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Magnetic properties of a structurally four-spin system $SrCo_2(PO_4)_2$

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ABSTRACT

Magnetic properties of a structurally four-spin system $SrCo_2(PO_4)_2$ are firstly investigated by means of susceptibility, magnetization, and heat capacity measurements. Our experimental results show that $SrCo_2(PO_4)_2$ is a typical three-dimensional antiferromagnet with a magnetic ordering at $T_N = \sim 23$ K. Although Co^{2+} ions of $SrCo_2(PO_4)_2$ have a high spin state and exhibit a large orbital moment contribution in an oxygen octahedral environment, similar to those of $(Ba, Sr, Pb)Co_2(VO_4)_2$, field-induced magnetic transitions are not observed.

Compounds with a general formula of $AM_2(XO_4)_2$ (A = Ba, Sr, Pb; M = Cu, Co, Ni, Fe, Mn; X = P, V) have attracted much attention in solid state physics, due to the discovery of their rich and interesting magnetic behaviors [1–24]. Among them, for $S = 1/2$ systems, $SrCu_2(PO_4)_2$ and $PbCu_2(PO_4)_2$ are spin-gap systems with a realization of a linear four-spin cluster model [1, 2], while $BaCu_2(VO_4)_2$ shows a spin singlet ground state with a large spin-gap, which can be described as an one-dimensional (1D) alternating spin chain system or an isolated spin dimer system [3–7]. For $S = 1$ systems, $SrNi_2(VO_4)_2$ and $PbNi_2(VO_4)_2$ are suggested to belong to 1D Haldane spin chain systems [8,9], which provide an interesting issue on quantum critical behaviors between spin-liquid and Neel ordered states [10,11], while $BaNi_2(VO_4)_2$ is likely a prototype of two-dimensional XY system [12–14]. For $S = 3/2$ systems, $BaCo_2(VO_4)_2$, $SrCo_2(VO_4)_2$, and $PbCo_2(VO_4)_2$ are found to be 1D Ising spin systems with large magnetic anisotropy [15–22], which display an interesting field-induced quantum phase transition. For $S = 2$ and $5/2$ systems, $SrFe_2(PO_4)_2$ and $BaMn_2(VO_4)_2$ are found to be canted antiferromagnets with weak ferromagnetism [23,24].

$SrCo_2(PO_4)_2$ is also one of this family mentioned above and crystallizes in a triclinic structure of space group $P\bar{1}$ with $a =$ 5.014(2) Å, $b = 8.639(4)$ Å, $c = 9.691(1)$ Å, $\alpha = 118.04(3)°$, $\beta = 75.09(4)°$, and $\gamma = 86.90(4)°$ [25]. As shown in Fig. 1, one of the most remarkable structural features is that magnetic Co^{2+} ions have two crystallographic sites of Co(1) and Co(2), in which all of the Co(1)O$_5$ trigonal bipyramids form dimeric Co(1)$_2$O$_{10}$ groups via edge-sharing, and dimeric Co(1)$_2$O$_{10}$ groups connect with Co(2)O$_4$ tetrahedra to form four-spin clusters with Co(2)-Co(1)-Co(1)-Co(2) units via corner-sharing. Further, four-spin clusters connect to each other through PO$_4$ tetrahedra to form chains running along the b-axis and Sr ions locate inside between the chains. Such structural features in $SrCo_2(PO_4)_2$ are clearly different from those in $(Ba, Sr, Pb)Co_2(VO_4)_2$ with a screw chain structure along the c-axis [26–28]. However, to our best knowledge, no reports on magnetic properties of $SrCo_2(PO_4)_2$ can be found elsewhere. In this paper, we are the first to investigate the magnetic properties of $SrCo_2(PO_4)_2$ by means of magnetic susceptibility, magnetization and heat capacity measurements.

A polycrystalline sample was synthesized by a standard solid-state reaction method using a mixture of high purity reagents of $SrCO_3$ (4N), $CoC_2O_4 \cdot 2H_2O$ (3N), and $NH_4H_2PO_4$ (3N) as the starting materials in the molar ratio of 1:2:2. The mixture was ground carefully, homogenized thoroughly with ethanol (99%) in an agate mortar, and then packed into an alumina crucible and calcined at 930 °C in air for 40 h with several intermediate grindings. Finally, the product was pressed into pellets and sintered at 950 °C for 20 h, and then cooled to room temperature at a rate of 100 K/h. No impurity phase was observed by powder X-Ray diffraction (XRD) measurement using $CuK\alpha$ radiation. The

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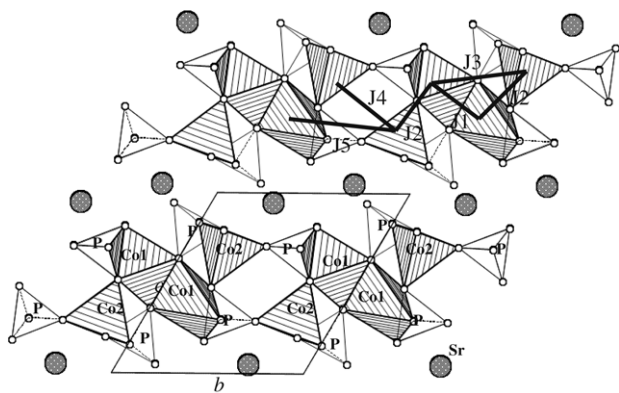*E-mail addresses:* hezz@fjirsm.ac.cn, hcz1988@hotmail.com (Z. He).

Fig. 1. Crystal structure of $SrCo_2(PO_4)_2$. Large and small balls represent Sr and O, respectively. Main exchange paths are seen.

structural parameters were refined by the Rietveld method using the RIETAN-2000 program [29], being in good agreement with those reported previously [25]. The magnetic measurements were preformed using a superconducting quantum interference device (MPMS5S, Quantum Design) magnetometer and the heat capacity was measured by a relaxation method using a commercial physical property measurement system (PPMS, Quantum Design).

The temperature dependences of the magnetic susceptibility and corresponding reciprocal one of polycrystalline $SrCo_2(PO_4)_2$ are shown in Fig. 2. The susceptibility increases with decreasing temperature, while a sharp peak is observed around ∼23 K, showing onset of antiferromagnetic (AF) ordering. A Curie-like upturn is seen below ∼10 K, indicating a contribution from free moment due to structural defect. A typical Curie–Weiss behavior is observed above 40 K, giving the Curie constant $C =$ 6.316(9) emu K/mol and Weiss constant $\theta = -23.68(4)$ K. The effective magnetic moment (μ_{eff}) is calculated to be 5.026(7)μ_B, which is much larger than the value 3.87(3) μ_B for $S = 3/2$ with a g factor of 2. This indicates that Co^{2+} ions in $SrCo_2(PO_4)_2$ have a high spin state and exhibit a large orbital moment contribution in the oxygen octahedral environment, which is similar to those in $(Ba, Sr, Pb)Co_2(VO_4)_2$ [15,18,28]. Also, the negative Weiss constant suggests that the interactions between Co^{2+} ions are AF.

The results of heat capacity measurements in $H = 0$ from 50 to 2 K are shown in Fig. 3. A clear sign of a λ-like feature is seen at around 23 K, agreeing with the peak temperature in susceptibility data. This gives concrete evidence of a long-range AF ordering at ∼23 K. As shown in Fig. 3(b), heat capacity data above 35 K can be fitted well by $C_p = \gamma T + \beta T^3$ with $\gamma = 0.3788(8)$ J mol^{-1} K^{-1} and $\beta = 1.758(2) \times 10^{-4}$ J mol^{-1} K^{-4}. Since $SrCo_2(PO_4)_2$ is an insulator, it is reasonable to arrange γT for the magnetic contribution from spin systems and βT^3 for the lattice one from phonons. The β value gives a Debye temperature of 415.4(1) K and the entropy change for this λ-like anomaly at ∼23 K is roughly estimated to be $\Delta S = \sim$10.43 J/mol K, corresponding to 93.4% of $R\ln(2S + 1)$ expected for spin-3/2 systems. Such slight underestimation of spin entropy might be due to an overestimation of lattice contribution. However, this is quite different from the heat capacity feature in $(Ba, Sr, Pb)Co_2(VO_4)_2$ in which most of the entropy of the systems has been lost through the short-range magnetic correlation as shown by a broad peak in their magnetic susceptibilities [15,18,28]. We also note that the heat capacity feature in $SrCo_2(PO_4)_2$ is in good agreement with $T_N \approx -\theta$ as seen in magnetic susceptibility, showing that the system is a typical three-dimensional antiferromagnet without spin fluctuation.

Magnetization (M) as a function of applied field (H) at 2 K is shown in Fig. 4. The linear behavior of magnetization and no magnetization saturation are seen, which are in good agreement with the AF ground state in the system. We note that
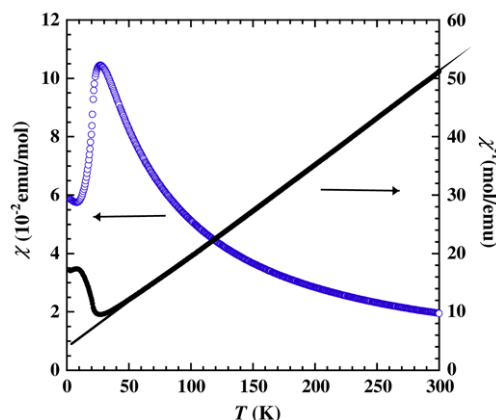

Fig. 2. The temperature dependences of the magnetic susceptibility and the corresponding reciprocal one of polycrystalline $SrCo_2(PO_4)_2$.
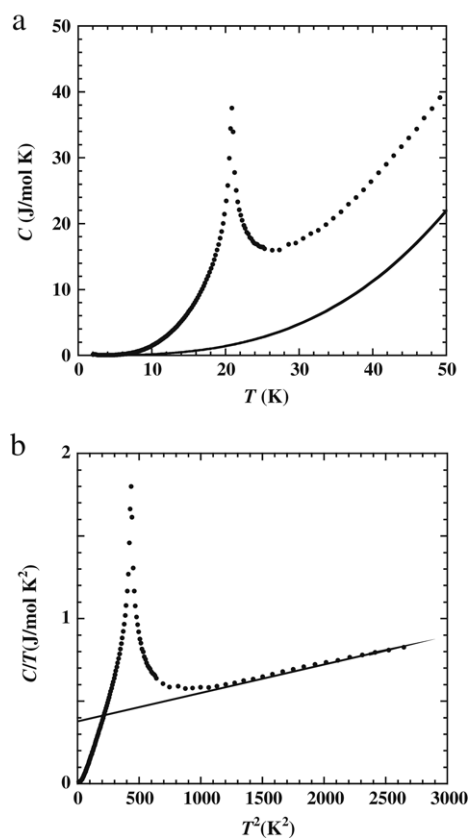

Fig. 3. (a) Heat capacity (C_p) measured in zero magnetic field. The solid line represents the lattice contribution (C_l). (b) The plot of C_p/T vs T^2.

although Co^{2+} ions in $SrCo_2(PO_4)_2$ also exhibit a large orbital moment contribution similar to those in $(Ba, Sr, Pb)Co_2(VO_4)_2$, field-induced magnetic phase transitions are not observed.

Our experimental results of susceptibility, magnetization and heat capacity measurements clearly show that $SrCo_2(PO_4)_2$ is a typical three-dimensional (3D) antiferromagnet with a magnetic ordering at $T_N = \sim$23 K. We found that $SrCo_2(PO_4)_2$ belongs to the family of $SrCo_2(XO_4)_2$ and its magnetic Co^{2+} ions also exhibit a high spin state of $S = 3/2$ with a large orbital moment contribution, which is quite similar to those in $(Ba, Sr, Pb)Co_2(VO_4)_2$. However, field-induced magnetic phase transitions are not observed in the system. As shown in Fig. 1, there are five different exchange paths in intra-chains: intra-cluster of four-spin Co1–O–Co1 (J1),
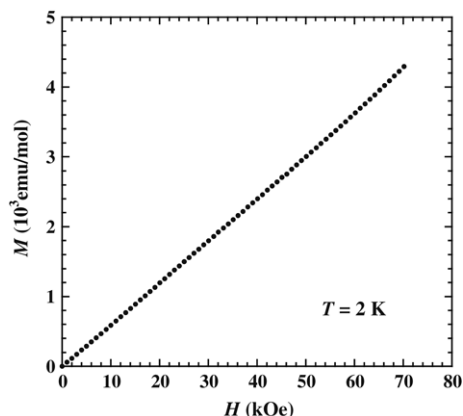
Fig. 4. Magnetization as a function of applied field H at 2 K.

Co1–O–Co2 (J2), and Co1–O–P–O–Co2 (J3); inter-cluster of four-spin Co2–O–P–O–Co2 (J4) and Co2–O–P–O–Co1 (J5). If inter-chain exchange paths are also taken into consideration, $SrCo_2(PO_4)_2$ looks to be one of quite complicated spin systems, which is clearly different from $(Ba, Sr, Pb)Co_2(VO_4)_2$. We suggest that a typical 3D magnetic behavior in $SrCo_2(PO_4)_2$ is related to its structural features. Compared with different magnetic properties between $SrCo_2(PO_4)_2$ and $(Ba, Sr, Pb)Co_2(VO_4)_2$, it is well-known that nonmagnetic P^{5+} or V^{5+} ions would play an important role in the family of $AM_2(XO_4)_2$.

Conclusions

Polycrystalline samples of $SrCo_2(PO_4)_2$ with good quality have been synthesized by a standard solid-state reaction method. Susceptibility, magnetization and heat capacity measurements showed that $SrCo_2(PO_4)_2$ is a typical 3D spin-3/2 antiferromagnet with a magnetic ordering at $\sim$23 K. Although magnetic Co^{2+} ions in $SrCo_2(PO_4)_2$ exhibit a high spin state of $S = 3/2$ with a large orbital moment contribution, field-induced magnetic phase transitions are not observed in the system.

References

[1] A.A. Belik, M. Azuma, A. Matsuo, M.-H. Whangbo, H.-J. Koo, J. Kikuchi, T. Kaji, S. Okubo, H. Ohta, K. Kindo, M. Takano, Inorg. Chem. 44 (2005) 6632.
[2] A.A. Belik, M. Azuma, A. Matsuo, T. Kaji, S. Okubo, H. Ohta, K. Kindo, M. Takano, Phys. Rev. B 73 (2006) 024429.
[3] Z. He, T. Kyômen, M. Itoh, Phys. Rev. B 69 (2004) 220407.
[4] K. Ghoshray, B. Pahari, B. Bandyopadhyay, R. Sarkar, A. Ghoshray, Phys. Rev. B 71 (2005) 214401.
[5] C.S. Lue, B.X. Xie, Phys. Rev. B 72 (2005) 052409.
[6] H.-J. Koo, M.-H. Whangbo, Inorg. Chem. 45 (2006) 4440.
[7] S.S. Salunke, A.V. Mahajan, I. Dasgupta, Phys. Rev. B 77 (2008) 012410.
[8] B. Pahari, K. Ghoshray, R. Sarkar, B. Bandyopadhyay, A. Ghoshray, Phys. Rev. B 73 (2006) 012407.
[9] Y. Uchiyama, Y. Sasago, I. Tsukada, K. Uchinokura, A. Zheludev, T. Hayashi, N. Miura, P. Böni, Phys. Rev. Lett. 83 (1999) 632.
[10] Z. He, Y. Ueda, J. Phys. Soc. Japan 77 (2008) 013703.
[11] A. Zheludev, T. Masuda, I. Tsukada, Y. Uchiyama, K. Uchinokura, P. Boni, S.H. Lee, Phys. Rev. B 62 (2000) 8921.
[12] N. Rogado, Q. Huang, J.W. Lynn, A.P. Ramirez, D. Huse, R.J. Cava, Phys. Rev. B 65 (2002) 144443.
[13] M. Heinrich, H.A. Krug von Nidda, A. Loidl, N. Rogado, R.J. Cava, Phys. Rev. Lett. 91 (2003) 137601.
[14] W. Knafo, C. Meingast, K. Grube, S. Drobnik, P. Popovich, P. Schweiss, P. Adelmann, Th. Wolf, H. Von Loehneysen, Phys. Rev. Lett. 99 (2007) 137206.
[15] Z. He, D. Fu, T. Kyômen, T. Taniyama, M. Itoh, Chem. Mater. 17 (2005) 2924.
[16] Z. He, T. Taniyama, T. Kyômen, M. Itoh, Phys. Rev. B 72 (2005) 172403.
[17] Z. He, T. Taniyama, M. Itoh, Appl. Phys. Lett. 88 (2006) 132504.
[18] Z. He, T. Taniyama, M. Itoh, Phys. Rev. B 73 (2006) 212406.
[19] Z. He, T. Taniyama, M. Itoh, J. Yamaura, Y. Ueda, Solid State Commun. 141 (2007) 667.
[20] Z. He, Y. Ueda, M. Itoh, Solid State Commun. 142 (2007) 404.
[21] S. Kimura, H. Yashiro, K. Okunishi, M. Hagiwara, Z. He, K. Kindo, T. Taniyama, M. Itoh, Phys. Rev. Lett. 99 (2007) 087602.
[22] S. Kimura, T. Takeuchi, K. Okunishi, M. Hagiwara, Z. He, K. Kindo, T. Taniyama, M. Itoh, Phys. Rev. Lett. 100 (2008) 057202.
[23] A.A. Belik, M. Azuma, M. Takano, B.I. Lazoryak, Chem. Mater. 16 (2004) 4311.
[24] Z. He, Y. Ueda, M. Itoh, Solid State Commun. 141 (2007) 22–24.
[25] B. ElBali, A. Boukhari, E.M. Holt, J. Aride, Crystallogr. Spectrosc. Res. 23 (1993) 1001.
[26] R. Wichmann, Hk. Müller-Buschbaum, Z. Anorg. Allg. Chem. 534 (1986) 153.
[27] D. Osterloh, Hk. Müller-Buschbaum, Z. Naturforsch. B 49 (1994) 923.
[28] Z. He, Y. Ueda, M. Itoh, J. Solid State Chem. 180 (2007) 1770.
[29] F. Izumi, T. Iketa, Mater. Sci. Forum 321–324 (2000) 198.