hamiltonian for the edge-shared $Ir^{4+}O_6$ octahedra, which is dominated by the quantum compass interaction,

$$H^{(\gamma)} = -JS^\gamma_i S^\gamma_j, \quad (6)$$

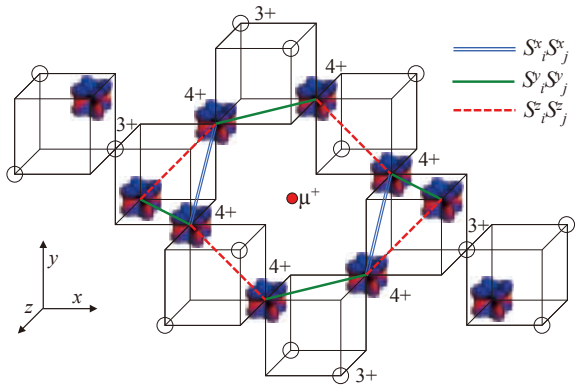

Fig. 3: Octamer configuration associated with charge order in $CuIr_2S_4$. Exchange interaction $S^{\gamma}_i S^{\gamma}_j$ for each Ir^{4+} pair is shown by lines along the respective $\gamma\gamma$ bond ($\gamma = x, y, z$).

where S^{γ}_i ($\gamma = x, y, z$) denotes the γ-component of the S = 1/2 pseudospin operator $\mathbf{S}_i$ defined for the J_{eff} = 1/2 ground state, $J \sim 2J_{\text{H}}/3U$ where J_{H} and U are the Hund's coupling and on-site Coulomb energy, and the entire energy is scaled by $4t^2/U$ with t being the *dd*-transfer integral through an intermediate anion [10]. The form of exchange interaction depends on the spatial orientation of a given bond, leading to highly anisotropic (Ising type) interaction between Ir ions.

It is noteworthy that, upon substituting IrO_6 with IrS_6, $CuIr_2S_4$ in the insulating phase would serve as an ideal stage of the quantum compass model, as it partly comprises the edge-shared $Ir^{4+}S_6$ network. More importantly, the compass interaction is projected to the Kitaev model on the Ir^{4+} octamers [10,11] in the case of charge order without dimerization. As shown in Fig. 3, an Ir^{4+} octamer consists of a honeycomb unit and two triangular units, on which every Ir^{4+} ion occupies a node of two (or three) nonequivalent bonds with each being perpendicular to one of the cubic axes x, y, z. Thus the iridium pseudospins (accompanying effective moments) are subject to strong geometrical frustration due to competing exchange interactions favoring different spatial orientations.

From this revised viewpoint, the lattice dimerization and associated structural phase transition in a thiospinel compound $CuIr_2S_4$ [12] are naturally understood as a relief of magnetic frustration upon charge order. In this regard, it is interesting to note that the dimerization occurs for the Ir^{4+} pairs connected by one particular kind of bond on an octamer [12], e.g., yy or zz bond (shared by triangular units) in Fig. 3. This suggests that, while the Kitaev ground state might be destroyed by the lattice dimerization (due to enhanced exchange interaction for the corresponding bond), the magnetic frustration is only partially removed. In any case, such a situation would be drastically different from the spin-singlet ground state predicted within the conventional scenario where spins are independent of orbital degrees of freedom [13], and may require a reconsideration of the origin of metal-insulator transition.

Our recent μSR study suggested that the lattice dimerization does not accompany "spin dimerization" to form the singlet-ground state, and that the ground state would be better understood as a spin-glass state of novel origin induced by partial removal of magnetic frustration specific to strong SO coupling [15]. Typical examples of μSR spectra in $CuIr_2S_4$ at various temperatures are shown in Fig. 4a. One can observe a slow Gaussian damping at 200 K, which is expected for muons exposed to random local magnetic fields from nuclear magnetic moments (primarily from ^{63}Cu and ^{65}Cu in $CuIr_2S_4$). Below ~100 K, fast exponential depolarization sets in, where the depolarization rate ( ) as well as the relative amplitude (a) of the depolarizing component develop with decreasing temperature. These spectra are analyzed by curve fitting using the form

$$A(t) = A_0\{a \cdot \exp[-(\lambda t)]^{\beta} + (1-a)\}G^{\text{KT}}{}_z(\Delta t), \qquad (7)$$

where A_0 is the initial asymmetry, β is the power for the "stretched" exponential damping, and $G^{\text{KT}}{}_z(\Delta t)$ is the Kubo-Toyabe relaxation function with being the line width determined by the nuclear dipolar fields. Equation (7) gives excellent reproduction of data with a tendency of smaller β at lower temperatures. From a comparison of the deduced [= 0.150(1) μs^{-1}] with calculated second moments of Cu and Ir nuclei, we conclude that the muon site is located at the center of the $Ir^{3+/4+}$ octamers [(1/8,1/8,1/8) O_h site situated at the center of a S^{2-}_6 octahedron, shown in Fig. 3, where is calculated to be 0.152 μs^{-1}]. The nearly exponential damping in the time domain corresponds to a Lorentzian-type distribution of internal magnetic field at the muon site, indicating the onset of highly disordered magnetism. The response of μSR spectra to a longitudinal field (parallel to initial muon polarization, Fig. 4b) implies that the internal field is quasistatic at 2 K within the time window of μSR (< 10^{-4} s). The form within the square brackets of Eq. (7) is then replaced with a physically more meaningful form using the relaxation function for spin glass,

$$\sim f\{1/3+(2/3)\exp[-(\lambda t)]^{\beta}\} + (1-f), \qquad (8)$$

where f [= 0.435(5) ~$3a/2$ at 2 K] is the true fractional yield for muons probing the inhomogeneous magnetic field B whose density distribution $P(B)$ is represented by the Fourier transform of the stretched exponential damping.

It is notable that f (at 2 K) is close to 1/2, implying that the specimen exhibits spatial phase separation into magnetic and non-magnetic domains with nearly equal fraction. Since muons surrounded only by Ir^{3+} ions at the nearest-neighboring sites exhibit slow Gaussian damping due to nuclear random local fields, the result provides evidence for the segregation of Ir charge state into Ir^{3+} and Ir^{4+} clusters. This is also perfectly in line with the presumption that implanted muons occupy the O_h sites at the center of Ir^{3+} and Ir^{4+} octamers according to statistical probability of one to one.

The spin-glass-like state of Ir^{4+} octamers suggests the presence of frustration and associated degeneracy in the electronic ground state of $CuIr_2S_4$, strongly supporting the "revised view" in which the SO interaction leads to geometrical frustration. The super-Lorentzian density distribution of $P(B)$ disfavors the scenario of attributing the origin of inhomogeneity to random orientation of Ir pseudospins having a common effective moment size m = <$\mathbf{S}_i$> on an Ir^{4+} octamer (those nearest-neighboring to muons), because a Gaussian distribution is expected in such a situation, as has been observed in the vanadium spinel compound $Li_{1-x}Zn_xV_2O_4$ (which also exhibits a spin-glass-like magnetic ground state for $x > 0.05$) [15]. This may imply a qualitative difference in the electronic state upon partial removal of geometrical frustration arising from the SO interaction. A crude estimation can be made for the Ir^{4+} effective moment size as a mean value by comparing λ^{β} [= 2.03(8) MHz at 2 K] with hyperfine parameter (δ_μ) calculated using the second moment of the magnetic fields from $\mathbf{S}_i$. Using a dipolar field approximation, we obtain δ_μ = 41.7 $\mu s^{-1}/\mu_B$, which yields m = 0.049(2) μ_B. This is much smaller than the moment size (~0.36 μ_B) observed in the ordered phase of Sr_2IrO_4 [9]. The small value of m as well as its highly inhomogeneous character comparable to magnetic dilute alloys suggest the influence of geometrical frustration and/or closeness to the spin-liquid ground state.

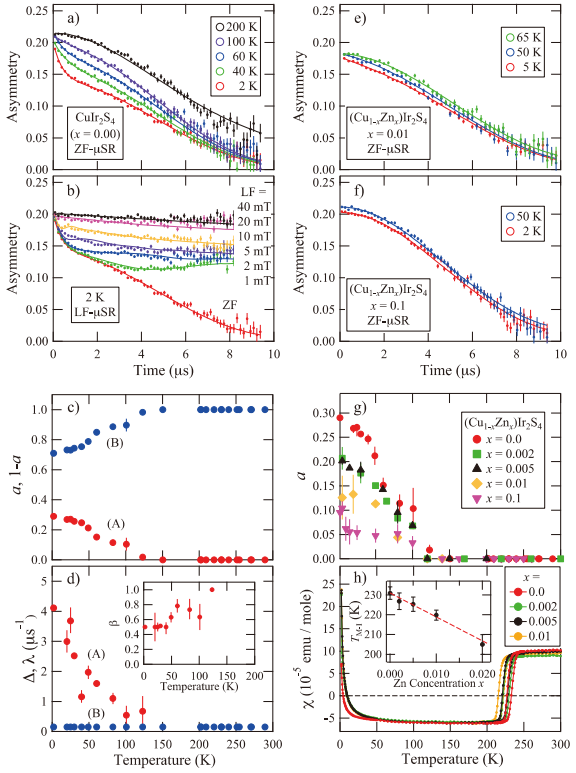

Fig. 4: (a) Time-dependent μSR spectra observed at several temperatures in powder samples of $CuIr_2S_4$ under zero external field. (b) μSR spectra at 2 K under various longitudinal fields. (c) Temperature dependence of the partial μ-e decay asymmetry, one for the component showing fast exponential damping (A) and the other showing Gaussian damping (B). (d) Depolarization rate of the respective components as a function of temperature. (e) μSR spectra in $Cu_{1-x}Zn_xIr_2S_4$ under zero external field with x = 0.01, and (f) x = 0.1. (g) Relative amplitude of the component showing fast exponential damping (A) as a function of temperature. (h) Magnetic susceptibility (χ) of $Cu_{1-x}Zn_xIr_2S_4$ samples used for μSR measurements. Inset shows the temperature of metal-insulator transition determined by χ.

The magnetic ground state exhibits another intriguing feature that the quasistatic local magnetism is strongly suppressed by substitution of Cu with Zn. As shown in Fig. 4e-g, Zn content as small as x = 0.01 is sufficient to eliminate the signal showing exponential damping. Meanwhile, the magnetism turns out to be robust against off-stoichiometric composition for Ir and Cu. This unusual sensitivity of the ground state to the hole-filling supports the idea that there exists inter-octamer correlation. A preliminary theoretical study based on the Heisenberg-Kitaev model [16] indicates that an isolated Ir^{4+} octamer may not retain magnetic moments regardless of partial dimerization [17], suggesting that the inter-octamer correlation is a crucial factor in stabilizing the spin-glass-like ground state. Such interoctamer correlation would also provide a qualitative explanation for the superstructure (i.e., alternative stacking) of Ir^{3+} and Ir^{4+} octamers observed in $CuIr_2S_4$.

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