Possible multipolar ordering in spin-orbital-entangled d^2 system on a face-centered-cubic lattice

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The interplay of strong spin-orbit coupling (SOC) and electron correlation in heavy transition-metal compounds containing $4d$ and $5d$ elements has been revealed to give rise to unprecedented electronic states of matter. In such systems, strong SOC produces spin-orbit-entangled $J_{\rm eff}$ states of d-electrons. The interactions between spin-orbital-entangled objects are distinct from those in spin-only systems, and a plethora of novel electronic phases has been predicted to emerge. In d^2 configurations, SOC yields $J_{\rm eff} = 2$ quintet states. When the $J_{\rm eff} = 2$ states are placed on a face-centered-cubic (FCC) lattice, multipolar ordering phenomena such as charge quadrupolar and magnetic octupole orderings are expected to emerge.[1,2)]

To explore such multipolar orderings of d-electrons, we focused on cubic tungsten halides A_2WCl_6 (A = K, Rb, Cs) with a $5d^2$ configuration of W^{4+} ions. The regular WCl_6 octahedra form an FCC lattice. In these compounds, the magnetic susceptibility $\chi(T)$ shows a Curie-Weiss behavior at high temperatures, and the effective moments are close to the value expected for $J_{\rm eff} = 2$ ($\mu_{\rm eff} \sim 1.22\ \mu_{\rm B}$). K_2WCl_6 displays an anomaly in specific heat $C(T)$ at approximately 180 K, which corresponds to a structural transition from cubic to tetragonal, but no further anomaly was observed at lower temperatures. Rb_2WCl_6 and Cs_2WCl_6 show no pronounced anomaly in $C(T)$ and $\chi(T)$ down to 2 K, although a deviation from the Curie-Weiss behavior is observed at approximately 100 K. The magnetic ground state of these materials is thus not clear yet.

One of the possible ground states is the formation of magnetic octupolar ordering, which has been suggested for d^2 double-perovskite oxides.[3)] In those oxides, although any signature of magnetic dipolar ordering was found in $\chi(T)$ and neutron diffraction, a clear oscillatory signal was observed in muon spin rotation (μSR) measurements, indicating time-reversal-symmetry breaking. The other possibility, especially for K_2WCl_6, is that the structural transition lifts the degeneracy of the $J_{\rm eff} = 2$ quintet and selects the non-magnetic $J^z_{\rm eff} = 0$ singlet ground state (*i.e.*, charge quadrupole order), which can be regarded as a spin-orbital nematic state in analogy with the $S^z = 0$ spin-nematic state. In this case, the time-reversal-symmetry is retained, and no oscillatory signal is expected in μSR.

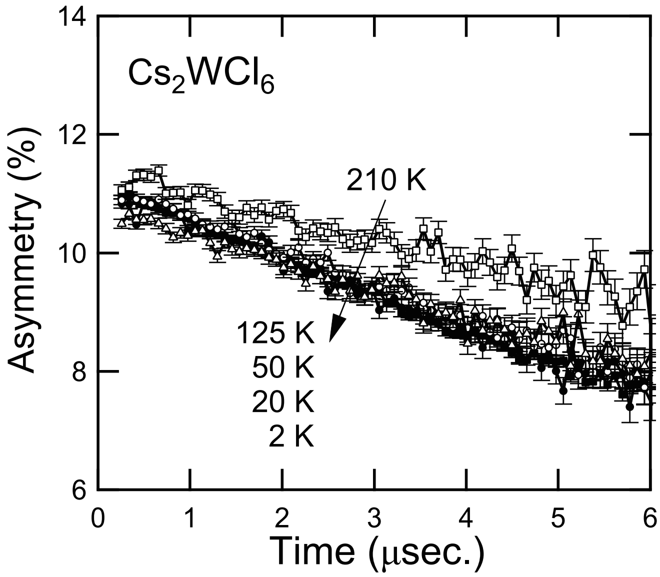

Fig. 1. Zero-field time spectra of muon asymmetry for Cs_2WCl_6 at several temperatures.

In order to investigate the ground states, we performed a μSR measurement on powder samples of A_2WCl_6 (A = K, Rb, Cs) using ARGUS, ISIS. For all the samples, the time dependence of muon asymmetry at low temperatures only shows a monotonic decrease, indicating a nonmagnetic ground state. Figure 1 shows the result for Cs_2WCl_6. The time dependence of muon asymmetry at zero magnetic field did not show any pronounced change down to 2 K. For K_2WCl_6, the relaxation rate λ, obtained by fitting with a Lorentzian curve, shows a kink at approximately 180 K, where a structural transition occurs. No such anomaly was found in Cs_2WCl_6 or Rb_2WCl_6.

This result excludes the presence of magnetic dipolar or octupolar ordering in A_2WCl_6. The question of whether the $J_{\rm eff} = 2$ moments remain fluctuating or form a quadrupolar ordering with a spin-singlet ground state remains open. We expect that the ground states of these compounds can be clarified in combination with other measurements, especially the analysis of low-temperature crystal structures.

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