Percolated-Induced Ferrimagnetism

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Abstract. A percolated-induced ferromagnetic moment in KNi$_{1-x}$Zn$_x$F$_3$ for $x = 0.57$, which is Heisenberg-type diluted three-dimensional magnet, is studied by electron spin resonance. Below $T_C \simeq 24$ K, ferrimagnetic resonance spectra appeared as expected. On the other hand, in KCo$_{1-x}$Zn$_x$F$_3$ for $0.49 \leq x < 1$, which are Ising-type diluted three-dimensional magnets, a percolated-induced ferromagnetic moment did not appear. This difference may play an important key role in Coulomb repulsion between Zn$^{2+}$ ions because KNi$_{1-x}$Zn$_x$F$_3$ consists of simple cubic lattice, on the other hand tetragonal distortion exists in KCo$_{1-x}$Zn$_x$F$_3$.

1. Introduction

Transparent-bulk ferromagnets are useful for optical isolators in widely optical information networks. Recently numerous investigations\cite{1-3} have been carried out for realizing a higher Curie temperature $T_C$ in diluted-magnetic semiconductors (DMS). The discovery of transparent ferromagnets at room temperature, in Co-doped rutile and anatase TiO$_2$\cite{4,5}, has triggered intensive studies on semiconductors of various oxides doped with magnetic ions. We challenge a method that is different from DMS: magnetic conversion from transparent antiferromagnets to transparent random ferrimagnets, with spontaneous ferromagnetic moment by a diluted percolation method.

In this study, we report on single-crystal transparent random ferrimagnets based on a theoretical prediction by Todate\cite{6}. According to this prediction, a percolation method using non-magnetic ions in simple cubic (SC) antiferromagnets causes an inhomogeneous spin arrangement, because six up/down spins are formed dominantly around non-magnetic ions. Considering Coulomb repulsion, non-magnetic ions are not favor to replacements side by side. As illustrated in Fig. 1, since non-magnetic ions tend to replace every other two magnetic ions at $x = 0.4-0.6$, the numbers of up and down spins are not equal, even if non-magnetic ions are homogenously dispersed in SC antiferromagnets. Since the percolation limit in SC is $x = 0.3117$, a magnetic long-range order may occur. As a result of Coulomb repulsion between non-magnetic ions, ordered spin arrangement forms a random ferrimagnet with spontaneous ferromagnetic moment. If this scenario is true, transparent antiferromagnets convert to transparent random ferrimagnets with spontaneous ferromagnetic moment. This idea is epoch-making and no experimental studies have been conducted.
2. Experimental procedure

We have already reported that perovskite nickel fluorides $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$, which are $S = 1$ Heisenberg-type diluted three-dimensional antiferromagnets, show random ferrimagnets below $T_C = 24 \pm 2$ K for $x = 0.57$ and $26 \pm 2$ K for $x = 0.51$, as shown in Fig. 2[7]. In this study, we performed electron spin resonance (ESR) to clarify appearance of the spontaneous ferromagnetic moment below $T_C$. We further prepared $\hat{s} = 1/2$ Ising-type diluted three-dimensional antiferromagnets, $\text{KCo}_x\text{Zn}_{1-x}\text{F}_3$ ($0.49 \leq x < 1$), at temperature $T$ and external magnetic field $H$, and performed dependence of magnetization $M$ measurements using a superconducting quantum-interference device (SQUID) magnetometer.

Single-crystals of $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ and $\text{KCo}_x\text{Zn}_{1-x}\text{F}_3$ were grown by the Bridgman method. Transparent yellow-green for $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ and light-purple for $\text{KCo}_x\text{Zn}_{1-x}\text{F}_3$ single crystals were obtained. The values of $x$ were determined by energy dispersive X-ray fluorescence spectrometer (EDX, 20 kV acceleration voltage), which is attached to environmental scanning electron microscope (E-SEM, Philips E-SEM 30). Almost all samples were found to be homogeneous, and the scattered values of $x$ were less than $\pm 1-2$ %.

3. Experimental results and discussion

3.1. Heisenberg-type diluted three-dimensional magnets

Figure 3 shows ESR spectra at 24 GHz of $\text{KNi}_x\text{Zn}_{1-x}\text{F}_3$ for $x = 0.57$. Since the symmetrical ESR spectra appear above $T_C$, we found no contaminations of magnetic impurities. Below $T_C$, on the other hand, the antisymmetrical ESR spectra appear and the ESR intensities rapidly increase with decreasing $T$, similar to the $M(T)$ curves shown in Fig. 2. These tendencies indicate ferrimagnetic resonance rather than ferromagnetic resonance because line width in ferromagnetic resonance is generally sharp at low $T$. When we assume typical ferrimagnetic resonance, a resonance condition of the lower field mode is expressed as $\omega_1 = |\gamma_{\text{eff}}|(H + H_{\text{effA}})$, where $\gamma_{\text{eff}}$ and $H_{\text{effA}}$ are effective gyromagnetic ratio and magnetic anisotropy ($H_{\text{effA}} \geq 0$). Thus ferrimagnetic resonance field shifts toward lower field side owing to magnetic anisotropic field. As can be seen in Fig. 3, its tendency is very small because $\text{KNiF}_3$ is a typical Heisenberg SC antiferromagnet[8]. Further from the small shifts of resonance field, demagnetization field can be ignored.

3.2. Ising-type diluted three-dimensional magnets

Figure 4 shows the $M(T)/H$ curves of $\text{KCo}_x\text{Zn}_{1-x}\text{F}_3$ for various values of $x$ at $H = 100$ Oe. The $M(T)/H$ curve for $x = 1$ and the antiferromagnetic transition temperature, $T_N = 114$ K, are consistent with previous reports[9,10]. In $\text{KCo}_x\text{Zn}_{1-x}\text{F}_3$ for $0.49 \leq x \leq 1$, the orbital...
Figure 2. The $M(T)/H$ curve for $x = 0.57$. The FC (field cooled) data and the ZFC (zero-field cooled) data were collected after applying $H = 5$ Oe at 50 K and 5 K, respectively. $T_C = 24 \pm 2$ K was obtained.

Figure 3. ESR spectra for various temperatures for $x = 0.57$. The resonance field of DPPH is necessary to determine $g$ values.

Figure 4. Temperature dependence of $M(T)/H$ in KCoxZn1−xF3 for 0.49 $\leq x \leq 1$ at $H = 100$ Oe. Each diamagnetic moment is NOT subtracted from $M$.

Figure 5. Transition temperatures normalize at $T_N(x = 1) = 114$ K for various values of $x$. The solid line is the fitting line, and then the percolation limit is obtained to be $x = 0.33 \pm 0.02$.

angular momentum of the Co$^{2+}$ ion is not quenched by the octahedral coordinated crystal field. Thus, large diamagnetic moments appear: KCoF$_3$ was reported to be $5 \times 10^{-3}$ emu/mol\[11\]. Although diamagnetic contribution is NOT subtracted from the experimental values of $M$ in Fig. 4, ferromagnetic-like $M(T)$ behavior did not appear. There were no difference between the field cooled (FC) data and the zero-field cooled (ZFC) data which were collected after applying $H = 100$ Oe at 150 K and 5 K, respectively. Furthermore, the $M(H)$ curves for $x = 0.59$ and...
0.49 did not show a hysteresis loop. We determined the value of $T_N$ by the points of inflection of the $M(T)$ curvature. As a result, $x$ dependence of $T_N$ is shown in Fig. 5, and then the percolation limit is obtained to be $x = 0.33 \pm 0.02$, experimentally. This value agrees well with the theoretical prediction limit ($x = 0.3117$). As a result, Co$^{2+}$ ions are well-substituted for Zn$^{2+}$ ions, homogeneously but a percolated-induced ferromagnetic moment did not appear in KCo$_x$Zn$_{1-x}$F$_3$.

Since Co$^{2+}$ ion at high spin state is Kramers doublet, spin-lattice coupling is very large compared with Ni$^{2+}$ ion. According to the X-ray experimental results in KCo$_x$Mg$_{1-x}$F$_3$ for $x = 0.88$ and 0.75[12], a structural-phase transition from cubic to tetragonal crystal structure occurs below temperatures which exhibit three-dimensional long-range order. In KNiF$_3$, on the other hand, no magnetostrictions or structural-phase transitions occur[8-10]. As a result of comparing KNi$_x$Zn$_{1-x}$F$_3$ with KCo$_x$Zn$_{1-x}$F$_3$, we found that appearance of a percolated-induced ferromagnetic moment plays an important key role in keeping the balance of the Coulomb repulsion between non-magnetic ions in SC lattice.

In conclusion, spontaneous ferromagnetic moment appeared in KNi$_x$Zn$_{1-x}$F$_3$ for $x = 0.57$ from ESR measurements, and magnetic conversion from transparent antiferromagnet KNiF$_3$ to transparent random ferrimagnets, with spontaneous ferromagnetic moment by the diluted percolation method, was carried out. On the other hand, in KCo$_x$Zn$_{1-x}$F$_3$ for $0.49 \leq x < 1$, a percolated-induced ferromagnetic moment did not appear because the tetragonal distortion exists. As a result, percolated-induced ferrimagnetism was found to be valid for SC lattice.

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