IOP Publishing Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **19** (2007) 145221 (6pp) doi:10.1088/0953-8984/19/14/145221

Re-entrant spin-glass behaviour of geometrically frustrated $SrFe_3(PO_4)_3O$

A A Belik[1], **N Tsujii**[1], **Q Huang**[2], **E Takayama-Muromachi**[1] **and**
M Takano[3]

[1] National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044, Japan
[2] NIST Center for Neutron Research, MD 20899, USA
[3] Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan

E-mail: Alexei.Belik@nims.go.jp

Received 4 August 2006
Published 23 March 2007
Online at stacks.iop.org/JPhysCM/19/145221

Abstract

Four anomalies of magnetic origin were observed at $T_1 = 10.7$ K, $T_2 = 11.7$ K, $T_f = 22.4$ K, and $T_c = 23.5$ K in $SrFe_3(PO_4)_3O$ with a geometrically frustrated magnetic lattice using different techniques. $SrFe_3(PO_4)_3O$ shows features typical of re-entrant spin glass with the freezing temperature T_f in zero static magnetic field and the Curie temperature T_c. These features are the sharp upturn of the dc magnetization and ferromagnetic hysteresis loops on the $M(H)$ curves below T_c, frequency-dependent rounded maxima on both the $\chi'(T)$ and $\chi''(T)$ curves at different positions, a very small anomaly of specific heat at T_f, and strong suppression of spin-glass behaviour by magnetic fields above 0.1 T. High-field magnetization measurements revealed the existence of a 1/3-magnetization plateau above 25 T at $T = 1.7$ K. Magnetic reflections were observed below T_c on neutron powder diffraction patterns. Additional magnetic reflections appeared below T_2.

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

1. Introduction

Investigations of random magnets have attracted much attention from researchers for several decades [1–7]. Spin-glass (SG) freezing is associated with the randomness of exchange interactions due to a random distribution of magnetic impurities or due to crystallographic disorder. In stoichiometric ordered compounds, SG behaviour, which is observed very rarely, can originate for certain topological reasons [6, 7]. Therefore, investigations of SG transitions caused by geometrical frustration is one of the most interesting topics in magnetism.

The systems with SG characteristics at low temperatures after a ferromagnetic (FM) transition at a higher temperature are referred to as re-entrant spin glasses or cluster spin

0953-8984/07/145221+06$30.00

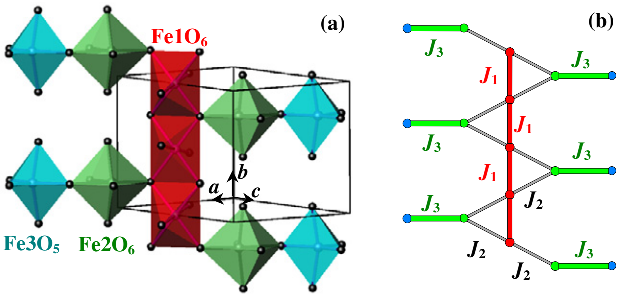

Figure 1. (a) Fragment of the crystal structure of $SrFe_3(PO_4)_3O$. (b) Schematic presentation of the magnetic interaction pattern in $SrFe_3(PO_4)_3O$.

glasses [3, 4]. The competing FM and antiferromagnetic (AFM) interactions are the origin of the re-entrant phenomena [1].

In this work, we report on magnetic properties of $SrFe_3(PO_4)_3O$ studied by ac susceptibility, dc magnetization, specific heat, and neutron powder diffraction. $SrFe_3(PO_4)_3O$ shows the features typical of re-entrant spin glasses with a freezing temperature $T_f = 22.4$ K, a Curie temperature $T_c = 23.5$ K, and additional magnetic anomalies at 10.7 and 11.7 K. As far as we are aware, $SrFe_3(PO_4)_3O$ is the first ordered phosphate which exhibits re-entrant SG behaviour.

2. Experiment

$SrFe_3(PO_4)_3O$ was prepared from a stoichiometric mixture of $FePO_4$ and $SrCO_3$ by the solid-state method. The mixture was pressed into a pellet at 200 kgf cm^{-2} and then allowed to react at 1273 K (heating rate 200 K h^{-1}, cooling with a furnace) on a Pt plate for 130 h with four intermediate grindings. X-ray powder diffraction showed that the sample was monophasic.

$SrFe_3(PO_4)_3O$ crystallizes in a monoclinic system (space group $P2_1/m$) with $a = 7.5395$ Å, $b = 6.3476$ Å, $c = 10.3161$ Å, and $\beta = 99.740°$ [8]. Three crystallographically different Fe sites (Fe1, Fe2, and Fe3) exist in the crystal structure. The $Fe1O_6$ octahedra share two edges (O1–O6) with each other to create one-dimensional (1D) chains, $\{Fe1O_4\}_n$ (figure 1). The $Fe2O_6$ octahedron is linked with the $Fe3O_5$ polyhedron through a vertex (O3) and with the $\{Fe1O_4\}_n$ chain (through the O1 atom). The 1D chains shown in figure 1(a) are connected with each other by PO_4 groups forming a three-dimensional network. Depending on the sign and strength of exchange interactions, J_1–J_3 (figure 1(b)), geometrical frustration is possible in this system.

dc magnetic measurements were performed on a Quantum Design SQUID magnetometer (MPMS XL) between 2 and 400 K under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. Isothermal magnetization curves were recorded between −50 and +50 kOe at 5, 10, 15, 20, 22, 35, and 110 K using the MPMS XL. Frequency-dependent ac susceptibility measurements at different static magnetic fields were performed with a Quantum Design PPMS instrument in the temperature range of 2–50 K (on cooling) at frequencies (f) of 10, 10^2, 5×10^2, 10^3, 5×10^3, and 10^4 Hz and an applied oscillating magnetic field (H_{ac}) of 1 Oe. Specific heat, $C_p(T)$, was recorded between 1.8 and 300 K (on cooling) at zero magnetic field by a pulse relaxation method using a commercial calorimeter (Quantum Design PPMS). High-field magnetization curves were recorded at 1.7 K between 0 and 300 kOe using a hybrid magnet of NIMS.

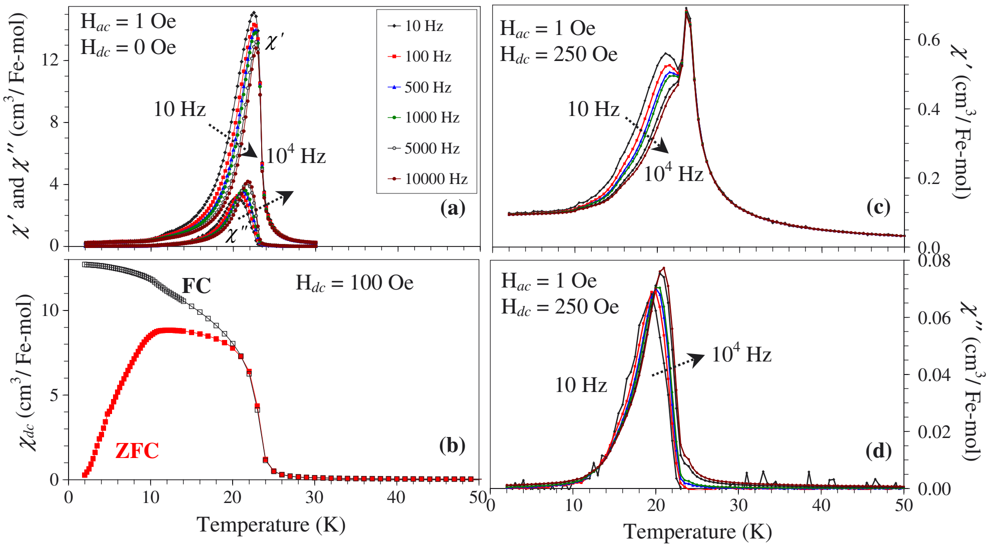

Figure 2. The real $\chi'(T)$ ((a) and (c)) and imaginary $\chi''(T)$ ((a) and (d)) parts of the ac susceptibility as a function of temperature at frequencies $f = 10$, 100, 5×10^2, 10^3, 5×10^3, and 10^4 Hz. Measurements were performed on cooling at static fields $H_{\mathrm{dc}} = 0$ Oe (a) and 250 Oe ((c) and (d)) using an ac field with the amplitude $H_{\mathrm{ac}} = 1$ Oe. (b) The ZFC and FC dc susceptibilities measured at 100 Oe.

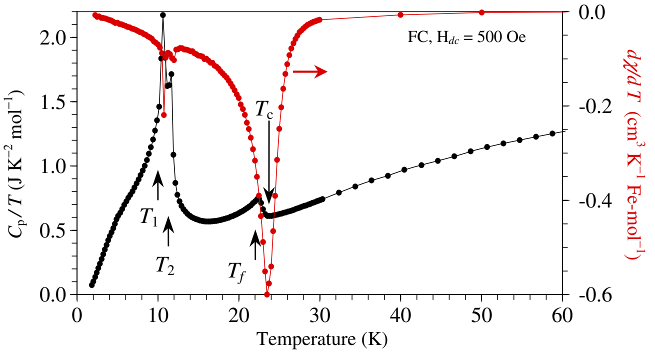

Figure 3. The C_p/T versus T curve measured at zero magnetic field and the FC $\mathrm{d}\chi/\mathrm{d}T$ versus T curve measured at 500 Oe between 2 and 60 K.

The neutron powder diffraction data for $SrFe_3(PO_4)_3O$ were collected using the BT-1 high-resolution powder diffractometer at the NIST Center for Neutron Research, employing a Cu (311) monochromator to produce a monochromatic neutron beam of wavelength 1.5403 Å. The intensities were measured in steps of 0.05° in the 2θ range 3°–168°.

3. Results and discussion

The temperature dependence of the dc susceptibility ($\chi = M/H$) at 100 Oe is displayed in figure 2(b). Both ZFC and FC curves increase sharply at $T_c = 23.5$ K, indicating the onset of a transition with FM origin. T_c represents the temperature defined as the peak position of the FC $\mathrm{d}\chi/\mathrm{d}T$ versus T curve (see figure 3). The difference between the ZFC and FC curves is observed below 21 K. The χ^{-1} versus T curve shows significant curvature from the linear behaviour at 40–400 K typical of ferrimagnets. A fit of the high-temperature region (300–400 K) to a simple Curie–Weiss law gave $\mu_{\mathrm{eff}} = 5.15\ \mu_{\mathrm{B}}$ per Fe^{3+} ion and a Weiss constant of $\theta = -274$ K. The effective magnetic moment (μ_{eff}) is smaller than the expected value of 5.59 μ_{B} for a high-spin Fe^{3+} ion. The reduced value of μ_{eff} is reminiscent of ferrimagnetic interactions even at such high temperatures. The negative Weiss constant indicates that the main interaction between Fe^{3+} ions is AFM. The $\mathrm{d}\chi/\mathrm{d}T$ versus T curve (figure 3) has additional small anomalies at $T_1 = 10.7$ K and $T_2 = 12.0$ K with negative gradients.

The in-phase ($\chi' = M'/H_{\mathrm{ac}}$) and out-of-phase ($\chi'' = M''/H_{\mathrm{ac}}$) components of the ac susceptibility at zero static magnetic field exhibit evident maxima with intensities and positions depending on frequency. With increasing frequency, the peak positions are shifted to higher temperatures, the peak intensity of $\chi'(T)$ is suppressed, and the peak intensity of $\chi''(T)$ is increased (figure 2(a)). These features are reminiscent of SG behaviour [9]. The spin freezing temperature (T_{f}), defined as the peak position of the $\chi'(T)$ curve at $f = 10$ Hz, is 22.4 K. Note that the maxima on the $\chi'(T)$ and $\chi''(T)$ curves occur at different temperatures; for example, the peak on the $\chi''(T)$ curve at $f = 10$ Hz is observed at 20.5 K. In addition, the maxima are not cusped but rather rounded. All these features show that $\mathrm{SrFe_3(PO_4)_3O}$ behaves not as a canonical SG but as a re-entrant SG [3]. Similar behaviour is observed in static magnetic fields of 100 and 250 Oe (figure 2). However, the peaks related to the SG behaviour are strongly suppressed by the static field and actually no frequency dependence is observed on the $\chi'(T)$ and $\chi''(T)$ curves at $H_{\mathrm{dc}} \geqslant 1$ kOe. This corresponds to the fact that magnetic energy becomes sufficient to overcome the energy barrier (or blocking temperature) between possible equilibrium positions of magnetic moments. At 250 Oe, a clear peak on the $\chi'(T)$ curves is detected at T_{c} (figure 2(c)). This peak is overlapped with SG features at lower static magnetic fields.

In spin glasses, a criterion, $\delta T_{\mathrm{f}} = \Delta T_{\mathrm{f}}/(T_{\mathrm{f}}\Delta \log_{10} f)$, has often been used for comparing the frequency dependence of T_{f}. With the values $T_{\mathrm{f}} = 22.40(2)$ K at $f = 10$ Hz and $T_{\mathrm{f}} = 22.64(4)$ K at $f = 10^4$ Hz, we obtain $\delta T_{\mathrm{f}} = 0.0036$. This value is comparable with those reported for some spin glasses [4, 6, 9]. The frequency dependence of T_{f} is also analysed by the empirical Vogel–Fulcher law, a well-known testing equation for the SG phenomenon [9]:

$$f = f_0 \exp[-E_{\mathrm{a}}/k_{\mathrm{B}}(T_{\mathrm{f}} - T_0)] \tag{1}$$

where E_{a} is activation energy, k_{B} is the Boltzmann constant, f_0 is characteristic frequency, and T_0 is Vogel–Fulcher temperature. Assuming the variation of χ' to a Gaussian function near T_{f} to determine T_{f} and taking $f_0 = 10^{13}$ Hz typical in SG systems, we obtain reasonable fitting parameters $T_0 = 21.70(5)$ K and $E_{\mathrm{a}}/k_{\mathrm{B}} = 19.2(1)$ K (at $H_{\mathrm{dc}} = 0$ Oe). Therefore, the frequency dependence of T_{f} is well described by the Vogel–Fulcher law. In addition, we observed time-dependent magnetic properties such as relaxation that follows the logarithmic law, indicating non-equilibrium magnetic behaviour.

Figure 3 shows the temperature dependence of specific heat divided by temperature, C_p/T, in zero magnetic field. Two sharp large peaks at T_1 and $\approx T_2$ and one broad small peak at T_{f} (for $H_{\mathrm{dc}} = 0$ Oe) are observed. No other anomalies are found between 1.8 and 300 K. Only the small anomaly is present near the freezing temperature and no peaks are observed at T_{c}.

The isothermal magnetization curves, $M(H)$, are depicted in figure 4. Clear FM hysteresis loops are observed at 5–22 K, while no hysteresis is seen above T_{c}. Remanent moments and coercitive fields at 20 and 22 K are very small. The high-field measurements show the 1/3 magnetization plateau with the values of 5 μ_{B} per formula unit of $\mathrm{SrFe_3(PO_4)_3O}$. Therefore, these data support the existence of an intermediate ferrimagnetic state.

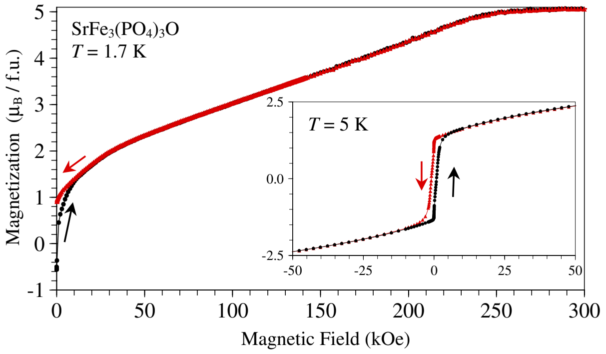

Figure 4. Isothermal magnetization curves (M versus H) at 1.7 K between 0 and 300 kOe. The inset shows the M versus H curve at 5 K between −50 and 50 kOe.

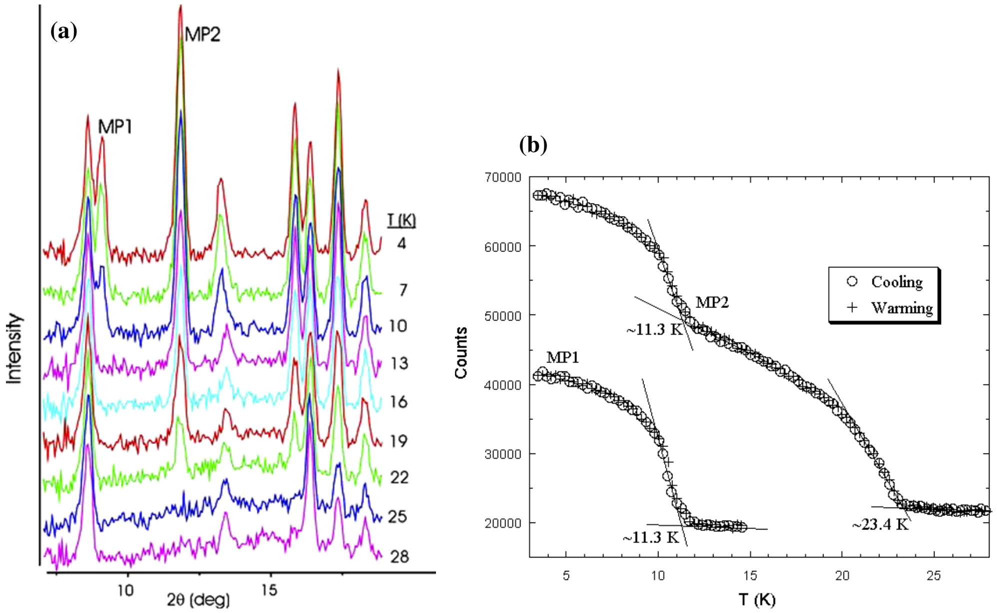

Figure 5. (a) Fragments of neutron diffraction patterns at different temperatures. MP1 and MP2 denote the magnetic reflections. (b) Temperature dependence of the intensity of the MP1 and MP2 magnetic reflections.

Neutron diffraction measurements show that magnetic reflections appear below T_c (figure 5), indicating the onset of long-range ordering. Additional magnetic reflections appear below T_1 (or T_2).

A spin glass is a collection of magnetic moments whose low-temperature state is frozen and disordered. To produce such a state, two conditions are necessary: frustration and partial randomness of interaction between magnetic moments. Because there is no structural and positional disorder in $SrFe_3(PO_4)_3O$ [8], the origin of re-entrant SG behaviour should lie in the competition between FM and AFM interactions. The determination of magnetic structures of $SrFe_3(PO_4)_3O$ is in progress. It will help to determine the sign of exchange constants in $SrFe_3(PO_4)_3O$ and the magnitude of the ordered magnetic moments.

It is known that strong frustration exists in 1D spin-$n/2$ chains. Such a type of chains formed by the $Fe1O_6$ octahedra is present in the structure of $SrFe_3(PO_4)_3O$ (figure 1(a)). There is also competition between AFM-type interactions (dominant at high temperatures) and FM-type interactions (dominant at low temperatures). Frustration in the 1D chains and competition between AFM and FM interactions may introduce the formation of magnetic clusters with randomly frustrated exchange interactions between them, necessary for the re-entrant SG state. Note that SG behaviour was also observed in other ordered compounds, e.g. $Co_2(OH)(PO_4)$ [6] and Ca_3CoXO_6 (X = Rh, Ir, and Co) [7].

In conclusion, four anomalies of magnetic origin can be observed at 10.7, 11.7, 22.4, and 23.5 K in $SrFe_3(PO_4)_3O$ using different magnetic techniques. $SrFe_3(PO_4)_3O$ shows the typical features of re-entrant spin-glass behaviour.

References

[1] Jonason K, Mattsson J and Nordblad P 1996 *Phys. Rev. Lett.* **77** 2562
[2] Suzuki I S and Suzuki M 2006 *Phys. Rev.* B **73** 094448
[3] Goldfarb R B, Rao K V and Chen H S 1985 *Solid State Commun.* **54** 799
[4] Li D X, Nimori S, Shiokawa Y, Haga Y, Yamamoto E and Onuki Y 2003 *Phys. Rev.* B **68** 172405
[5] Tien C, Feng C H, Wur C S and Lu J J 2000 *Phys. Rev.* B **61** 12151
[6] Rojo J M, Mesa J L, Lezama L, Pizarro J L, Arriortua M I, Rodriguez Fernandez J, Barberis G E and Rojo T 2002 *Phys. Rev.* B **66** 094406
[7] Rayaprol S, Sengupta K and Sampathkumaran E V 2003 *Phys. Rev.* B **67** 180404(R)
[8] Morozov V A, Pokholok K V, Lazoryak B I, Malakho A P, Lachgar A, Lebedev O I and Van Tendeloo G 2003 *J. Solid State Chem.* **170** 411
[9] Mydosh J A 1993 *Spin Glass: An Experimental Introduction* (London: Taylor and Francis)