# Short-range magnetic order in the frustrated antiferromagnet $Cu_5(PO_4)_3(OH)_4$ (pseudomalachite)

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Geometrically frustrated magnets have recently been attracting much interest, because they are expected to exhibit new physical states including spin liquid. Almost every frustrated magnet studied so far, *e.g.*, kagomé, triangular, and pyrochlore lattices, are based on triangular units. The spin frustrated effect, however, is not restricted to a triangle but appears if antiferromagnetic spins are on a polygon with odd-number edges such as a pentagon. A lattice containing pentagons as its unit can afford a new category for the spin frustration effect. $Cu_5(PO_4)_3(OH)_4$ (mineral name: pseudomalachite) is an orthorhombic crystal[1)] with three crystallographically inequivalent sites of copper. Layers consisting of face-shared $CuO_6$ octahedrons extend in the *bc* plane and are separated by interlayer $PO_4$ tetrahedrons. A spin network in the *bc* plane formed by $Cu^{2+}$ ions ($S = 1/2$) has a unique structure composed of triangles and pentagons.

We measured the magnetic susceptibility, specific heat, and high-field magnetization of pseudmalachite using natural mineral samples.[2)] The sign of the Weiss temperature is found to be negative, indicating that the dominant interaction is antiferromagnetic. The specific heat $C(T)$ has a broad maximum at $T_f \approx 4.2$ K, where $\chi(T)$ shows a peak anomaly.

The relative change of $C(T)$ at $T_f$ is very small if this transition is a long-range magnetic order.

The entropy change associated with the magnetic order was estimated to be approximately 5.5 J/(K·mol),

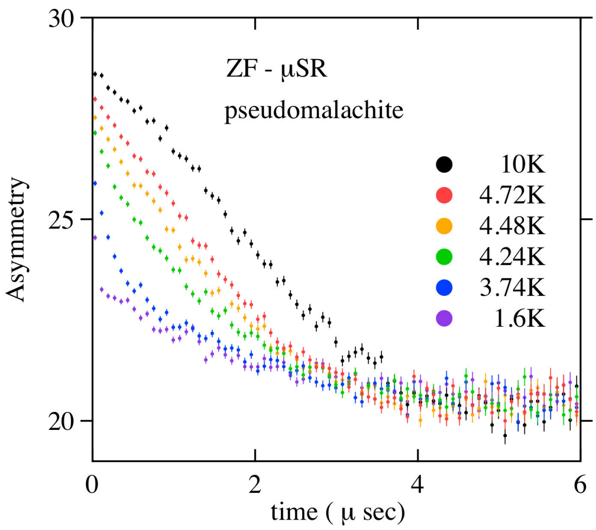


Fig. 1. ZF-$\mu$SR spectra of pseudomalachite.

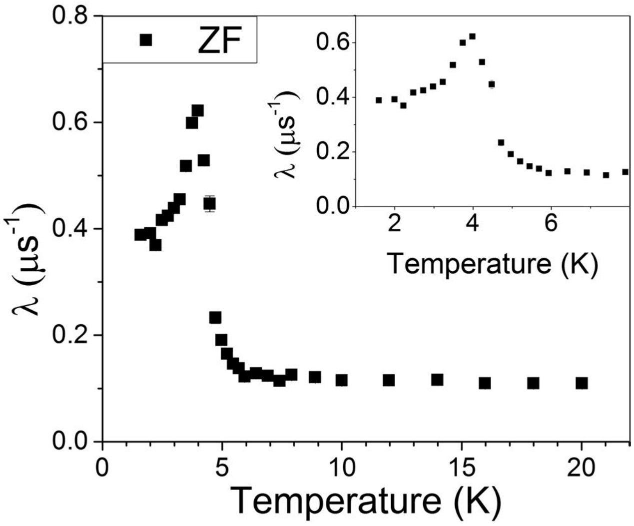


Fig. 2. Temperature dependence of the relaxation rate $\lambda$.

which is only one-fifth of the expected value $5R \ln 2 \approx 28.8$ J/(K·mol). In order to clarify the magnetic ordering transitions in this frustrated magnet, measurements using a microscopic and dynamic probe is highly desired.

Figure 1 shows the zero-field muon spin relaxation (ZF-$\mu$SR) spectra measured down to 1.6 K. At relatively high temperatures, the spectra follow Gaussian curves.

Below approximately 4.2 K, the initial asymmetry begins to decrease, and the form of the spectra changes from the Gaussian to an exponential curve following $\exp(-\lambda/t)$, where $\lambda$ is the relaxation rate. Figure 2 shows the temperature dependence of the relaxation rate obtained from a fit to the observed spectra. $\lambda$ has a distinct peak at approximately 4 K, where the anomaly was observed in the specific-heat data. These observed results clearly indicate that the magnetic phase transition occurs at $T_f$.

The spectrum below $T_f$, however, does not show any spin rotation, suggesting that the internal field is dynamic, rather than static. Furthermore, even in the lowest-temperature spectrum, spin relaxation remains, and finite spin fluctuations seem to be present in the ordered phase. These findings are consistent with our macroscopic indication that the transition is not a long-range order but has the character of a short-range order, which originates from the geometrical spin frustration effect of the peculiar spin network of pseudomalachite.

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References

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