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High-frequency ESR measurements of the Co spinel compound SiCo_2O_4

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Abstract

The new Co spinel compound SiCo_2O_4 has been synthesized using the high-pressure synthesis technique. High-frequency ESR measurements of powder samples of SiCo_2O_4 have been performed using a pulsed magnetic field up to 16 T in the temperature range from 1.8 to 80 K. A broad absorption line of the EPR spectrum, which is observed at 80 K, becomes sharper as the temperature decreases towards the Néel temperature $T_N = 15$ K. On the other hand, below the Néel temperature, T_N , two absorption lines appear at around 2 T due to the critical field resonances. The spin dynamics of the Co spinel compound SiCo_2O_4 are discussed in connection with other frustrated systems.

1. Introduction

The pyrochlore lattice has attracted much attention from the viewpoint of spin frustration [1]. In particular, $\text{R}_2\text{Ti}_2\text{O}_7$ ($\text{R} = \text{Ho}, \text{Dy}$) pyrochlores have been intensively studied in connection with the ground state of ice [2, 3]. The spin configuration of the R ion tetrahedron has a 2-in–2-out structure due to small ferromagnetic interactions and large magnetic dipole interactions, which originate from the large magnetic moment of the rare earth ions. Therefore, $\text{R}_2\text{Ti}_2\text{O}_7$ is called a dipolar spin ice system [4, 5]. The dipolar spin ice system is interesting in that the spin frustration is constructed by the magnetic dipole interaction as a long-range interaction. On the other hand, the investigation of a spin ice system, which is dominated by the exchange interaction as a short-range interaction, for instance the 3d ion pyrochlore lattice, would be interesting. The most frustrated 3d ion pyrochlore systems are known as spinels. In the spinel compounds of general formula AB_2O_4 , the A and B ions can be either magnetic or non-magnetic ions. The B ions occupy the octahedral sites while the A ions sit in tetrahedral

ones. From the viewpoint of the geometry of the frustration, the B sites of the spinels can be considered as belonging to a pyrochlore lattice. The most famous frustrated 3d ion spinel systems are Cr^{3+} systems such as MCr_2O_4 ($M = \text{Zn}, \text{Cd}, \text{Mg}$) [6–11]. As the Cr^{3+} ion is not so anisotropic, the 2-in–2-out structure is difficult to be realized in Cr^{3+} spinel. Therefore, we decided to investigate Co spinels, which are expected to have a large anisotropy and a stronger exchange interaction than the magnetic dipole interaction, because the magnetic moment of a 3d electron system is smaller than that of Dy^{3+} or Ho^{3+} ions. In this paper, we consider SiCo_2O_4 . The crystal structure of SiCo_2O_4 , which is synthesized under ambient pressure, is an olivine structure [12]. However, the author TS succeeded in obtaining the high-pressure phase of SiCo_2O_4 , which has the spinel structure according to powder x-ray diffraction measurements [13]. The Co^{2+} ions in SiCo_2O_4 occupied the spinel B sites, which form the pyrochlore lattice. From the x-ray measurements the CoO_6 symmetry is tetragonal at room temperature. Moreover, structural changes are not observed below T_N in low-temperature x-ray measurements. From the Co–O bond length, which is estimated to be 210 pm from x-ray measurements [13], the Co^{2+} ions are expected to be in a weak crystal field [14]. Therefore, the Co^{2+} ions in SiCo_2O_4 are expected to be very anisotropic [15]. The magnetic susceptibility curve of a powder sample shows a peak due to an antiferromagnetic transition at around 15 K. The Weiss temperature is estimated to be 52 K, which suggests that the magnetic interaction is ferromagnetic. The magnetization curve at 2 K shows a metamagnetic transition at around $H_c \sim 2$ T. This suggests a larger anisotropy, which comes from the Ising-type nature of the Co^{2+} ion. Therefore, the spin frustration effect is expected to be the Co^{2+} tetrahedron like the Ho^{3+} tetrahedron of $\text{Ho}_2\text{Ti}_2\text{O}_7$ from the ferromagnetic interaction between Co ions and the Ising-type anisotropy. The investigation of the spin frustration effect in spinel SiCo_2O_4 is important in understanding the role of the magnetic dipole interaction on the spin ice $\text{R}_2\text{Ti}_2\text{O}_7$. In this paper, submillimetre and millimetre wave ESR measurements of spinel SiCo_2O_4 powder samples have been performed. The spin dynamics of SiCo_2O_4 will be discussed in connection with other frustrated spinel systems.

2. Experimental details

The powder samples of SiCo_2O_4 were synthesized by the high-pressure synthesis technique. Examples of using high-pressure synthesis are described in [16]. Powder x-ray diffraction measurement showed that a single phase SiCo_2O_4 with the spinel structure was successfully synthesized [13]. It has a cubic symmetry with a lattice constant 814 pm and the space group is $Fd\bar{3}m$. The high-frequency ESR measurements of spinel SiCo_2O_4 were performed using pulsed magnetic fields up to 16 T in the frequency range from 60 to 315 GHz. The observed temperature range was from 1.8 to 80 K. The details of our experimental setup are described in [17, 18].

3. Results and discussion

Figure 1 shows the temperature dependence of the ESR spectra for (a) 160 GHz and (b) 315 GHz. As we are dealing with a powder sample, broad absorption features are seen in the spectra. In the high-temperature range a very broad absorption line is observed at around $g = 5.0$. In general, the g -values of the Co^{2+} ion are known as very anisotropic and are typically 3–6 [15]. In a previous paper, we estimated the g -values of $g_A = 6.7$ and $g_B = 4.5$ from the frequency–field relation of ESR absorptions above the saturation field at 1.8 K [19]. Basically, the g -values above the saturation field become the same values of the g -values in the paramagnetic state. Therefore, the expected EPR absorption line is anisotropic, although

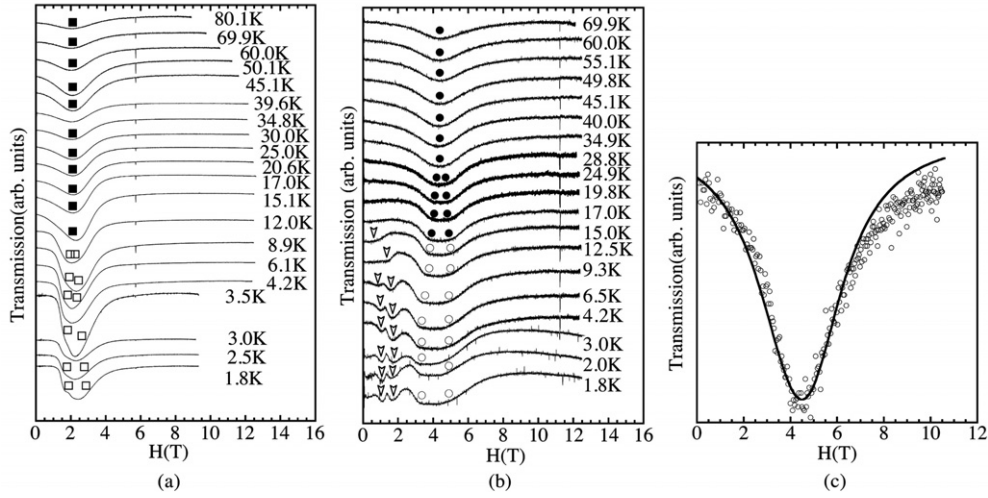


Figure 1. Temperature dependence of ESR spectra of SiCo_2O_4 at (a) 160 GHz and (b) 315 GHz. The sharp absorption line shows DPPH which is the field marker of $g = 2.03$. (c) EPR absorption line of SiCo_2O_4 observed at 315 GHz and 69.9 K. Open circles correspond to the observed data and the solid line corresponds to the powder pattern simulation.

the EPR absorption line obtained at high temperature shows a symmetric EPR line shape. This suggests that the EPR lines are very broad absorption lines. As the powder pattern EPR absorption lines reflect the integral of the angular dependence, we can analyse the absorption lines by the method described in [20]. To estimate the intrinsic linewidth of the EPR absorption, powder pattern simulations were performed for 315 GHz at 69.9 K. We consider the line shape as a Lorentzian shape and use the g -values $g_{\parallel} = 6.7$ and $g_{\perp} = 4.5$, which are consistent with the g -values for the Co^{2+} ion in a tetragonal crystal field [15]. The best-fit simulation curve is obtained by using the linewidth $\Delta H_{\parallel} = \Delta H_{\perp} = 1.87$ T, as shown in figure 1(c). The powder pattern simulation suggests that it is possible to interpret a broad symmetric absorption of the EPR line as two broad anisotropic EPR absorptions. The symmetric EPR line shapes take on a rectangular shape as the temperature decreases. This suggests that the intrinsic linewidths of the ESR lines become sharper as the temperature decreases. On the other hand, below the Néel temperature $T_N = 15$ K two absorption lines appear at around 2 T for 315 GHz and two shoulders appear for 160 GHz. These two anomalies correspond to the critical field resonances at the metamagnetic phase transitions [19]. The temperature dependence of the integrated intensity for the whole absorption lines are shown in figure 2. The integrated intensity for 160 GHz follows the magnetic susceptibility and shows typical behaviours of the magnetic susceptibility of an antiferromagnetic phase transition for the powder sample. On the other hand, as the resonance field for 315 GHz is higher than the applied magnetic field of the magnetic susceptibility measurements, the integrated intensity does not follow the magnetic susceptibility. This is because the saturation field is about 3 T, from the magnetization measurements at 2 K. However, distinct changes of the integrated intensity for the whole absorption lines at 315 GHz are observed at $T_N = 15$ K. The temperature dependence of the g -values is shown in figure 3. The error in the g -value estimation is estimated to be linewidth over ten. Although the g -values of 160 GHz stay constant from 80 to 15 K, they are split into two values due to the Néel state below T_N . As the sample is powder and the intrinsic linewidths are broad, the g -values for 160 GHz do not resolve into two resonances in the

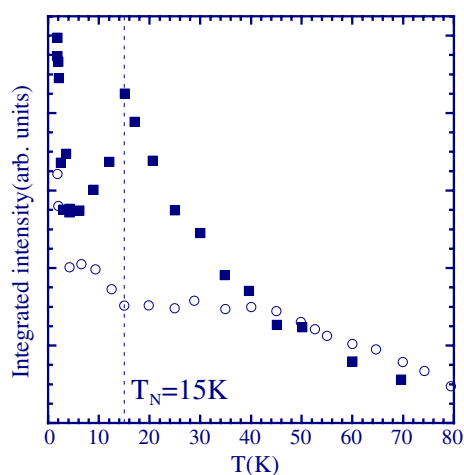


Figure 2. Temperature dependence of the integrated intensity for the whole absorption lines. Closed rectangles and open circles indicate 160 and 315 GHz, respectively. The broken line indicates $T_N = 15$ K.

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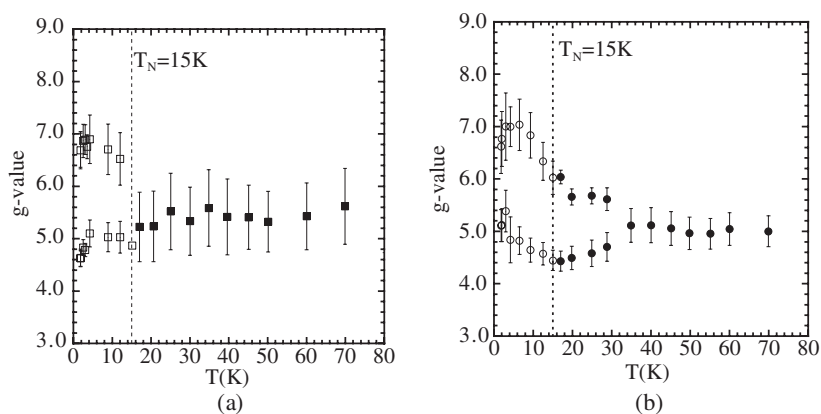


Figure 3. Temperature dependence of the g -values for (a) 160 GHz and (b) 315 GHz. Error bars indicate the linewidth.

high-temperature region. On the other hand, as the frequency 315 GHz is higher than 160 GHz, the ESR absorption line shape changes to rectangular below 30 K. This shows that the g -values for 315 GHz are resolved into two components of g -values below 30 K. However, judging from the powder simulation of the EPR absorption at 69.9 K, we can consider that a broad symmetric absorption line includes two broad absorption lines, which have $g_{\parallel} = 6.7$ and $g_{\perp} = 4.5$. Therefore, the starting temperature of the splitting is not so clear. Moreover, the change of line shape at 30 K should be considered as sharpening absorption line. To obtain the intrinsic linewidth is difficult because of the broadened spectra; therefore we take the linewidth of the whole absorption line, marked by rectangle and circle symbols in figures 1(a) and (b), and they are shown in figure 4. Although the linewidths of 160 and 315 GHz stay constant from 80 to 15 K, the linewidths below T_N for 160 and 315 GHz become

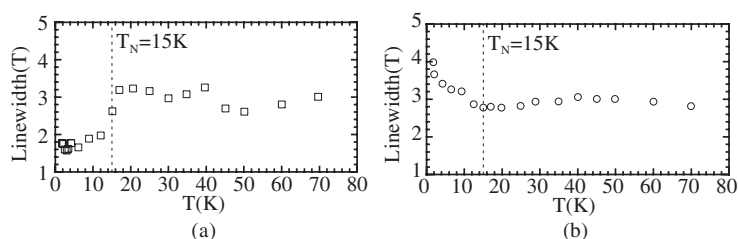


Figure 4. Temperature dependence of the linewidth for the whole linewidth at (a) 160 GHz and (b) 315 GHz.

narrow and broad, respectively. As the edges of the line shape for 315 GHz become sharper below 30 K, the intrinsic linewidths are expected to become sharper below 30 K. Typical ESR behaviour of an antiferromagnet shows linewidth broadening at around T_N . Although the g -shifts are observed at 315 GHz, linewidth broadenings are not observed at 315 and 160 GHz. Therefore, the behaviour of SiCo_2O_4 at T_N is different from typical antiferromagnetic ordering. We consider the critical behaviour of SiCo_2O_4 in comparison with another frustration system. The ESR absorption line shapes of the Cr^{3+} spinel LiCrTiO_4 powder were also symmetric and similar to those of SiCo_2O_4 [21]. But the linewidth becomes broader and g -shifts are observed in LiCrTiO_4 as the temperature decreases. The same tendencies of the linewidth and the g -value were observed in the *Kagome* lattice system $\text{SrCr}_x\text{Ga}_{12-x}\text{O}_{19}$ [22, 23]. In general, it is considered that the spin frustration affects the linewidth and the g -value of the ESR spectrum. On the other hand, the same Cr^{3+} spinel frustration system ZnCr_2O_4 shows a constant g -value as the temperature decreases [9]. In ZnCr_2O_4 antiferromagnetic ordering has occurred with the crystal structure phase transition at $T_N = 13$ K [6–8]. Although g -shifts are observed in SiCo_2O_4 , the behaviour of the linewidth is different from that among the chromium systems LiCrTiO_4 , $\text{SrCr}_x\text{Ga}_{12-x}\text{O}_{19}$ and ZnCr_2O_4 . The reason for this may come from the difference of the magnetic anisotropy of the Cr^{2+} ion and the Co^{2+} ion. To clarify the behaviours of the ESR absorption for the pyrochlore frustration system with ferromagnetic interaction at the critical temperature, ESR measurements of DyTi_2O_7 or HoTi_2O_7 are required.

4. Conclusion

High-frequency ESR measurements of the spinel SiCo_2O_4 have been performed in the temperature range from 1.8 to 80 K. Distinct g -shifts and changes of the linewidth are observed at T_N . However, the linewidth broadening towards T_N could not be observed. Not all behaviours of SiCo_2O_4 coincide with the typical behaviour of a frustrated system. However, the critical behaviour of SiCo_2O_4 at T_N is different from typical antiferromagnetic ordering. To investigate the spin frustration effect in the spinel SiCo_2O_4 in more detail, single crystals are required.

Acknowledgments

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