International Conference on Strongly Correlated Electron Systems 2014 (SCES2014) IOP Publishing
Journal of Physics: Conference Series **592** (2015) 012106 doi:10.1088/1742-6596/592/1/012106

Spin-orbit dilution effects on the magnetism of frustrated spinel $Ge(Co_{1-x}Mg_x)_2O_4$

Ryotaro Agata, Shota Takita, Takashi Ishikawa, and Tadataka Watanabe
Department of Physics, College of Science and Technology (CST), Nihon University, Chiyoda-ku, Tokyo 101-8308, Japan

E-mail: tadataka@phys.cst.nihon-u.ac.jp

Abstract. We investigated magnetic properties of spinel oxides $Ge(Co_{1-x}Mg_x)_2O_4$ with $x = 0 \sim 0.5$ to study the spin-orbit dilution effects on the magnetism of spin-orbit frustrated spinel $GeCo_2O_4$. We discovered that the magnetic moment per single Co^{2+} ion is decreased with increasing nonmagnetic Mg^{2+} concentration, which indicates the spin-orbit decoupling caused by the spin-orbit dilution. Additionally, small-amount substitution of Mg^{2+} for Co^{2+} causes the rapid increase of the positive Weiss temperature indicating the enhancement of ferromagnetic interactions, while the Mg^{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 $GeCo_2O_4$.

1. Introduction

Geometrical frustration is a concept which provides an intriguing playground for condensed matter physics. Cubic spinels AB_2O_4 with magnetic B ions have attracted much interest in light of the geometrical frustration which is inherent in the B-site sublattice of corner sharing tetrahedra (pyrochlore lattice). Cobaltite spinel $GeCo_2O_4$ consists of magnetic Co^{2+} ions ($3d^7$) with threefold degeneracy of t_{2g} orbitals on the octahedral B sites as shown in Fig. 1, and non-magnetic Ge^{4+} ions on the tetrahedral A sites. Thus it is expected that this compound provides a rich field for the orbital physics in the magnetically frustrated system.

$GeCo_2O_4$ exhibits the occurrence of an antiferromagnetic transition at Néel temperature 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 θ_W = 81.0 K indicating the dominant contribution of the ferromagnetic interactions [4]. For $GeCo_2O_4$, recent ultrasound velocity measurements and inelastic neutron scattering

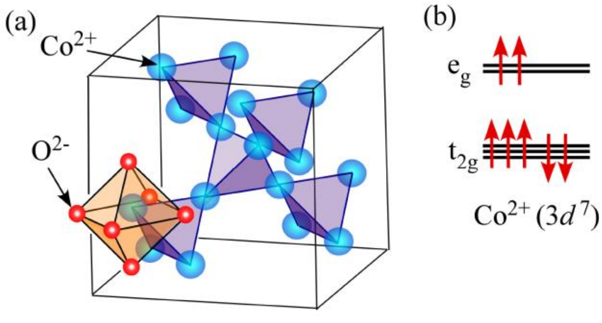
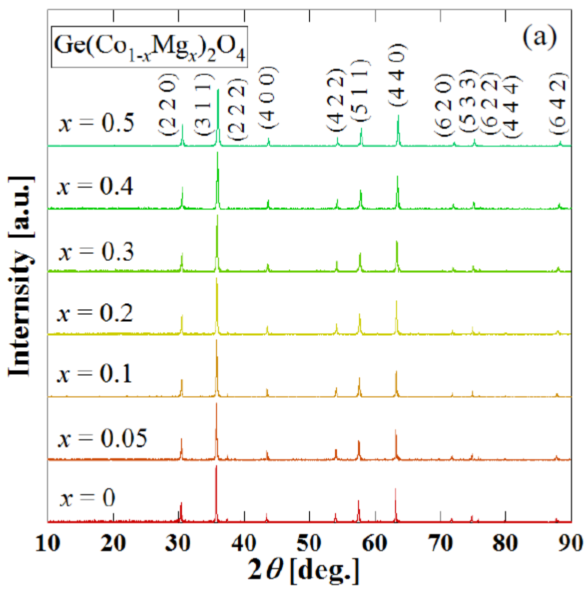


Figure 1. (a) Pyrochlore lattice of the *B*-site Co^{2+} ions in cubic spinel $GeCo_2O_4$. Octahedral O^{2-} ligands surrounding a *B*-site Co^{2+} ion are also illustrated. (b) High-spin state of Co^{2+} ($3d^7$) in the octahedral crystal field.



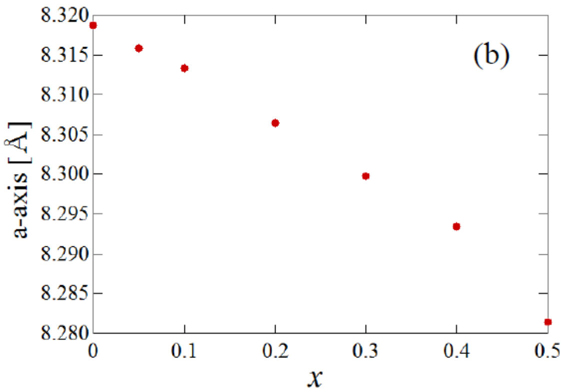


Figure 2. (a) Powder XRD patterns of Ge($Co_{1-x}Mg_x$)$_2$O$_4$ (x = 0 ~ 0.5). (b) *a*-axis length of Ge($Co_{1-x}Mg_x$)$_2$O$_4$ as a function of Mg concentration x (x = 0 ~ 0.5).

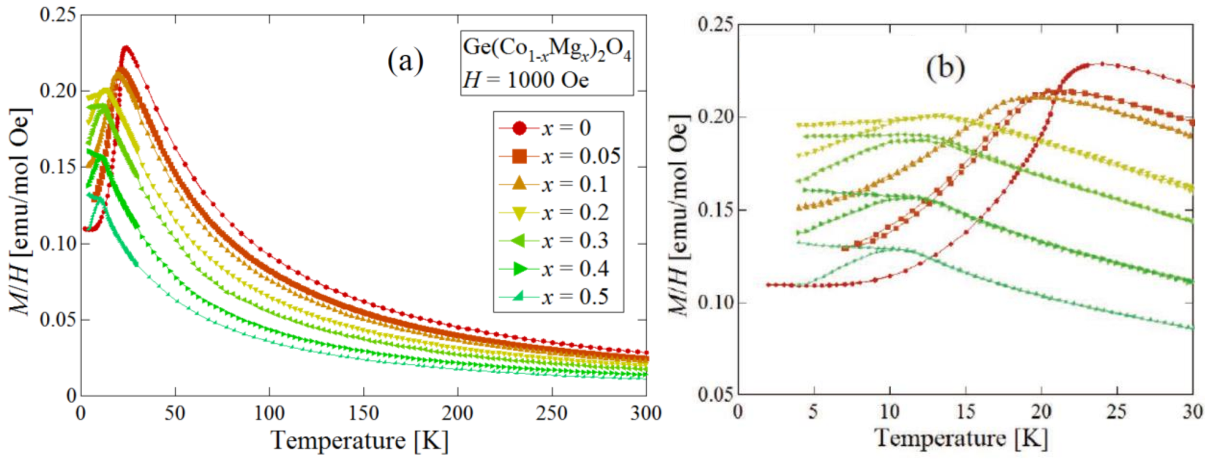


Figure 3. Temperature dependence of FC and ZFC magnetic susceptibilities with H = 1000 Oe in Ge($Co_{1-x}Mg_x$)$_2$O$_4$ (x = 0 ~ 0.5). (a) T < 300 K and (b) T < 30 K.

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 $GeCo_2O_4$.

2. Experimental

Polycrystalline samples of Ge($Co_{1-x}Mg_x$)$_2$O$_4$ (x = 0 ~ 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 ^oC followed by 24 hours at 950 ^oC. 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

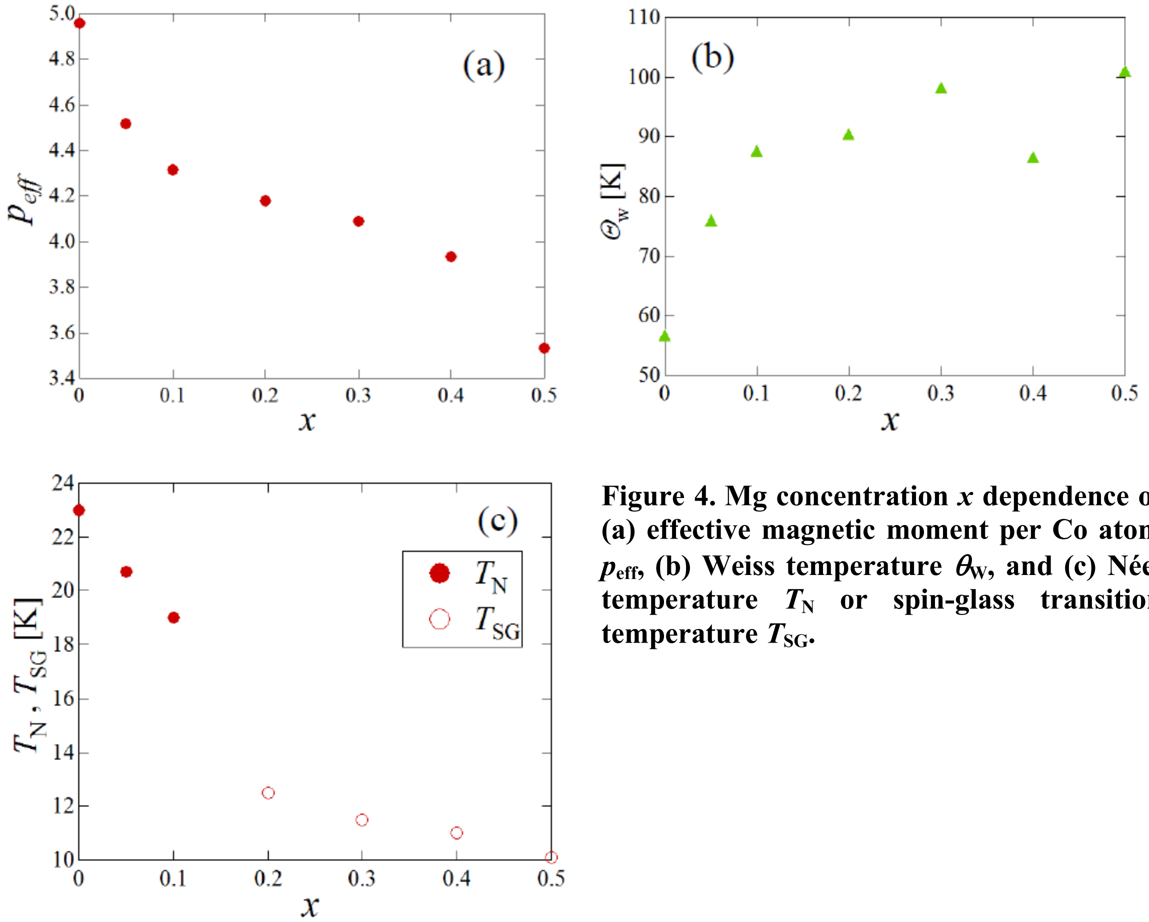


Figure 4. Mg concentration *x* dependence of (a) effective magnetic moment per Co atom p_{eff}, (b) Weiss temperature θ_{W}, and (c) Néel temperature T_{N} or spin-glass transition temperature T_{SG}.

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 ~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 *x* 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_{eff}, Weiss temperature θ_{W}, and Néel temperature T_{N} or spin-glass transition temperature T_{SG} as a function of Mg concentration *x*, respectively. Here, p_{eff} and θ_{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 θ_{W} obtained from the Curie-Weiss analysis [4].

Thus, in the present study, we discuss the Mg-doping effects on the magnetic susceptibility of $GeCo_2O_4$ 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 $p_{eff} \sim 5.0\mu_B$ 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 $p_{eff} \sim 3.6\mu_B$ 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 θ_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 θ_W and T_N (T_{SG}) respectively shown in Figs. 4 (b) and (c) strongly suggests the reinforcement of ferromagnetic frustration in $GeCo_2O_4$.

It is noted that the ultrasound velocity measurements in $GeCo_2O_4$ 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 $Ge(Co_{1-x}Mg_x)_2O_4$ with $x = 0 \sim 0.5$ to study the spin-orbit dilution effects on the magnetism of the spin-orbit frustrated spinel $GeCo_2O_4$. The magnetic susceptibilities in $Ge(Co_{1-x}Mg_x)_2O_4$ suggest that the spin-orbit dilution causes the spin-orbit decoupling and the reinforcement of ferromagnetic frustration in $GeCo_2O_4$. Further experimental and theoretical works are expected to verify the orbital-spin frustration and its reinforcement by the spin-orbit dilution in $GeCo_2O_4$.

5. Acknowledgement

This work was partly supported by Grant-in-Aid for Scientific Research (C) (25400348) from MEXT of Japan, and by Nihon University College of Science and Technology Grants-in-Aid for Fundamental Science Research.

References

[1] Hubsch J and Gavoille G 1987 *J. Magn. Magn. Mater.* **66**, 17.
[2] Diaz S, de Brion S, Chouteau G, Canals B, Simonet V, and Strobel P 2006 *Phys. Rev. B* **74**, 092404.
[3] Hoshi T, Aruga-Katori H, Modals M, and Takagi H 2007 *J. Magn. Magn. Mater.* **310**, e448.
[4] Diaz S, de Brion S, Holzapfel M, Chouteau G, and Strobel P 2004 *Physical B* **346-347**, 146.
[5] Watanabe T, Hara S, and Ikeda S 2008 *Phys. Rev. B* **78**, 094420.
[6] Watanabe T, Hara S, Ikeda S, and Tomiyasu K 2011 *Phys. Rev. B* **84**, 020409(R).
[7] Tomiyasu K, Crawford M K, Adroja D T, Manuel P, Tominaga A, Hara S, Sato H, Watanabe T, Ikeda S, Lynn J W, Iwasa K, and Yamada K 2011 *Phys. Rev. B* **84**, 054405.
[8] Lashley J C, Stevens R, Crawford M K, Boerio-Goates J, Woodfield B F, Qiu Y, Lynn J W, Goddard P A, and Fisher R A 2008 *Phys. Rev. B* **78**, 104406.