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Long-range antiferromagnetic ordering in $Cu_2NiB_2O_6$

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Abstract

Magnetic properties of peculiar structural-type borate $Cu_2NiB_2O_6$ are investigated by means of ac susceptibility, dc magnetization, and heat capacity measurements. This material is isostructural to $Cu_2CoB_2O_6$, of which the structural configuration is composed of quasi-one-dimensional six-columns ribbons. Our experimental results show that this material displays an antiferromagnetic phase transition at ~15 K, which differs from $Cu_2CoB_2O_6$ showing spin-glass behavior below 5 K. The different magnetic ground states in these compounds may be attributed mainly to the subtle balance of the exchange energy in the scalene triangles.
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Keywords: $Cu_2NiB_2O_6$; Borate; Magnetic materials; Geometrical frustration

1. Introduction

Geometrically frustrated magnetic systems have provided a great deal of attention to experimental and theoretical studies due to their fascinating magnetic phenomena. Geometrical frustration generally arises when spatial arrangement of the spins in a specific lattice such as equilateral triangle and tetrahedron cannot simultaneously minimize all the interaction energies. In this regard, many researches are focusing on compounds with Kagome (two-dimensional) or pyrochlore (three-dimensional) structures, which show exotic ground states such as spin glasses, spin liquids and spin ices [1].

Since magnetic properties are closely related to the crystal structure of magnetic compounds, the compounds with the same crystal structure likely display similar magnetic ground states. This is well recognized in pyrochlore compounds which show geometrically frustrated spin-glass behavior in general [1–3]. Such magnetic characteristic are also found in warwickites, a large family of oxyborates formulated as $M^{2+}M^{3+}OBO_3$, due to their similar structural feature, where divalent and trivalent ions M^{2+} and M^{3+} are either same or different metal elements [4–8]. For example, homometallic warwickites such as Fe_2OBO_3 [6] and Mn_2OBO_3 [7] show clear magnetic phase transitions at 155 and 26 K, while heterometallic warwickites such as $MgFeOBO_3$ and $MnScOBO_3$ show no magnetic phase transition, but display typical spin-glass behavior below 11 and 2.7 K, due to their disordered atomic arrangement, respectively [8].

Recently, we investigated the magnetic properties of a new type borate $Cu_2CoB_2O_6$, of which the structural configuration is composed of quasi-one-dimensional six columns ribbons similar to warwickites [9,10]. As shown in Fig. 1(a), all metal ions are atomically ordered at each site due to a large Jahn–Teller effect of Cu^{2+} ions [11]. Our studies found that $Cu_2CoB_2O_6$ displays spin-glass behavior below 5 K and suggested that the origin of the spin-glass behavior might result from geometrical frustration due to the triangles built by the ribbons, based on the analysis of the crystal structure [12]. In this paper, in order to gain concrete information about the geometrical frustration in the scalene triangle, we investigate the magnetic properties of $Cu_2NiB_2O_6$ [13], a newly synthesized ribbon borate compound with the same structure as $Cu_2CoB_2O_6$, in terms of ac susceptibility, dc magnetization and heat capacity measurements under the same condition as in our previous study.

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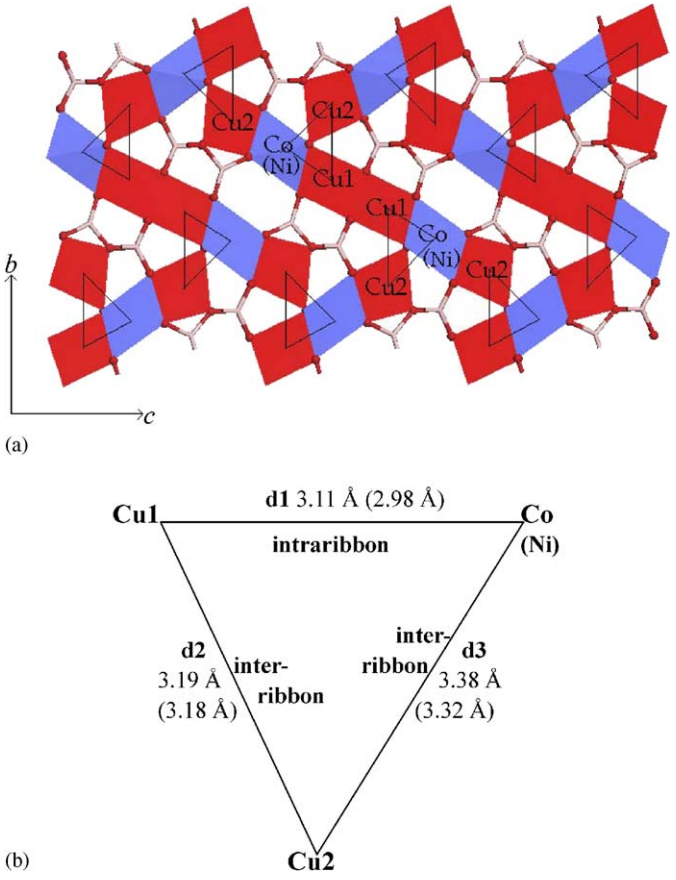

Fig. 1. (a) The crystal structure of $Cu_2CoB_2O_6$ (or $Cu_2NiB_2O_6$) viewed from the b–c plane, showing the six-column ribbons, the metal ions sites and the peculiar triangles. (b) Three different distances: $d1$, intraribbon Cu1–Co (Cu1–Ni); $d2$, interribbon Cu2–Cu1 (Cu2–Cu1) and $d3$, interribbon Cu2–Co (Cu2–Ni) in the non-equilateral triangles of $Cu_2CoB_2O_6$ and ($Cu_2NiB_2O_6$), are depicted.

2. Experiment

A polycrystalline sample of $Cu_2NiB_2O_6$ was prepared by means of a conventional solid-state reaction method. Appropriate amounts of CuO (4 N), $NiC_2O_4 \cdot 2H_2O$ (3 N), and excess B_2O_3 (3 N) were thoroughly ground with ethanol in an agate mortar and calcined in air at 1173 K for 72 h with several intermediate grindings. The product was washed in hot water to remove residual boron oxide, dried and pressed into pellets, then sintered at 1203 K for 24 h and cooled down to room temperature at a rate of about 100 K/h. The sample was confirmed to be a single phase by powder X-ray diffraction (XRD) measurements using a MXP18AHF X-ray diffractometer with graphite monochromatized Cu$K\alpha$ radiation at room temperature. The crystal structure was refined by the Rietveld method using the RIETAN-2000 program [14]. Chemical analysis of samples was performed using an EPMA system (JEOL JSM-5600 • Oxford Link ISIS). The ac magnetic susceptibilities were measured with an amplitude of 10 Oe at frequencies from 100 to 10,000 Hz. dc magnetizations were measured in applied fields up to 9 T in the low-temperature range. Heat capacities were measured by a relaxation method. All of the measurements were performed using a commercial quantum design physical property measurement system (PPMS).

3. Results and discussion

As shown in Fig. 2, the experimental XRD pattern of $Cu_2NiB_2O_6$ agrees well with the pattern calculated using the Rietveld method with the structural parameters of $Cu_2CoB_2O_6$, showing no impurity phase in the system. The reliability factors of $R_{wp} = 4.56$, $R_p = 2.98$ and $S = 2.23$ are obtained. The lattice constants of $a = 3.205(9)$ Å, $b = 14.838(1)$ Å, $c = 9.064(6)$ Å and $\beta = 93.77(8)^\circ$, which were determined using Si powder as an internal standard, are in good agreement with those reported previously [13]. Further, chemical analysis shows that the molar ratio of Cu and Ni in $Cu_2NiB_2O_6$ sample is very close to 2:1, which is similar to that of Cu and Co in $Cu_2CoB_2O_6$ sample we studied previously. These results indicate that $Cu_2NiB_2O_6$ sample has high quality. Although it is difficult to distinguish Cu and Ni by normal X-ray scattering, we note that Rietveld refinement using different occupation ratio of Ni and Cu sites in $Cu_2NiB_2O_6$ still gives a subtle increase in the residuals between the experimental and calculated data. Similar to $Cu_2CoB_2O_6$, structural analysis of single crystal clearly indicated that the atomic positions of Cu and Ni ions in $Cu_2NiB_2O_6$ are highly ordered due to the large Jahn–Teller distortion of Cu ions [13]. Such structural feature of copper-oxides is also reported in Ref. [15].

The temperature dependences of ac magnetic susceptibility and the corresponding reciprocal susceptibility measured at 100 Hz are shown in Fig. 3. The susceptibility

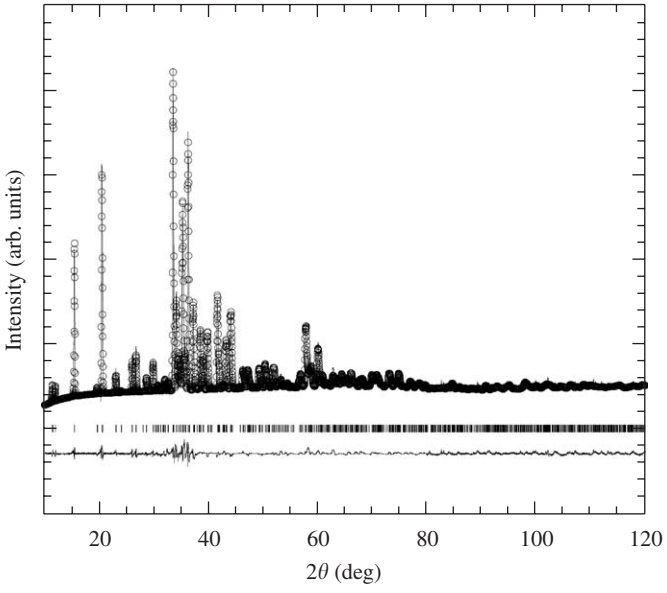

Fig. 2. Observed (open circles) and calculated (solid line) XRD pattern for $Cu_2NiB_2O_6$ at room temperature. The difference is shown at the bottom and Bragg reflections are indicated by vertical marks.

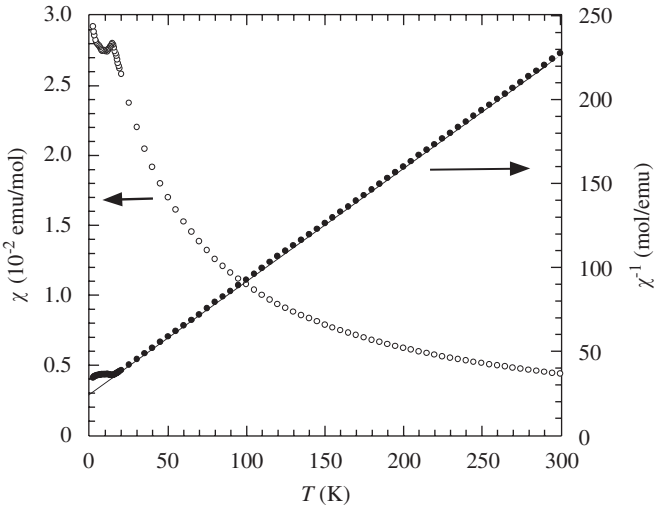

Fig. 3. The ac magnetic susceptibility (open circles) and inverse susceptibility (closed circles) of $Cu_2NiB_2O_6$ measured in an excitation field of 10 Oe at 100 Hz.

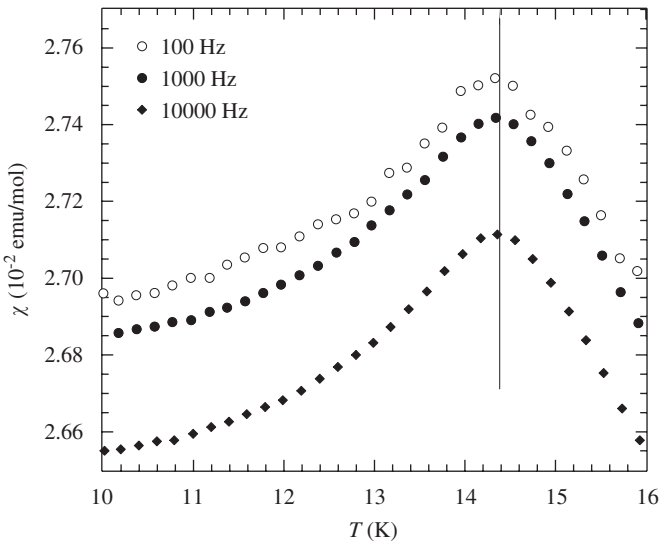

Fig. 4. The real part of ac susceptibility χ at different excitation frequencies. The solid line is a guide for the eyes.

follows Curie–Weiss behavior well above 15 K and exhibits a sharp peak near 15 K, indicating a magnetic phase transition. The Curie constant $C = 1.48(0)$ emu K/mol and Weiss temperature $\theta = -36.8(4)$ K were obtained from the reciprocal susceptibility. The effective magnetic moment is calculated to be $3.44(4)\mu_B$ which is close to $3.74\mu_B$ calculated assuming that Cu and Ni have $S = 1/2$ and 1 spin states. The negative Weiss temperature indicates that the dominant interactions are antiferromagnetic (AF). In order to understand the nature of this magnetic ordering, ac susceptibility curves were measured at several different frequencies as shown in Fig. 4. Clearly, the peak temperature is independent on frequency, suggesting that the phase transition at 15 K is not spin-glass freezing but AF ordering. Magnetization vs. magnetic field curves obtained at $T = 2$ and 12 K in Fig. 5 show that the magnetization increases linearly and does not saturate even in 9 T. Furthermore, no hysteresis and remnent magnetization are observed. These features are also consistent with the suggestion that the magnetic transition at 15 K is of an AF type.

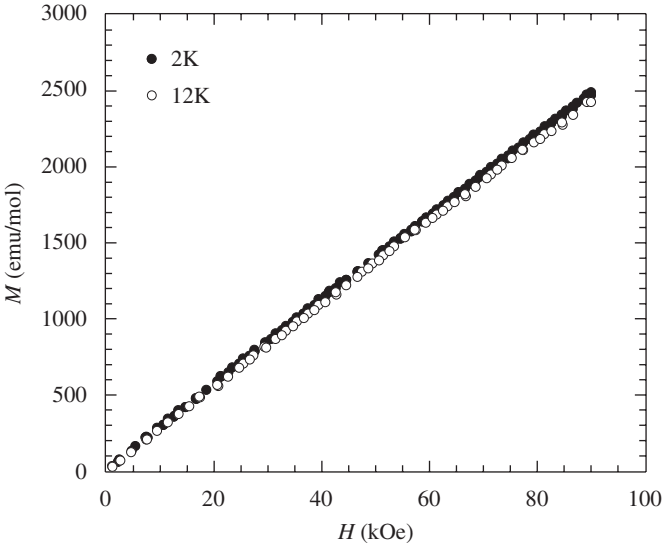

Fig. 5. Magnetization vs. applied field curves for $Cu_2NiB_2O_6$ at $T = 2$ and 12 K.

Further evidence for AF ordering is also obtained from heat capacity data. The results of heat capacity measurements in $H = 0$ are shown in Fig. 6. Apparently, there is a clear sign of λ-like feature around 15 K which corresponds to the temperature of the magnetic susceptibility peak. This is clear evidence that the magnetic anomaly at 15 K is not due to a spin-glass transition but an AF phase transition. The entropy integrated over this anomaly amounts to $\Delta S = \sim 2.2$ J/mol K. Also, there is a kink in the heat capacity at ~5 K, however, the origin of this anomaly is unclear.

Our experimental results of ac magnetic susceptibility, dc magnetization and heat capacity have revealed that $Cu_2NiB_2O_6$ displays AF phase transition at ~15 K, which obviously differs from $Cu_2CoB_2O_6$ showing spin-glass behavior below 5 K. In order to clarify the nature of the different magnetic ordering in these similar systems, we investigate the structural configuration of six-column ribbons in $Cu_2NiB_2O_6$ and $Cu_2CoB_2O_6$ in details. As seen in Fig. 1(a), the structures of $Cu_2NiB_2O_6$, $Cu_2CoB_2O_6$ and warwickites can be described as a similar assembly of triangles built by the ribbons. The triangle is not equilateral with three different distances ($d3 > d2 > d1$) between the magnetic elements in the triangles (Fig. 1(b)), which is obviously different from the triangular lattices in Kagome and pyrochlore structures. It is well known that the Hamiltonian for exchange interaction between any two spins (S_1 and S_2) can be expressed as $H = -2JS_1S_2$, where the magnitude and the sign of the exchange constant J are

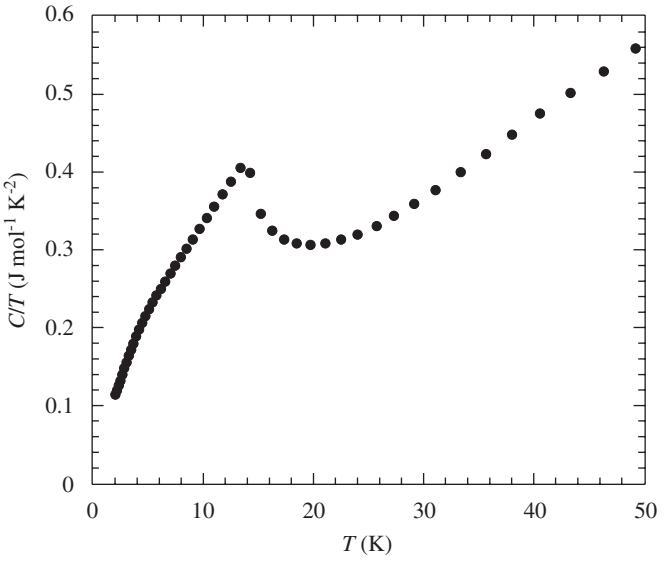

Fig. 6. The heat capacity of $Cu_2NiB_2O_6$ obtained at 0 T from 2 to 50 K.

determined by the bonding geometry according to the Goodenough rules [16].

We now discuss various possible conditions of spin arrangements in a non-equilateral triangle. While the same magnetic ions occupy all the sites of a non-equilateral triangle, the AF interactions energy between the spins are quite different due to their different exchange constants J arising from different coupling distances and angles. As a result, spin frustration does not likely occur. A good example of this description can be seen in $Cu_3B_2O_6$ with similar triangles, showing an AF phase transition at low temperature [17]. However, if the two different magnetic ions occupy the sites in a non-equilateral triangle, the situation should be completely different from that of the same magnetic atoms. Because the magnitude of the AF interaction energy between the two magnetic ions is actually determined by spin moments S and exchange constants J based on the coupling distance at the same coupling angle, it is reasonable to believe that the magnitudes of two AF interaction energy in the triangles may be close or same ($H_i \approx H_j$), assuming appropriate spin moments ($S_i > S_j$) and coupling distances ($d_i > d_j$) corresponding to coupling constants ($J_i < J_j$). In this case, spin frustration may occur in the triangles. A typical example with the non-equilateral triangles built by different magnetic ions Fe^{2+} and Fe^{3+} ions is discussed in Ref. [18], showing the characteristic spin-glass behavior due to geometric frustration in triangles. Recently, we found that the ordered ribbon borate $Cu_2CoB_2O_6$ displays spin-glass behavior below 5 K and suggested that $Cu_2CoB_2O_6$ is also an example of geometrically frustrated system in non-equilateral triangles built by different magnetic Cu^{2+} and Co^{2+} ions, due to the AF interribbon interactions of Cu1–Cu2 (3.19 Å) and Co–Cu2 (3.38 Å) in the peculiar triangles with the same or close magnitudes at very close coupling angles of 116° and 117° [12].

It has been pointed out that magnetic behaviors of warwickites are determined by both intraribbon and interribbon interactions, where interribbon interactions between magnetic ions in different ribbons dominate the three-dimensional magnetic behavior such as spin-glass transition [8]. Therefore, similar to warwickites, magnetic orderings in $Cu_2NiB_2O_6$ and $Cu_2CoB_2O_6$ may likely be associated with the interribbon interactions. Here, we put emphasis on discussing why isostructural $Cu_2NiB_2O_6$ does not exhibit spin-glass behavior, but displays AF ordering at ~15 K instead. As shown in Fig. 1(b), when Ni^{2+} substitutes for Co^{2+} in the triangles of this compound, a small change of the coupling distances between Cu and Ni ions could change the exchange coupling J, which induce a change of the interaction energies H between ions of the triangles. Further, because Ni^{2+} ($S = 1$) and Co^{2+} ($S = 3/2$) have different spin moments, the AF interaction energy of interribbon Ni–Cu2 in the triangles should be different from that of Co–Cu2. In addition, Ni^{2+} ions have all t_{2g} orbitals full in their high spin state, while Co^{2+} ions remain an empty t_{2g} orbital. As reported in the spinel compounds $GeNi_2O_4$ and $GeCo_2O_4$ [19], it is suggested that such orbital filling effects may also affect the interactions between ions of the triangles. Therefore, it is reasonable that this substitution induces a change in the subtle balance between the triangles, resulting in that $Cu_2NiB_2O_6$ displays AF ordering, while $Cu_2CoB_2O_6$ displays spin-glass behavior.

It is well known that the value of $|\theta_{CW}|/T_{ord}$ can be an empirical measure of spin frustration in a magnetic system, where θ_{CW} is the Weiss temperature and T_{ord} is the ordering temperature. For typical geometrically frustrated materials, the $|\theta_{CW}|/T_{ord}$ values larger than 10 have been observed, and this value is empirically used as a criterion for the presence of spin frustration [2]. If we compare $|\theta_{CW}|/T_{ord}$ of ~13 for $Cu_2CoB_2O_6$ with that of ~2.5 for $Cu_2NiB_2O_6$, the substitution of Ni^{2+} for Co^{2+} ions is clearly shown to decrease the spin frustration in the triangles. This interpretation is also compatible with the results that $Cu_2CoB_2O_6$ displays spin-glass behavior and $Cu_2NiB_2O_6$ shows AF ordering. It should also be noted that the different magnetic properties of $Cu_2CoB_2O_6$ and $Cu_2NiB_2O_6$ are not due to the random arrangement of magnetic ions since these compounds have no random occupation of magnetic ions in the triangles, and the results in turn could reveal that the origin of spin-glass in $Cu_2CoB_2O_6$ should be spin frustration in the triangles.

4. Conclusion

We have shown that $Cu_2NiB_2O_6$ displays an AF transition at ~15 K, which differs from the isostructural $Cu_2CoB_2O_6$ showing spin-glass behavior below 5 K. For $Cu_2NiB_2O_6$ and $Cu_2CoB_2O_6$, there are the same triangles built by the ribbons with two different magnetic ions Cu, Co and Cu, Ni, respectively. When Ni^{2+} ($S = 1$) substitutes for Co^{2+} ($S = 3/2$) in the triangles, spin frustration

does not occur in $Cu_2NiB_2O_6$ due to the fact that the AF interaction energies between magnetic ions in the triangles become non-equivalent. Therefore, it is well understood that $Cu_2NiB_2O_6$ exhibits AF ordering, whereas $Cu_2CoB_2O_6$ shows spin-glass behavior. These interesting findings not only support our suggestion that the origin of spin-glass behavior in $Cu_2CoB_2O_6$ results from geometrical frustration in the triangles built by ribbons with Cu^{2+} and Co^{2+}, but also provide a basis for searching for new types geometrically frustrated magnetic materials.

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References

[1] J.E. Greedan, J. Mater. Chem. 11 (2001) 37.
[2] P. Schiffer, A.P. Ramirez, Comments Condens. Matter Phys. 18 (1996) 21.
[3] M.J. Harris, M.P. Zinkin, Mod. Phys. Lett. B 10 (1996) 417.
[4] J.C. Fernandes, R. B Guimaraes, M.A. Continentino, H.A. Borges, J.V. Valarelli, A. Lacerda, Phys. Rev. B 50 (1994) 16754.
[5] J.P. Attfield, A.M.T. Bell, L.M. Rodriguez-Martinez, J.M. Greneche, R.J. Cernik, J.F. Clarke, D.A. Perkins, Nature (London) 396 (1998) 655.
[6] M.A. Continentino, A.M. Pedreira, R.B. Guimaraes, M. Mir, J.C. Fernandes, R.S. Freitas, L. Ghivelder, Phys. Rev. B 64 (2001) 014406.
[7] R.J. Goff, A.J. Williams, J.P. Attfield, Phys. Rev. B 70 (2004) 014426.
[8] R.B. Guimaraes, J.C. Fernandes, M.A. Continentino, H.A. Borges, C.S. Moura, J.B.M. da Cunha, C.A. dos Santos, Phys. Rev. B 56 (1997) 292.
[9] R. Norrestam, Z. Kristallogr. 189 (1989) 1.
[10] R. Norrestam, M. Kritikos, A. Sjodin, J. Solid State Chem. 114 (1995) 311.
[11] J. Schaefer, K. Bluhm, Z. Anorg. Allg. Chem. 620 (1994) 1051.
[12] Z. He, T. Kyômen, M. Itoh, Phys. Rev. B 70 (2004) 134431.
[13] M. Johnsson, M. Kritikos, Y. Kihn, P. Millet, Mater. Res. Bull. 38 (2003) 1725.
[14] F. Izumi, T. Iketa, Mater. Sci. Forum 321–324 (2000) 198.
[15] M.P. Shores, E.A. Nytko, B.M. Bartlett, D.G. Nocera, J. Am. Chem. Soc. 127 (2005) 13462.
[16] J.B. Goodenough, Phys. Rev. 100 (1955) 564.
[17] K. Hudo, T. Noji, Y. Koike, J. Phys. Soc. Jpn. 70 (2001) 935.
[18] C.N.R. Rao, G. Paul, A. Choudhury, E.V. Sampathkumaran, A.K. Raychaudhuri, S. Ramasesha, I. Rudra, Phys. Rev. B 67 (2003) 134425.
[19] S. Diaz, S. de Brion, G. Chouteau, P. Canals, J.R. Carvajal, H. Rakoto, J.M. Broto, J. Appl. Phys. 97 (2005) 10A512.