Single-Crystal Growth of Spinel Type GeNi$_2$O$_4$ and GeCo$_2$O$_4$ by FZ Method and their AC Susceptibility

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Abstract. Cubic spinel GeNi$_2$O$_4$ and GeCo$_2$O$_4$ compounds exhibit field-induced magnetic anisotropy below the antiferromagnetic transition temperature. GeNi$_2$O$_4$ has two antiferromagnetic like transitions at 12.1 K and 11.4 K. Structural phase transitions (PT) which may lower the symmetry and relief frustration of magnetic spins are expected at the temperatures. However, this cubic material does not undergo a structural PT. On the other hand, GeCo$_2$O$_4$ has a structural PT from high-temperature cubic symmetry to low-temperature tetragonal one at the temperature. Although GeCo$_2$O$_4$ demonstrates antiferromagnetic ordering, derived Weiss temperature is ferromagnetic (11.9 K). In order to understand those intriguing ground states in detail, we have measured AC susceptibility below 1 K. The results show there are no other phase transitions above 150 mK for both compounds.

1. Introduction
The spinel structure AB$_2$O$_4$ is cubic, where the A site expresses a diamond lattice, and the B site a pyrochlore lattice as shown in Fig.1. In general, a triangle lattice or a pyrochlore lattice has magnetic frustration if spins at the lattice have an antiferromagnetic interaction. Therefore many interesting magnetic properties like spin ices or spin liquids were reported for compounds with such lattices [1].

GeNi$_2$O$_4$ with the integer spin (Ni$^{2+}$, 3d$^8$, $S=1$) has two antiferromagnetic transitions, whose temperatures are very close, $T_{N1} = 12.1$ K and $T_{N2} = 11.4$ K [2]. In high magnetic field above 0.7 T and below $T_{N1}$, an induced magnetic anisotropy arises by the field. Below 0.7 T, not only the magnitude of magnetic susceptibility but the transition temperatures are isotropic, which means the two transitions can be observed for $<001>$, $<011>$ and $<111>$. However, above 0.7 T, the transition at $T_{N1}$ is observed only for the field along $<001>$ and $<110>$, and the transition at $T_{N2}$ is observed only for the field along $<110>$ and $<111>$. Based on those results, there is a possibility that this material changes its spin arrangement drastically in high magnetic field [3]. The most important feature is that this cubic material does not show any evidence for structural PT in synchrotron X-ray and neutron scattering measurements.

GeCo$_2$O$_4$ with the half-integer spin (Co$^{2+}$, 3d$^7$, $S=3/2$) has also an antiferromagnetic transition with $T_N = 20.8$ K. GeCo$_2$O$_4$ reveals a structural PT from cubic to tetragonal symmetry by the lattice distortion along $<001>$ at $T_N$. Despite its antiferromagnetic ground
state, the derived Weiss temperature is ferromagnetic (11.9 K) from the Curie-Weiss fitting for the temperature dependence of the susceptibility. It is naively conceivable that there are some ferromagnetic interactions for different combination of the spins.

Although several spin structures were suggested for both materials, neutron scattering studies using large single crystals were not carried out, which should be performed to clear the details of the structures [4, 5].

2. Experiment

Single crystals of GeNi$_2$O$_4$ and GeCo$_2$O$_4$ were grown by a floating-zone method. Details of the crystal growth are described elsewhere [6]. All samples were single-phased, determined by powder x-ray diffraction (XRD) with a CuKα source.

We measured the AC susceptibility for the single crystal of both materials by an adiabatic demagnetization cryostat (CMR) from 150 mK to 2 K, and by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) from 2 K to 40 K. The directions of AC magnetic field ($10^{-4}$ T) and static field (1 T and 2 T) are parallel. In this study, we did not align the sample along the magnetic field.

Figure 1. (a) Diamond lattice (A site) in a spinel structure. (b) Pyrochlore lattice (B site) in a spinel structure.

Figure 2. (a) An imaginary part of AC susceptibility at 2 T and 12 Hz around $T_{N1}$ and $T_{N2}$. (b) A real part of AC susceptibility at 0 T and 123 Hz between 150 mK and 2 K.
3. Results and Discussion

Figure 2(a) shows the temperature dependence of an imaginary part of AC susceptibility for GeNi$_2$O$_4$. No anomalies have been observed at $T_{N_1}$ and $T_{N_2}$. This indicates that the transitions at $T_{N_1}$ and $T_{N_2}$ do not involve ferromagnetic dissipative components in addition to spin-glass magnetic phases. Figure 2(b) shows the temperature dependence of the AC susceptibility from 2 K to 150 mK. Any magnetic transitions have never been recognized. This result leads to the probable fact that this compound keeps its cubic structure down to 150 mK, if a magnetic transition is associated with structural PT. GeCo$_2$O$_4$ demonstrates similar results to those for GeNi$_2$O$_4$ as shown in Fig. 3. Other and new transitions have not been confirmed. Observed gradient of the data in Fig. 2(b) and Fig. 3(b) may originate from the equipment background.

Considering the obtained results, the magnetic ground states for both compounds can be concluded as the antiferromagnet without ferromagnetic and spin-glass ingredients. It is expected that the remained entropy due to magnetic frustration in cubic GeNi$_2$O$_4$ below $T_{N_2}$ may give rise to an extraordinary magnetism.

4. Conclusion

It has been shown that both materials do not show any signs in the imaginary part of susceptibility around transition temperatures. Below 4 K, we have confirmed that there are no other magnetic transitions for both compounds. Those indicate that ferromagnetic component or spin-glass like phases do not exist in the ground state magnetic phases of GeNi$_2$O$_4$ and GeCo$_2$O$_4$. Especially for GeNi$_2$O$_4$, it should be noted that cubic symmetry may remain down to 150 mK.

References

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