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Melting of antiferromagnetic ordering in spinel oxide $CoAl_2O_4$

T Suzuki[1], **H Nagai**[1], **M Nohara**[1,2] **and H Takagi**[1,2]

[1] Department of Advanced Materials Science, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan
[2] CREST, Japan Science and Technology Agency (JST), Japan

E-mail: kk67104@mail.ecc.u-tokyo.ac.jp

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Abstract

The magnetic and thermal properties of the spinel oxides CoB_2O_4 have been studied for B = Rh, Co and Al. The compounds consist of magnetic Co^{2+} ($S = 3/2$) in the A site and non-magnetic B^{3+} in the B site, which form diamond and pyrochlore sublattices, respectively. We found that the ratio of the Curie–Weiss temperature to the magnetic ordering temperature, $|\Theta_{CW}|/T_N$, depends strongly on B^{3+} cations. $CoRh_2O_4$ was a typical antiferromagnet with $|\Theta_{CW}|/T_N = 31\ K/25\ K = 1.2$. The ratio was enhanced up to $|\Theta_{CW}|/T_N = 110\ K/30\ K = 3.7$ for Co_3O_4 (B = Co) and $|\Theta_{CW}|/T^* = 89\ K/9\ K = 10$ for $CoAl_2O_4$, indicating the evolution of magnetic frustration. The specific heat for $CoAl_2O_4$ exhibited a broad peak at $T^* = 9$ K and $T^{2.5}$ behaviour at low temperatures, suggesting the most frustrated magnet $CoAl_2O_4$ is in the critical vicinity of a quantum melting point of the antiferromagnetically ordered state.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The spinels are one of the most familiar magnetic compounds. The spinels have the general formula AB_2X_4, where A and B are metal cations and X is an anion. The B site forms a three-dimensional network of corner-sharing tetrahedra, known as the pyrochlore lattice, which has been a paramount playground for geometrical frustration. Interesting phenomena such as spin ice [1, 2] and clusters of spins [3] have been observed.

Recently, Fritshch *et al* have reported strong magnetic frustration in the spinel sulfides ASc_2S_4 for magnetic cations of A = Fe and Mn [4]. A spin and orbital liquid state has been proposed for $FeSc_2S_4$ [5]. $MnSc_2S_4$ exhibits spiral magnetic ordering [6]. Interestingly, the B site Sc^{3+} is non-magnetic in these compounds. The A site in spinels forms a diamond lattice, and the diamond lattice is not subjected to the geometrical frustration intrinsically. In order to understand the intriguing A-site frustration, Krimmel *et al* proposed that the A site in spinels forms a unique frustrated lattice due to the multiple exchange paths of A–X–B–X–A [4–6].

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It is still an open question whether the oxide spinels exhibit A-site frustration or not, mainly due to chemical difficulties. Tristan *et al* reported magnetic frustration on the oxide spinels MAl_2O_4 with M = Co, Fe and Mn [7]. However, these oxides exhibit considerable chemical mixing between M and Al to form $(M_{1-x}Al_x)[Al_{2-x}M_x]O_4$, and the magnetic properties are strongly influenced by the inversion parameter x.

Here, we focus on the normal spinel oxides CoB_2O_4 with B = Rh, Co and Al. The A site is occupied by magnetic Co^{2+} with $S = 3/2$. The B-site cations are non-magnetic because of the t_{2g}^6 electronic configurations in the low-spin state for Rh^{3+} and Co^{3+} [8, 9]. We found that the ratio of the Curie–Weiss temperature to the magnetic ordering temperature, $|\Theta_{CW}|/T_N$, depends strongly on B^{3+} cations. $CoRh_2O_4$ was a typical antiferromagnet with $|\Theta_{CW}|/T_N = 31\ K/25\ K = 1.2$. The ratio was enhanced up to $|\Theta_{CW}|/T_N = 110\ K/30\ K = 3.7$ for B = Co and $|\Theta_{CW}|/T^* = 89\ K/9\ K = 10$ for B = Al, indicating the presence of A-site magnetic frustration in oxide spinels. The specific heat for $CoAl_2O_4$ exhibited a broad peak at $T^* = 9$ K and $T^{2.5}$ behaviour at low temperatures, suggesting that $CoAl_2O_4$ is in the critical vicinity of a quantum melting point of the antiferromagnetically ordered state.

2. Experimental details

Polycrystalline samples of CoB_2O_4 with B = Rh, Co and Al were prepared by a solid-state reaction from the binary oxides Co_3O_4 (99.9%), Rh_2O_3 (99.9%) and Al_2O_3 (99.99%). $CoAl_2O_4$ is known as a normal spinel with minor inversion between Co^{2+} and Al^{3+} [10]. In order to reduce the inversion, the $CoAl_2O_4$ sample was slowly cooled from 700 to 400 °C at a rate of 2 °C h^{-1} and annealed at 400 °C for 150 h. Powder x-ray diffraction was performed by using Cu Kα radiation. Rietveld analyses were performed by utilizing the program RIETAN [11] to determine the inversion parameter. Magnetic susceptibility was measured between 2 and 300 K by using a SQUID magnetometer (MPMS, Quantum Design). Specific heat was measured by a thermal relaxation method (PPMS, Quantum Design).

3. Results and discussion

Figure 1 shows the powder x-ray diffraction patterns for CoB_2O_4 with B = Rh, Co and Al. The diffraction patterns indicate a single phase of cubic spinels. We determined the inversion parameter x, which is defined by $(Co_{1-x}B_x)^{\text{A-site}}[B_{2-x}Co_x]^{\text{B-site}}O_4$, from Rietveld analysis. $CoRh_2O_4$ shows no evidence of inversion between Co and Rh within an experimental error of 2%, in agreement with a previous report [12]. For $CoAl_2O_4$, we estimated $x = 0.04(2)$, indicating that the inversion is negligibly small for the present sample. This value of x is markedly smaller than those reported previously [7, 10].

Figure 2 shows the temperature dependence of the inverse magnetic susceptibility $1/\chi$ and the specific heat divided by temperature C/T for $CoRh_2O_4$. Above about 40 K, $1/\chi$ obeys Curie–Weiss behaviour, $1/\chi = (T - \Theta_{CW})/C_{Curie}$. We estimate a Curie–Weiss temperature of $\Theta_{CW} = -31(1)$ K and an effective moment of $\mu_{eff} = 4.31(3)\ \mu_B$, consistent with the $S = 3/2$ moment of Co^{2+} [8]. C/T exhibits a λ-type anomaly at $T_N = 25$ K, at which χ exhibits a peak, indicating antiferromagnetic ordering. The frustration parameter, defined by the ratio $f = |\Theta_{CW}|/T_N$, is as small as $f = 1.2$. Thus, $CoRh_2O_4$ is a typical antiferromagnet with $T_N \sim |\Theta_{CW}|$.

Figure 3 shows the temperature dependence of $1/\chi$ and C/T for Co_3O_4 (B = Co). The Curie–Weiss temperature of $\Theta_{CW} = -110(5)$ K and the Néel temperature of $T_N = 30$ K give an estimate for the frustration parameter of $f = 3.7$. This value is moderately larger than unity,

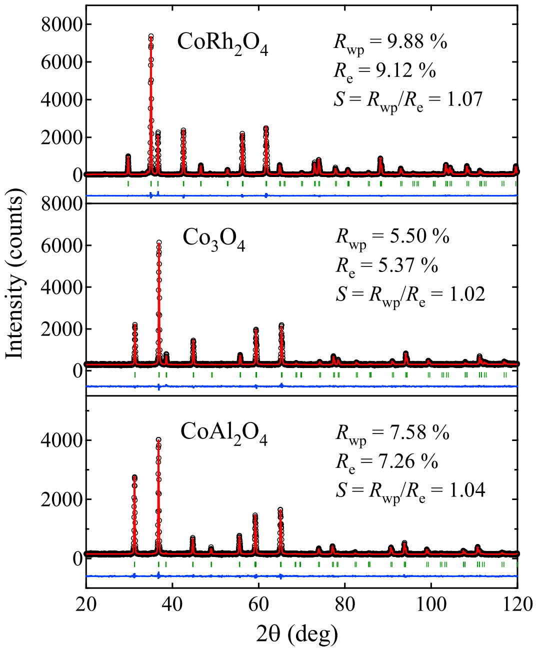

Figure 1. X-ray diffraction patterns of CoRh$_2$O$_4$, Co$_3$O$_4$ and CoAl$_2$O$_4$. The measured data (open circles) are compared with the calculated Rietveld patterns (solid lines). The difference spectra below the data show the absence of any impurity phases. R_{wp} and R_e indicate the weighted profile and expected reliability factors, respectively. Small values of $S = R_{wp}/R_e$ (>1) suggest that the refinements were well performed.

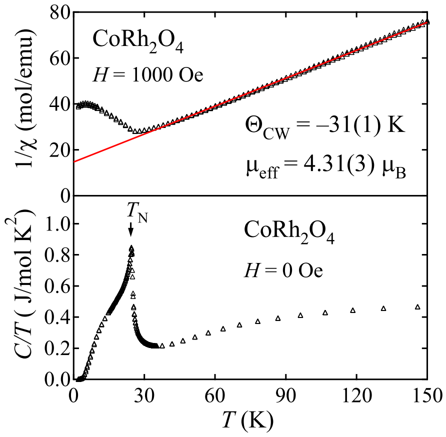

Figure 2. Inverse magnetic susceptibility $1/\chi$ and specific heat divided by temperature C/T for CoRh$_2$O$_4$. The solid line represents a fit to the Curie–Weiss curve.

indicating the presence of magnetic frustration in Co$_3$O$_4$. As a result, $1/\chi$ deviates from Curie–Weiss behaviour below about 100 K, indicating an evolution of short-range antiferromagnetic ordering below the characteristic temperature of $T \sim |\Theta_{CW}|$. At $T_N = 30$ K long-range ordering emerges, as can be seen from the λ-type anomaly in the specific heat.

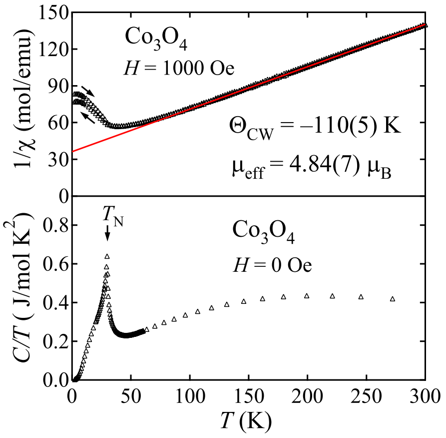

Figure 3. Inverse magnetic susceptibility $1/\chi$ and specific heat divided by temperature C/T for Co_3O_4. The solid line represents a fit to the Curie–Weiss curve.

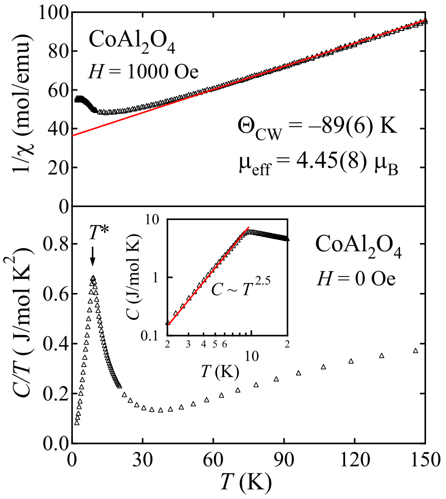

Figure 4. Inverse magnetic susceptibility $1/\chi$ and specific heat divided by temperature C/T for $CoAl_2O_4$. The solid line represents a fit to the Curie–Weiss curve. The inset shows the $T^{2.5}$ dependence of the specific heat C on a logarithmic scale.

The long-range magnetic ordering was drastically reduced for $CoAl_2O_4$ as can be seen from the temperature dependence of $1/\chi$ and C/T in figure 4. Although the Curie–Weiss temperature is as large as $\Theta_{CW} = -89(6)$ K, no clear signature of the long-range magnetic ordering was observed down to 2 K. Below about 60 K, $1/\chi$ deviates from Curie–Weiss behaviour and C/T starts increasing upon cooling, indicating an evolution of short-range antiferromagnetic ordering. By further lowering temperature, χ exhibits a broad peak at about 14 K and C/T at about $T^* = 9$ K. We tentatively determine the frustration parameter f from the ratio $|\Theta_{CW}|/T^*$. The large value of $f = 10$ demonstrates the presence of A-site frustration for the oxide spinel $CoAl_2O_4$. Disordered $CoAl_2O_4$ with an inversion parameter $x = 0.08$ exhibits a larger frustration parameter of $f = 22$ [7], probably due to the spin glass crossover at the reduced transition temperature of 4.8 K.

Table 1. Magnetic parameters of CoB_2O_4 for B = Rh, Co and Al.

	$CoRh_2O_4$	Co_3O_4	$CoAl_2O_4$
Curie–Weiss temperature, Θ_{CW} (K)	−31(1)	−110(5)	−89(6)
Ordering temperature, T_N or T^* (K)	25	30	9
Frustration parameter, $f = \|\Theta_{CW}\|/T_N$ or $\|\Theta_{CW}\|/T^*$	1.2	3.7	10
Effective moment, μ_{eff} (μ_B)	4.31(3)	4.84(7)	4.45(8)

Magnetic parameters for the oxide spinels CoB_2O_4 with B = Rh, Co and Al are summarized in table 1. Interestingly, the magnetic frustration in CoB_2O_4 depends strongly on the non-magnetic B^{3+} cations and the frustration parameter f increases as $B = Rh^{3+} < Co^{3+} < Al^{3+}$. As we mentioned above, the A-site frustration originates from the multiple exchange paths Co–O–B–O–Co [4–6]. We naturally expect that the exchange interactions along Co–O–B–O–Co depend strongly on the ionic radius of B^{3+} and the distortion of BO_6 octahedra, thus f is modified by B^{3+}. However, at present it is unclear why the largest f is realized for B = Al with the smallest ionic radius, which exhibits the largest distortion of BO_6.

We suggest for the present $CoAl_2O_4$ that the broad peak in χ and C/T at $T^* = 9$ K is not due to the simple spin glass crossover. The magnetic susceptibility exhibits no hysteresis between the field cooling (FC) and zero-field cooling (ZFC) processes below T^*. Correspondingly, peculiar features were observed in specific heat: a broad peak at around $T^* = 9$ K and the power-law of $T^{2.5}$ behaviour below T^*, as shown in the inset to figure 4. This behaviour is different from the T^2 behaviour observed below the spin glass transition temperature [7]. Our observations signal a gradual quenching of the magnetic entropy at around T^* and suggest that clean $CoAl_2O_4$ is in the critical vicinity of a melting point of a long-range antiferromagnetic ordered state at $T = 0$.

4. Summary

We have demonstrated the presence of A-site frustration for the oxide spinel $CoAl_2O_4$. The A-site frustration can be tuned by the non-magnetic B cations; the frustration parameter increases as $B = Rh^{3+} < Co^{3+} < Al^{3+}$ for CoB_2O_4 and reaches a large value of $f = 10$ for $CoAl_2O_4$. The most frustrated magnet $CoAl_2O_4$ exhibits no long-range magnetic ordering down to 2 K and the specific heat shows a broad peak at around $T^* = 9$ K and a $T^{2.5}$ power-law behaviour below T^*. These observations suggest that $CoAl_2O_4$ is in the critical vicinity of a quantum melting point of the Néel ordered state.

References

[1] Ramirez A P, Hayashi A, Cava R J, Siddharthan R and Shastry B S 1999 *Nature* **399** 333

[2] Bramwell S T and Gingras M J P 2001 *Science* **294** 1495

[3] Lee S-H, Broholm C, Ratcliff W, Gasparovic G, Huang Q, Kim T H and Cheong S-W 2002 *Nature* **418** 856

[4] Fritsch V, Hemberger J, Büttgen N, Scheidt E-W, Krug von Nidda H-A, Loidl A and Tsurkan V 2004 *Phys. Rev. Lett.* **92** 116401

[5] Krimmel A, Mücksch M, Tsurkan V, Koza M M, Mutka H and Loidl A 2005 *Phys. Rev. Lett.* **94** 237402

[6] Krimmel A, Mücksch M, Tsurkan V, Koza M M, Mutka H, Ritter C, Sheptyakov D V, Horn S and Loidl A 2006 *Phys. Rev.* B **73** 014413

[7] Tristan N, Hemberger J, Krimmel A, Krug von Nidda H-A, Tsurkan V and Loidl A 2005 *Phys. Rev.* B **72** 174404

[8] Blasse G 1963 *Philips Res. Rep.* **18** 383

[9] Roth W L 1964 *J. Phys. Chem. Solids* **25** 1

[10] Nakatsuka A, Ikeda Y, Yamasaki Y, Nakayama N and Mizota T 2003 *Solid State Commun.* **128** 85

[11] Izumi F and Ikeda T 2000 *Mater. Sci. Forum* **198** 321

[12] Cascales C and Rasines I 1984 *Mater. Chem. Phys.* **10** 199