Journal of the Physical Society of Japan
Vol. 75, No. 5, May, 2006, 054706
©2006 The Physical Society of Japan

Singlet Ground State and Magnetic Interactions in New Spin Dimer System $Ba_3Cr_2O_8$

Tomohiko NAKAJIMA*, Hiroyuki MITAMURA[1] and Yutaka UEDA

Materials Design and Characterization Laboratory, Institute for Solid State Physics,
University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581
[1]*Division of Physics under Extreme Conditions, Institute for Solid State Physics,*
University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581

(Received August 22, 2005; revised February 16, 2006; accepted February 24, 2006; published April 25, 2006)

We have successfully synthesized $Ba_3Cr_2O_8$ and investigated its crystal structure and magnetic properties. The crystal structure consists of Ba^{2+} cations and isolated CrO_4^{3-} tetrahedra; magnetic chromium ions exist as rare Cr^{5+} ($3d^1$, $S = 1/2$). An $S = 1/2$ compound $Ba_3Cr_2O_8$ was found to be a three-dimensional quantum spin system with a singlet ground state of dimer origin. From the analysis of magnetic susceptibility and high-field magnetization data, excitation gap is evaluated as $\Delta/k_B = 16.1\,K$ and intra- and interdimer exchange interactions are estimated as $J_0/k_B = 25.0\,K$ and $J'/k_B = 7.7\,K$, respectively. Comparing with a similar spin dimer compound $Ba_3Mn_2O_8$, $Ba_3Cr_2O_8$ has a more dominant intradimer interaction.

KEYWORDS: $Ba_3Cr_2O_8$, $S = 1/2$ spin singlet, magnetic property, high-field magnetization, excitation gap
DOI: 10.1143/JPSJ.75.054706

1. Introduction

Over the last decade, many spin dimer systems that have spin-singlet ground state have been extensively studied.[1–4] Among them, quantum phenomena associated with excited triplets (magnons) such as the Bose–Einstein condensation (BEC) of magnons,[2,4,5] and the Wigner crystallization of magnons[3] have attracted much attention. The former emerge as a field induced antiferromagnetic long-range ordering of transverse spin components. Such phenomenon of *magnon*-BEC was first experimentally observed in $TlCuCl_3$[4] in 2000. On the other hand, the Wigner crystallization of magnons was found to be realized in the orthogonal dimer system $SrCu_2(BO_3)_2$ with Shastry–Satherland lattice, showing the quantized magnetization plateaus phenomenologically.[3] These discoveries have accelerated the search for new spin dimer systems and new quantum phenomena.

In such current spin dimer study, recently, Uchida *et al.* have discovered a new spin dimer compound, i.e., $Ba_3Mn_2O_8$, with a gapped ground state.[6,7] This compound has an interesting framework of its crystal structure and exhibits magnetization plateau at half of its saturated magnetization. The crystal structure is shown in Fig. 1. Isolated tetrahedral MnO_4^{3-} and Ba^{2+} ions build the structure. The Mn ions reside as Mn^{5+} ($3d^2$, $S = 1$); this valence state is rare in manganese oxides. In this compound, Mn^{5+} ions set up double-layered triangular lattices, which are stacked along the c-axis with threefold periodicity. Uchida *et al.* concluded that the antiferromagnetic intradimer interaction J_0 [see Fig. 1(b)] is dominant and it is the origin of the spin gap. Moreover, they suggested that the interdimer interactions J_1, J_2, and J_3 are also antiferromagnetic and their total is almost equivalent to a magnitude of J_0. Very recently, Tsujii *et al.* have reported a magnetic field induced antiferromagnetic order in $Ba_3Mn_2O_8$ by specific heat measurement,[8] indicating a possible new *magnon*-BEC system.

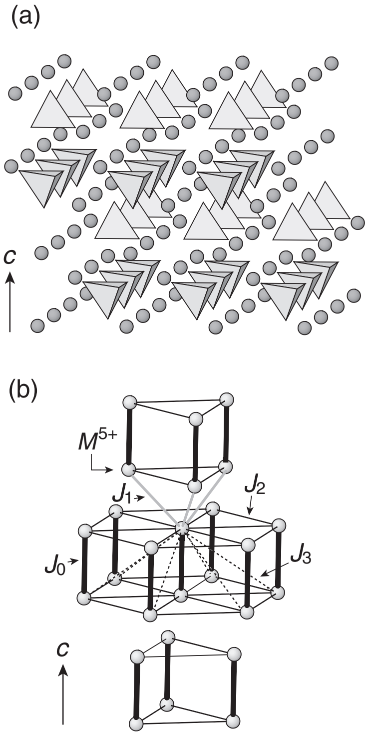

Fig. 1. (a) Schematic crystal structure of $Ba_3M_2O_8$ ($M = Cr$ and Mn) constructed from isolated MO_4 tetrahedra and Ba cations (solid balls). (b) Network of M^{5+} ions in crystal structure. The first, second, third, and fourth nearest neighbor exchange interactions J_0, J_1, J_2, and J_3 are expressed as thick, gray, thin, and dashed lines, respectively.

There exist some other compounds with the isostructure; $A_3M_2O_8$ ($A = Ca^{2+}$, Sr^{2+}, and Ba^{2+}, $M = V^{5+}$ and Cr^{5+}).[9–12] These compounds have been studied only from the viewpoint of crystal chemistry and have never been studied in terms of their physical properties. Among them, the compounds with Cr^{5+} are interesting, because the Cr^{5+}

---

[*] Present address: Materials Design and Characterization Laboratory, Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581. E-mail: t-nakaji@issp.u-tokyo.ac.jp

state is rare and quantum fluctuation would be mostly maximized in an $S = 1/2$ (Cr^{5+}: $3d^1$) system. In this work, we successfully prepared polycrystalline samples of $Ba_3Cr_2O_8$ with Cr^{5+} ($3d^1$, $S = 1/2$) and investigated their magnetic properties. $Ba_3Cr_2O_8$ is a new spin dimer compound with an energy gap of $\Delta/k_B \sim 16$ K between a spin singlet ground state and a triplet excited state, but it does not show any magnetization plateau in the magnetization curve in contrast to $Ba_3Mn_2O_8$.

2. Experimental

The polycrystalline samples of $Ba_3Cr_2O_8$ were prepared by a solid state reaction. The mixed powders of starting materials, $BaCO_3$ and Cr_2O_3, in an appropriate molar ratio were heated at 1223 K for 24 h in Ar gas for preliminary decarbonation and then heated at 1293 K for 24 h in an evacuating silica tube to avoid the oxidation of Cr^{5+} into Cr^{7+}. The obtained dark green product was checked to be a single phase of $Ba_3Cr_2O_8$ by X-ray diffraction. The crystal structure was refined by the Rietveld analysis of powder X-ray diffraction using RIETAN2000.[13] Magnetic susceptibility was studied using a SQUID magnetometer in a temperature range $T = 1.8{-}300$ K at 0.1 T. The high-field magnetization measurement was performed using an induction method with a multilayer pulse magnet at the Division of Physics under Extreme Conditions, Institute for Solid State Physics, University of Tokyo. Magnetization data were collected at $T = 1.6$ K in magnetic fields up to 46 T.

3. Results and Discussion

Figure 2 shows the X-ray diffraction pattern measured at room temperature. All the peaks responsible for $Ba_3Cr_2O_8$ can be successfully indexed in a trigonal $R\bar{3}m$ space group which is the same as in $A_3M_2O_8$ compounds. The lattice parameters are $a = 5.73906(5)$ Å, $c = 21.3757(2)$ Å, and $V = 609.72(1)$ Å^3, and the structural parameters refined by the Rietveld analysis are shown in Table I. From the structure data, the Cr^{5+}–Cr^{5+} distances corresponding to the exchange interaction J_i [see Fig. 1(b)] are calculated as $d_{J_0} = 3.934(6)$ Å, $d_{J_1} = 4.599(4)$ Å, $d_{J_2} = 5.7391(1)$ Å, and $d_{J_3} = 6.958(3)$ Å.

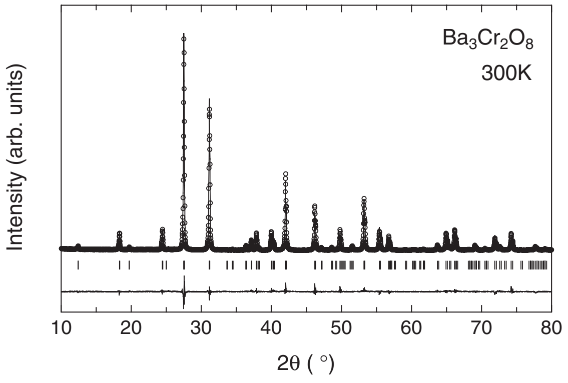

Fig. 2. X-ray diffraction pattern of $Ba_3Cr_2O_8$ at room temperature. The calculated and observed diffraction profiles are shown at the top with the solid line and cross markers, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between calculated and observed intensities. Data are refined in space group $R\bar{3}m$.

Table I. Refined structural parameters and selected bond distances of $Ba_3Cr_2O_8$ at room temperature.

$Ba_3Cr_2O_8$			
Space group: $R\bar{3}m$	Ba1	$3a$	$B_{iso} = 0.64(5)$ Å^2
$a = 5.73906(5)$ Å	Ba2	$6c$	$z = 0.20609(7)$
$c = 21.3757(2)$ Å			$B_{iso} = 0.52(3)$ Å^2
$V = 609.72(1)$ Å^3	Cr	$6c$	$z = 0.4079(1)$
$R_{wp} = 11.51\%$			$B_{iso} = 0.19(6)$ Å^2
$R_e = 8.81\%$	O1	$18h$	$x = 0.1656(5)$
$R_I = 6.40\%$			$z = 0.5666(2)$
$R_F = 4.26\%$			$B_{iso} = 0.95(1)$ Å^2
	O2	$6c$	$z = 0.3336(5)$
			$B_{iso} = 0.95(1)$ Å^2
Cr–Cr distances			
$d_{J_0} = 3.934(6)$ Å	$d_{J_1} = 4.599(4)$ Å		
$d_{J_2} = 5.7391(1)$ Å	$d_{J_3} = 6.598(3)$ Å		

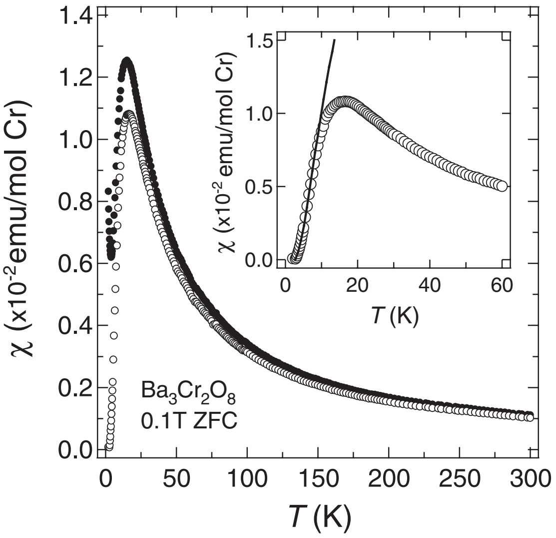

Fig. 3. Temperature dependence of magnetic susceptibility for $Ba_3Cr_2O_8$ measured under 0.1 T. The solid and open circles show raw data (χ_r) and net data (χ_M), respectively. χ_M is derived by subtracting the Curie tail from χ_r. The inset shows χ_M and the fitting curve (solid line) used for the rough estimation of spin gap.

Figure 3 shows the temperature (T) dependence of magnetic susceptibility (χ) for $Ba_3Cr_2O_8$ measured under 0.1 T. It shows a typical low dimensional behavior with a broad maximum at around 15 K. Above 65 K, raw data χ_r (solid circles in Fig. 3) obeys a Curie–Weiss law with Curie constant $C = 0.376(1)$ emu K/(Cr-mol), Weiss constant $\theta = -6.6(4)$ K, and temperature independent term $\chi_0 = -1.2(1) \times 10^{-4}$ emu/mol. The value of $P_{eff} = 1.73(8)$ μ_B obtained from the observed C is compatible with the calculated value of 1.73 μ_B for Cr^{5+} ($S = 1/2$) with g-factor = 2, and negative θ indicates an antiferromagnetic interaction among Cr ions. Upon decreasing temperature, χ_r exhibits a broad maximum at around 15 K and a sharp decrease below the temperature, that is, a gap-like behavior. χ_r increases again below 3.8 K. This upturn in χ_r obeys a Curie law and is ascribed to a small amount of impurity phase (approximately 0.2 mol% as spin 1/2 impurity). Net susceptibility χ_M obtained by subtracting the Curie tail from

χ_r is also shown as open circles in Fig. 3. χ_M exhibits a broad maximum at around 16 K and then decreases toward zero with decreasing temperature. This behavior of χ_M indicates a spin singlet ground state for $Ba_3Cr_2O_8$. We roughly estimated spin gap energy by fitting χ_M to the following equation at a low temperature range:

$$\chi_M = Ae^{(-\Delta/k_B T)} + \chi_0, \qquad (1)$$

where A is a constant, Δ is the magnitude of the spin gap, and χ_0 is the constant term caused by the diamagnetism of core electron shells and Van Vleck paramagnetism. The solid line in the inset of Fig. 3 shows the fitting using eq. (1). The parameters obtained from the fitting were $\Delta/k_B = 14.7(1)$ K and $\chi_0 = -1.8(2) \times 10^{-4}$ emu/mol.

To confirm a spin gapped ground state and to determine gap energy, we performed high-field magnetization measurements. Figure 4 shows (a) the magnetic field (H) dependence of magnetization (M) and (b) its field derivative (dM/dH) at 1.6 K for $Ba_3Cr_2O_8$. Up to 12 T, M slightly increases with a tendency to saturate at a small M, which originates in impurities. Above the magnetic field it rapidly increases and saturates at around $H_S = 23$ T. This behavior clearly indicates that the ground state is a gapped spin singlet and is then excited to the triplet state above the critical field $H_C = 12$ T. Energy gap Δ is estimated to be $\Delta/k_B = 16.1$ K using the following equation; $\Delta/k_B = g\mu_B H_C/k_B$, where $g = 2$. This value is consistent with 15 K roughly evaluated from the susceptibility data and the eq. (1). M saturates at around 1.8 μ_B which is less than the ideal value of $2.0\mu_B/2Cr^{5+}$. The origin of this reduction has not been known yet, although it would be partly due to the inclusion of impurity. Here, it should be noted that $Ba_3Cr_2O_8$ does not show any magnetization plateau in contrast to $Ba_3Mn_2O_8$. However, the value of 11 T between H_C and H_S suggests a considerable interaction among the triplets (magnons), that is, the system is not a simple isolated dimer system. If three-dimensional magnetic ordering occurs in the range of $H_C < H < H_S$, $Ba_3Cr_2O_8$ would be counted as a new BEC material in a boson system, where BEC phenomena would be understood more clearly than in $S = 1$ $Ba_3Mn_2O_8$. The measurements of the T-dependence of magnetization at $H_C < H$ and the synthesis of a single crystal are now in progress.

The present study reveals that $Ba_3Cr_2O_8$ has a spin gapped ground state. Because it is thought from the analogy with $Ba_3Mn_2O_8$ that the spin gap of $Ba_3Cr_2O_8$ originates in the nearest neighbor exchange interaction J_0 [see Fig. 1(b)], we first analyze χ_M using the Bleaney–Bowers equation [eq. (2)][14,15] for isolated dimers which is derived from the $S = 1/2$ Heisenberg Hamiltonian in eq. (3),

$$\chi_M = \frac{N_A \mu_B^2 g^2}{k_B T(3 + e^{J_0/k_B T})} + \chi_0 \qquad (2)$$

$$\mathcal{H} = \sum_{i,j} J_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j, \qquad (3)$$

where N_A is Avogadro's number, g and μ_B are g-factor and Bohr-magneton, respectively, and J_0 is the intra-dimer exchange coupling parameter. We fitted χ_M to the eq. (2) with g-factor as a variable parameter. The fitting curve is shown in Fig. 5(a). The best-fit gives $g = 1.909(2)$, $J_0/k_B = 25.07(4)$ K, and $\chi_0 = -0.5(1) \times 10^{-4}$ emu/mol. Intradimer interaction J_0/k_B (= 25.1 K) is much larger than gap energy Δ/k_B (= 16.1 K) estimated from H_C. This means that $Ba_3Cr_2O_8$ is not a simple isolated dimer system, which has also been deduced from the high-field magnetization

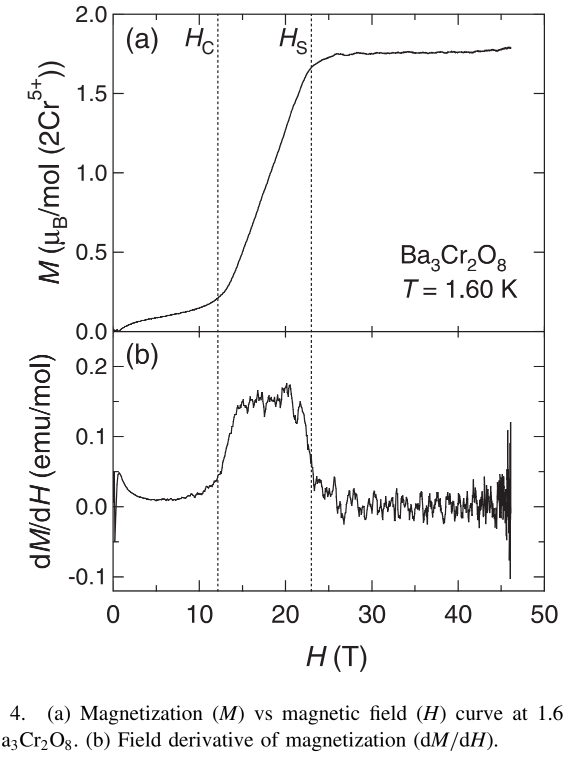

Fig. 4. (a) Magnetization (M) vs magnetic field (H) curve at 1.6 K for $Ba_3Cr_2O_8$. (b) Field derivative of magnetization (dM/dH).

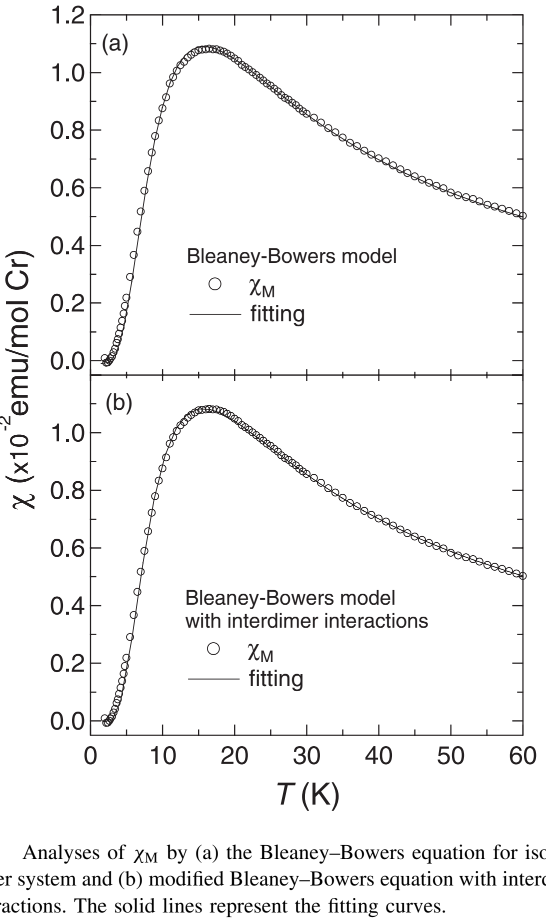

Fig. 5. Analyses of χ_M by (a) the Bleaney–Bowers equation for isolated dimer system and (b) modified Bleaney–Bowers equation with interdimer interactions. The solid lines represent the fitting curves.

measurements, and that interdimer interactions should be taken into consideration for the analysis of χ_M–T curve.

From the analogy with $Ba_3Mn_2O_8$, three kinds of interdimer interactions, namely, J_1, J_2, and J_3, can be considered, where J_1, J_2, and J_3 correspond to the second, third, and fourth nearest neighbor interactions [see Fig. 1(b)], respectively. We fitted χ_M to eq. (4) of the spin-dimer model with the interdimer interaction $J' = 3J_1 + 6J_2 + 6J_3$, which was used in the analysis of magnetic susceptibility for $Ba_3Mn_2O_8$.7)

$$\chi_M = \frac{N_A \mu_B^2 g^2}{k_B T(3 + e^{J_0/k_B T} + J'/k_B T)} + \chi_0 \tag{4}$$

The calculated curve well reproduces the observed χ_M in the temperature range of 6–300 K, as shown in Fig. 5(b). The parameters obtained from the best-fit are $g = 1.975(6)$, $J_0/k_B = 25.04(3)$ K, $J'/k_B = 7.69(9)$ K, and $\chi_0 = -1.9(2) \times 10^{-4}$ emu/mol. Thus, $Ba_3Cr_2O_8$ can be regarded as a coupled antiferromagnetic dimer system similar to $Ba_3Mn_2O_8$,6,7) where the interdimer interactions work effectively. The obtained interactions of $Ba_3Cr_2O_8$ are stronger (weaker) in the intradimer (in the interdimer) than those of $Ba_3Mn_2O_8$; $J_0/k_B = 17.4$ K and $J'/k_B = 24.9$ K.7) Because it is thought that the magnitude of intra- and interdimer interactions are proportional to their corresponding distances d_{J_i}, we compare d_{J_i} between $Ba_3Cr_2O_8$ ($d_{J_0} = 3.934$ Å, $d_{J_1} = 4.599$ Å, $d_{J_2} = 5.739$ Å, and $d_{J_3} = 6.958$ Å) and $Ba_3Mn_2O_8$ ($d_{J_0} = 3.984$ Å, $d_{J_1} = 4.569$ Å, $d_{J_2} = 5.711$ Å, and $d_{J_3} = 6.963$ Å16)). The d_{J_0} related to the intradimer interaction is shorter by 1.27% in $Ba_3Cr_2O_8$, whereas in the interdimer interactions, d_{J_1} and d_{J_2} are longer by 0.65 and 0.49%, respectively, and d_{J_3} is shorter by 0.07% in $Ba_3Cr_2O_8$ than those in $Ba_3Mn_2O_8$. These results suggest that $Ba_3Cr_2O_8$ has a stronger intradimer interaction and weaker interdimer interactions than those of $Ba_3Mn_2O_8$, which are in agreement with the results obtained from the analysis of magnetic susceptibility.

4. Conclusion

We have successfully synthesized $Ba_3Cr_2O_8$ and investigated its crystal structure and magnetic properties. The crystal structure consists of Ba^{2+} cations and isolated CrO_4^{3-} tetrahedra; the magnetic chromium ions exist as rare Cr^{5+} ($3d^1$, $S = 1/2$). An $S = 1/2$ compound, $Ba_3Cr_2O_8$ was found to be a three-dimensional quantum spin system with a singlet ground state of dimer origin. From the analysis of magnetic susceptibility and high-field magnetization data, excitation gap is evaluated as $\Delta/k_B = 16.1$ K and intra- and interdimer exchange interactions are estimated as $J_0/k_B = 25.0$ K and $J'/k_B = 7.7$ K, respectively. Comparing with a similar spin dimer compound $Ba_3Mn_2O_8$, $Ba_3Cr_2O_8$ has a more dominant intradimer interaction.

Acknowledgements

The authors thank T. Yamauchi, M. Isobe, Y. Matsushita, K. Ohgushi and H. Ueda for valuable discussion. This work is partly supported by Grants-in-Aid for Scientific Research (Nos. 407 and 758) and for Creative Scientific Research (No. 13NP0201) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

1) D. C. Johnston, J. W. Johnson, D. P. Goshorn and A. J. Jacobson: Phys. Rev. B **35** (1987) 219.
2) H. Tanaka, K. Takatsu, W. Shiramura and T. Ono: J. Phys. Soc. Jpn. **65** (1996) 1945.
3) H. Kageyama, K. Yoshimura, R. Stern, N. V. Mushnikov, K. Onizuka, M. Kato, K. Kosuge, C. P. Slichter, T. Goto and Y. Ueda: Phys. Rev. Lett. **82** (1999) 3168.
4) T. Nikuni, M. Oshikawa, A. Oosawa and H. Tanaka: Phys. Rev. Lett. **84** (2000) 5868.
5) T. Waki, Y. Morimoto, C. Michioka, M. Kato, H. Kageyama, K. Yoshimura, S. Nakatsuji, O. Sakai, Y. Maeno, H. Mitamura and T. Goto: J. Phys. Soc. Jpn. **73** (2004) 3435.
6) M. Uchida, H. Tanaka, M. I. Bartashevich and T. Goto: J. Phys. Soc. Jpn. **70** (2001) 1790.
7) M. Uchida, H. Tanaka, H. Mitamura, F. Ishikawa and T. Goto: Phys. Rev. B **66** (2002) 54429.
8) H. Tsujii, B. Andraka, M. Uchida, H. Tanaka and Y. Takano: Phys. Rev. B **72** (2005) 214434.
9) G. Liu and J. E. Greedan: J. Solid State Chem. **110** (1994) 274.
10) R. Gopal and C. Calvo: Phase Transition **38** (1992) 127.
11) H. J. Mattausch and H. K. Müller-Buschbaum: Z. Naturforsch. B **27** (1972) 739.
12) E. Cuno and H. K. Müller-Buschbaum: Z. Anorg. Allg. Chem. **572** (1989) 95.
13) F. Izumi and T. Ikeda: Mater. Sci. Forum **321–324** (2000) 198.
14) B. Bleaney and K. D. Bowers: Proc. R. Soc. London, Ser. A **214** (1952) 451.
15) K. Hara, M. Inoue, S. Emori and M. Kubo: J. Magn. Reson. **4** (1971) 337.
16) M. T. Weller and S. J. Skinner: Acta Crystallogr., Sect. C **55** (1999) 154.