Spin-orbit dilution effects on the magnetism of frustrated spinel Ge(Co\textsubscript{1-x}Mg\textsubscript{x})\textsubscript{2}O\textsubscript{4}

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Abstract. We investigated magnetic properties of spinel oxides Ge(\textit{Co}_{1-x}\textit{Mg}_x)\textsubscript{2}O\textsubscript{4} with \textit{x} = 0 \sim 0.5 to study the spin-orbit dilution effects on the magnetism of spin-orbit frustrated spinel GeCo\textsubscript{2}O\textsubscript{4}. We discovered that the magnetic moment per single Co\textsuperscript{2+} ion is decreased with increasing nonmagnetic Mg\textsuperscript{2+} concentration, which indicates the spin-orbit decoupling caused by the spin-orbit dilution. Additionally, small-amount substitution of Mg\textsuperscript{2+} for Co\textsuperscript{2+} causes the rapid increase of the positive Weiss temperature indicating the enhancement of ferromagnetic interactions, while the Mg\textsuperscript{2+} substitution suppresses the antiferromagnetic ordering resulting in the appearance of spin glass behavior. The present results suggest that the spin-orbit dilution causes the spin-orbit decoupling and the reinforcement of ferromagnetic frustration in GeCo\textsubscript{2}O\textsubscript{4}.

1. Introduction
Geometrical frustration is a concept which provides an intriguing playground for condensed matter physics. Cubic spinels \textit{AB}_2O_4 with magnetic \textit{B} ions have attracted much interest in light of the geometrical frustration which is inherent in the \textit{B}-site sublattice of corner sharing tetrahedra (pyrochlore lattice). Cobaltite spinel GeCo\textsubscript{2}O\textsubscript{4} consists of magnetic Co\textsuperscript{2+} ions (3\textit{d}\textsuperscript{7}) with threefold degeneracy of \textit{t}_{2g} orbitals on the octahedral \textit{B} sites as shown in Fig. 1, and non-magnetic Ge\textsuperscript{4+} ions on the tetrahedral \textit{A} sites. Thus it is expected that this compound provides a rich field for the orbital physics in the magnetically frustrated system. GeCo\textsubscript{2}O\textsubscript{4} exhibits the occurrence of an antiferromagnetic transition at Néel temperature \textit{T}_N = 21.0 K accompanied with cubic-to-tetragonal structural elongation [1, 2, 3]. On the other hand, the magnetic susceptibility in the paramagnetic state exhibits Curie-Weiss behaviour with the positive Weiss temperature \textit{\theta}_W = 81.0 K indicating the dominant contribution of the ferromagnetic interactions [4]. For GeCo\textsubscript{2}O\textsubscript{4}, recent ultrasound velocity measurements and inelastic neutron scattering...
experiments suggested that this compound is a promising candidate for the spin-orbit-coupled frustrated system [5, 6, 7]. In this paper, we investigate structural and magnetic properties of the nonmagnetic Mg-doped Ge(Co$_{1-x}$Mg$_x$)$_2$O$_4$ to study the spin-orbit dilution effects on the magnetism of GeCo$_2$O$_4$.

2. Experimental
Polycrystalline samples of Ge(Co$_{1-x}$Mg$_x$)$_2$O$_4$ ($x = 0 \sim 0.5$) were prepared by solid state reaction. Mixtures of stoichiometric amounts of GeO$_2$, CoO, and MgO powders were sealed into evacuated quartz tube, and heated for 40 hours at 800 °C followed by 24 hours at 950 °C. The crystal structure of the samples was analyzed by powder X-ray diffraction (XRD) measurements at room temperature using Cu Kα radiation. The magnetic susceptibility measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design Magnetic Property Measurement System (MPMS)) at temperatures from 3 K to 300 K with magnetic field of $H = 1000$ Oe in zero-field-cooled (ZFC) and field-cooled (FC) processes.

3. Results and Discussion

![Figure 2. (a) Powder XRD patterns of Ge(Co$_{1-x}$Mg$_x$)$_2$O$_4$ ($x = 0 \sim 0.5$). (b) $a$-axis length of Ge(Co$_{1-x}$Mg$_x$)$_2$O$_4$ as a function of Mg concentration $x$ ($x = 0 \sim 0.5$).](image1)

![Figure 3. Temperature dependence of FC and ZFC magnetic susceptibilities with $H = 1000$ Oe in Ge(Co$_{1-x}$Mg$_x$)$_2$O$_4$ ($x = 0 \sim 0.5$). (a) $T < 300$ K and (b) $T < 30$ K.](image2)
Figure 2 (a) shows the powder XRD patterns of the polycrystalline Ge(Co$_{1-x}$Mg$_x$)$_2$O$_4$ samples with $x = 0 \sim 0.5$. All the samples crystallize in the spinel-type structure without any additional peak. Figure 2 (b) shows the $a$-axis length of Ge(Co$_{1-x}$Mg$_x$)$_2$O$_4$ as a function of Mg concentration $x$. It is evident that the $a$-axis length of Ge(Co$_{1-x}$Mg$_x$)$_2$O$_4$ decreases with increasing Mg concentration $x$. These results ensure that the $B$-site Co atoms are properly replaced by Mg atoms.

Temperature dependence of the FC and ZFC magnetic susceptibilities with $H = 1000$ Oe in Ge(Co$_{1-x}$Mg$_x$)$_2$O$_4$ ($x = 0 \sim 0.5$) is shown in Fig. 3. As shown in Fig. 3 (a), all the samples exhibit Curie-Weiss behavior in the paramagnetic phase of $\sim 30$ K $< T <$ 300 K. Additionally, the low-temperature magnetic susceptibilities shown in Fig. 3 (b) reveal that the antiferromagnetic transition is suppressed with increasing the nonmagnetic Mg concentration up to $x = 0.1$, resulting in the appearance of the spin-glass-like behavior with the evolution of the irreversibility of magnetic susceptibility above $x = 0.2$.

On the basis of the magnetic susceptibilities shown in Fig. 3, Figs. 4 (a), (b), and (c) plot effective magnetic moment per Co atom $p_{\text{eff}}$, Weiss temperature $\theta_W$, and Néel temperature $T_N$ or spin-glass transition temperature $T_{SG}$ as a function of Mg concentration $x$, respectively. Here, $p_{\text{eff}}$ and $\theta_W$ are obtained by fitting the experimental data in $250$ K $< T <$ $300$ K to the linear Curie-Weiss law, and $T_{SG}$ is defined as the temperature below which the irreversibility in the magnetic susceptibility evolves. For GeCo$_2$O$_4$, the previous work of the measurements and analyses of the magnetic susceptibility and the specific heat claimed invalidity of the Curie-Weiss analysis of the magnetic susceptibility due to the dominant contribution of the low-lying crystal-field states compared to the magnetic correlations [8]. However, the recent inelastic neutron scattering experiments by using high-purity GeCo$_2$O$_4$ single crystals revealed the dominant contribution of the ferromagnetic correlations compared to the crystal-field states [7], which is compatible with the positive $\theta_W$ obtained from the Curie-Weiss analysis [4].
Thus, in the present study, we discuss the Mg-doping effects on the magnetic susceptibility of GeCo$_2$O$_4$ by utilizing the Curie-Weiss analysis, although we should take into account the contribution of the crystal-field states for the correct quantitative analysis.

Figure 4 (a) tells that $p_{\text{eff}} \sim 5.0 \mu_B$ at $x = 0$ is rapidly suppressed with Mg doping in $x = 0 \sim 0.1$, and gradually suppressed in $x = 0.2 \sim 0.5$ down to $p_{\text{eff}} \sim 3.6 \mu_B$ at $x = 0.5$ close to the spin-only value for the high-spin Co$^{2+}$ ($3.87 \mu_B$), which indicates the spin-orbit decoupling caused by the spin-orbit dilution. Additionally, Figs. 4 (b) and (c) tell that the Mg doping leads to the rapid increase of the positive $\theta_W$ in $x = 0 \sim 0.1$ indicating the enhancement of ferromagnetic interactions, while the Mg doping suppresses $T_N$ in $x = 0 \sim 0.1$ resulting in the appearance of spin glass behavior ($T_{SG}$) in $x > 0.2$. Thus the Mg concentration $x$ dependence of $\theta_W$ and $T_N$ ($T_{SG}$) respectively shown in Figs. 4 (b) and (c) strongly suggests the reinforcement of ferromagnetic frustration in GeCo$_2$O$_4$.

It is noted that the ultrasound velocity measurements in GeCo$_2$O$_4$ suggested the possible generation of the “ferromagnetic” geometrical frustration of Kugel-Khomskii (KK)-type orbital-spin interaction between the nearest-neighbor Co$^{2+}$ ions [5]. The present results might suggest that the spin-orbit dilution reinforces the orbital-spin frustration by the spin-orbit decoupling.

4. Summary

In summary, we investigated magnetic properties of the cobaltite spinel Ge(Co$_{1-x}$Mg$_x$)$_2$O$_4$ with $x = 0 \sim 0.5$ to study the spin-orbit dilution effects on the magnetism of the spin-orbit frustrated spinel GeCo$_2$O$_4$. The magnetic susceptibilities in Ge(Co$_{1-x}$Mg$_x$)$_2$O$_4$ suggest that the spin-orbit dilution causes the spin-orbit decoupling and the reinforcement of ferromagnetic frustration in GeCo$_2$O$_4$. Further experimental and theoretical works are expected to verify the orbital-spin frustration and its reinforcement by the spin-orbit dilution in GeCo$_2$O$_4$.

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