PHYSICAL REVIEW B VOLUME 60, NUMBER 14 1 OCTOBER 1999-II

High-pressure form of $(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$: A spin-$\frac{1}{2}$ antiferromagnetic alternating-chain compound with one kind of chain and a single spin gap

M. Azuma
Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611-0011, Japan
and CREST, Japan Science and Technology Corporation (JST), Kawaguchi, Saitama 332-0012, Japan

T. Saito and Y. Fujishiro
Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611-0011, Japan

Z. Hiroi* and M. Takano
Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611-0011, Japan
and CREST, Japan Science and Technology Corporation (JST), Kawaguchi, Saitama 332-0012, Japan

F. Izumi
National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

T. Kamiyama
Institute of Material Science, University of Tsukuba, Tennodai, Tsukuba, Ibaraki 305-8573, Japan

T. Ikeda
Institute of Applied Physics, University of Tsukuba, Tennodai, Tsukuba, Ibaraki 305-8573, Japan

Y. Narumi
CREST, Japan Science and Technology Corporation (JST), Kawaguchi, Saitama 332-0012, Japan
and KYOKUGEN, Osaka University, Toyonaka, Osaka 560-8531, Japan

K. Kindo
KYOKUGEN, Osaka University, Toyonaka, Osaka, 560-8531, Japan
and CREST, Japan Science and Technology Corporation (JST), Kawaguchi, Saitama 332-0012, Japan

(Received 14 April 1999)

$(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$, known as a quantum spin chain compound, was found to undergo a structural transition when treated at 2 GPa and 700 °C. The high-pressure phase as studied by powder x-ray and neutron diffractions comprises a unique kind of spin-1/2 Heisenberg alternating antiferromagnetic chain, in contrast with the ambient pressure phase containing two crystallographically different chains. Magnetic susceptibility, high-field magnetization, and specific-heat data showed the presence of a single spin gap of 23 (magnetization)–27 (susceptibility) K, not double as observed for the ambient pressure phase. This result is consistent with recent magnetization and NMR studies which indicated that the two kinds of chains of the ambient pressure phase have single, different spin gaps. [S0163-1829(99)00837-1]

I. INTRODUCTION

There is a growing interest in one-dimensional (1D) antiferromagnetic (AF) quantum spin systems with spin gaps like spin-1/2 alternating chains,[1] spin-1 chains (Haldane systems), and spin-1/2 spin ladders.[2] The recent discoveries of appropriate oxide systems such as CuGeO_3 (spin-Peierls),[3] $\mathrm{Y}_2\mathrm{BaNiO}_5$ (Haldane),[4] $\mathrm{SrCu}_2\mathrm{O}_3$,[5] and $\mathrm{Sr}_{14}\mathrm{Cu}_{24}\mathrm{O}_{41}$ (ladders)[6] have accelerated the keen interest because their thermal stability made it rather easy to finely tune the electronic properties by means of chemical doping.

$(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$ (VOPO), long known as an active catalyst for the selective oxidation of butane to maleic anhydride, comprises vanadium ions in the 4+ oxidation state with spin-1/2. The singlet ground state of this compound was found by Johnston *et al.*[7] They fitted the temperature dependence of magnetic susceptibility to a spin-1/2 Heisenberg alternating AF chain model. However, the structural features were suggestive of ''ladders,'' rather than alternating chains, with almost straight V-O-V bonds in the leg direction and two orthogonal V-O-V bonds in the rung direction. The susceptibility reinvestigated after the spin ladder model by Dagotto, Riera, and Scalapino[8] was found to follow the ladder model as well.[9] Anyway, the existence of a spin gap of 3.7 meV (43 K) was confirmed by means of neutron scattering on a powder sample.[10] Finally, a more recent neutron-scattering study on single crystals[11] showed the validity of the alternating chain model with a major AF interaction (J_1) between a pair of VO_5 pyramids bridged by PO_4 tetrahedra and a minor one (J_2) between a pair of edge sharing VO_5 pyramids. The interaction along the leg of the ladder was even ferromagnetic. Interestingly, the neutron-scattering

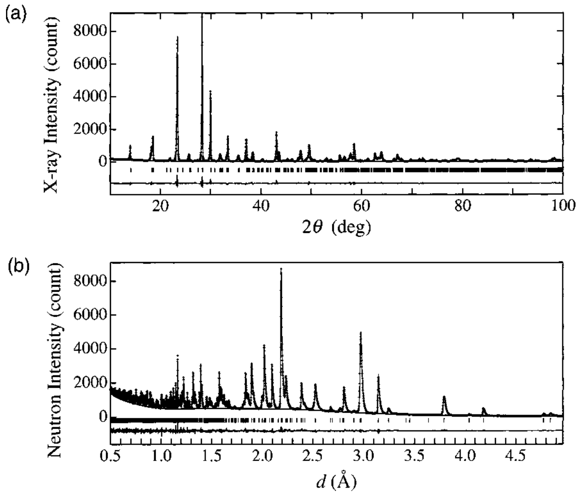

FIG. 1. Observed (+), calculated (solid line), and difference (below) XRD (a) and ND (b) patterns. The tick marks indicate the calculated peak positions.

study also revealed the existence of a second energy gap of about twice as large as the first one as predicted theoretically.[12] However, this compound comprises two slightly different chains,[13,14] making it difficult to determine whether these chains have single but different spin gaps or have the same double gaps. Recent high-field magnetization and NMR studies have shown the former is the case.[15]

We found that this compound undergoes a pressure-induced transition to a similar but simplified structure with a unique kind of chain. And magnetic susceptibility, high-field magnetization and specific-heat data consistently indicated that there is only a single spin gap of 23∼27 K. This high-pressure (HP) phase seems to be a good example of spin-1/2 Heisenberg AF chain with a weak alternation $(J_2/J_1 \sim 1)$.

II. EXPERIMENTAL

The starting material, that is, the ambient pressure (AP) form of VOPO, was prepared by a simple solid-state reaction as follows. Stoichiometric amounts of NH_4VO_3 and $NH_4H_2PO_4$ were mixed, pressed into pellets, and heated at 600 °C for one day in a flowing CO_2 stream. It was then treated at 700, 750, and finally at 850 °C for 24 h each with intermediate regrindings. The crystal structure and the magnetic property of the AP phase sample thus obtained were reported elsewhere.[14] The sample was then treated at 2 GPa and 700 °C for 30 min in a conventional cubic-anvil-type HP apparatus. Powder x-ray diffraction (XRD) data were collected with a Rigaku RINT 2000 diffractometer equipped with a monochromator (CuKα radiation). Neutron-diffraction (ND) data were taken on a high-resolution time-of-flight (TOF) neutron powder diffractometer Vega at the KENS pulsed spallation source. Rietveld analyses were carried out on these two sets of data in the same manner as for the AP phase[14] to refine the lattice parameters, atomic positions and isotropic atomic displacement parameters. An electron diffraction study was carried out on JEOL-2000EX.

The magnetic susceptibility was measured in an external magnetic field of 0.1 T from 2 to 400 K on heating after zero-field cooling with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS XL). The high-field magnetization was measured in a pulsed magnetic field up to 60 T at 1.3 K by an induction method using a multilayer pulse magnet at KYOKUGEN, Osaka University. Specific-heat data were taken by means of a pulse relaxation method using a commercial calorimeter (Quantum Design PPMS) from 1.8–30 K.

III. RESULTS AND DISCUSSION

A. Crystal structure

Structure refinement was carried out by repeating Rietveld analyses of XRD and ND data alternatingly. The reason is that vanadium atoms are almost ‘‘transparent’’ against neutrons, while oxygen atoms have relatively small atomic scattering factors for x rays. In each refinement with RIETAN (Ref. 16) structural parameters determined in the last refinement were used as initial ones, and this feedback process was repeated several times. In the final process, the atomic coordinates and the thermal parameters of all the atoms were first determined by using the XRD data, and then those of P and O atoms were refined by using the ND data, keeping those of the V atoms unchanged. The analyses were performed based on space group $Pnab$. According to electron diffraction, the reflection conditions are $k+l$ = even for $0kl$ reflections, k = even for $hk0$ reflections, and h = even for $h0l$ reflections, and it is only orthorhombic $Pnab$ that meets these conditions.

TABLE I. Atomic positions and atomic displacement parameters for the high-pressure phase of $(VO)_2P_2O_7$. Space group $Pnab$; $a=7.5801(2)$ Å, $b=9.5458(3)$ Å, $c=8.3629(3)$ Å, $Z=4$. ND: $R_{wp}=4.36$, $R_p=3.28$, goodness of fit = 1.26. XRD: $R_{wp}=7.35$, $R_p=5.50$, goodness of fit = 0.96. Parameters for the V atom were refined using the XRD data, while those for the P and O atoms were done using the ND data.

Atom	Site	x	y	z	B (Å)
V	8d	0.0356(1)	0.0042(2)	0.3107(1)	0.52(2)
P	8d	0.0419(2)	0.2016(1)	−0.0036(5)	0.41(2)
O1	8d	0.2472(7)	0.0283(1)	0.3188(1)	0.72(2)
O2	4c	0.25000	0.1684(1)	0.00000	1.05(3)
O3	8d	−0.0327(4)	0.1357(2)	0.1452(2)	0.50(4)
O4	8d	0.5277(4)	0.1469(2)	0.1562(3)	0.81(5)
O5	8d	−0.0243(1)	0.1356(1)	0.5017(4)	0.41(2)

TABLE II. Selected bond lengths and angles for the high-pressure phase of $(VO)_2P_2O_7$.

Atoms	Bond length (Å)	Atoms	Bond angle (deg)
V - O1	1.622(5)	V - O5 - V (J_2)	101.71
O4	1.938(2)	V - O4 - P	148.30
O3	1.939(2)	O4 - P - O3	115.64
O5	2.062(2)	V - O3 - P	139.52
O5	2.081(3)		
O1	2.209(5)		
P - O4	1.476(4)		
O3	1.505(4)		
O5	1.560(1)		
O2	1.609(1)		

Figure 1 shows the results of the Rietveld analyses. The observed, calculated, and difference patterns as well as the allowed reflections are displayed in the figure. Crystallographic data and the reliability factors are summarized in Table I. Note that the HP phase has a simple structure with only one V^{4+} site in comparison with the AP phase with multiple sites, four in the orthorhombic ($Pca2_1$) structure for a powdered sample[14] and eight in the monoclinic structure ($P2_1$) for a single crystal.[13] The selected bond distances and bond angles of the HP phase are summarized in Table II. Bond valence sum[17] calculated from these values was 4.10 for the vanadium and 5.01 for the phosphorus ions, which are quite reasonable values.

The crystal structures of the HP and AP phases are illustrated in Fig. 2. Both these are made of edge-sharing pairs of VO_5 pyramids and PO_4 tetrahedra, while the arrangement is simpler in the HP phase. In the AP form viewed along the *b* axis [see Fig. Fig. 2(c)] the pyramids are lined along the *c* axis in a manner of up-up-down-down-up-up and so are the tetrahedra. In contrast, the mode is up-down-up-down for the HP phase. Accordingly the *c* axis of the HP form is about a half of the AP phase.

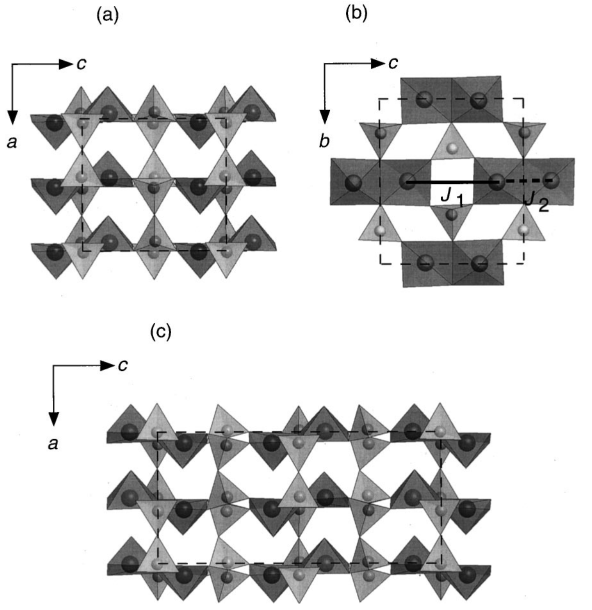

FIG. 2. Crystal structure of HP $(VO)_2P_2O_7$ illustrated along the *a* axis (a) and the *b* axis (b). The large and small spheres represent V and P ions, respectively. Crystal structure of the AP phase along the *b* axis is also shown for comparison (c).

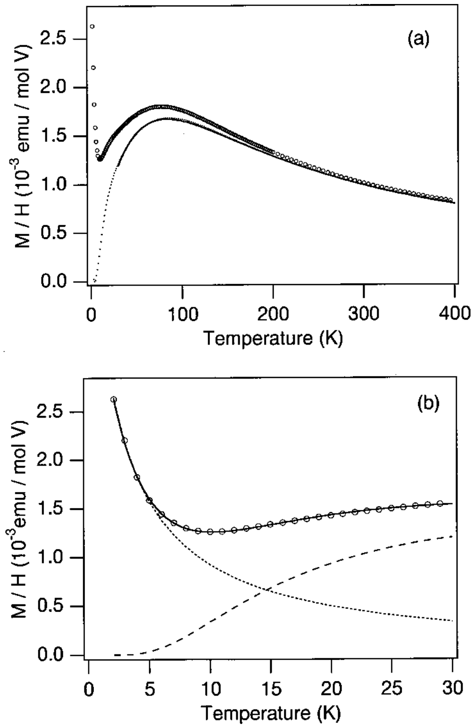

FIG. 3. Temperature dependence of magnetic susceptibility of HP $(VO)_2P_2O_7$ below 400 K (a). The open circles are the experimental raw data, while the data after subtraction of the Curie component are shown with dots. The solid line represents the fit to the alternation chain model. The data below 30 were fit to the equation given in text (b). The solid line represents the result of the fit, the long dashed line is the spin susceptibility and the short dashed line is the Curie term.

According to the inelastic neutron scattering study,[11] the AP phase has two major AF interactions along the *c* axis, one mediated by the two V-O-(P)-O-V paths (J_1) and the other through the almost orthogonal V-O-V paths (J_2) where $J_2/J_1 \sim 0.8$. The alternation of these interactions along the *c* axis leads to a spin-1/2 alternating chain, which seems to survive in the HP phase as marked in Fig. 2(b) with solid (J_1) and dashed (J_2) lines. Because of this structural similarity to the AP phase, the HP phase was also expected to be a gapped alternating AF system.

B. Magnetic susceptibility

Figure 3(a) shows temperature dependence of magnetic susceptibility of the HP phase. One can see a broad maximum centered around 90 K suggesting the 1D nature in magnetism and also a sudden increase below 10 K. Because magnetization at 2 K showed a linear field dependence up to 1 T and because there was no anomaly in the specific heat around 10 K, we concluded that the increase below 10 K was not due to ferromagnetism but was due to paramagnetic free moments.

The data below 30 K were fitted to an equation $\chi(T) = \chi_0 + C/(T-\theta) + aT^{-1/2}\exp(-\Delta/T)$ as seen in Fig. 3(b),

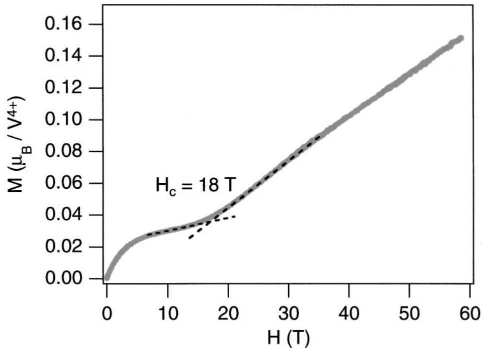

FIG. 4. Magnetization curve of HP $(VO)_2P_2O_7$ measured in pulsed magnetic field at 1.3 K.

where χ_0 is the T-independent term, $C/(T-\theta)$ is a Curie-Weiss term owing to the free moments and the $aT^{-1/2}\exp(-\Delta/T)$ term is the susceptibility of a 1D system with a spin gap Δ.[18] The best fit was obtained for the following set of parameters: $\chi_0=-2.0\times10^{-5}$ emu/mol V, $C=1.15\times10^{-2}$ emu/K mol V, $\theta=-2.2$ K, $a=1.6\times10^{-2}$, and $\Delta=27$ K. This C value corresponds to free spins of 3.1% of V^{4+}. On the other hand, it was 1.7% for the starting material, our AP VOPO.[14] We here note two possibilities, one chemical and the other structural, for the increase after the HP treatment. Excess oxygen might have been somehow introduced into the crystals though we did not use any oxidizer intentionally. The excess oxygen would create V^{5+} that breaks a singlet pair into one free spin. The possibility of the contamination of Au from the capsule can be ruled out. The HP treatment was performed at relatively low temperature, and the energy dispersive x-ray analysis did not detect any trace of such contamination. The other possibility is that crystal imperfections might have increased because the sample was quenched from 700 °C.

The temperature of the broad maximum, 90 K, was close to that of the AP phase, but the susceptibility maximum was smaller. These show that both J_1 and J_2 are similar between the AP and HP phases but J_2/J_1 $(=\alpha)$ is a little closer to unity for the HP phase. The data above 30 K could be well fitted to an analytical equation given by Hatfield[19] which is valid for a temperature range $T\geqslant0.25J_1$, and we obtained $J_1=137$ K, $\alpha=0.9$, and $g=2.01$. We could estimate the spin gap (Δ) as $\Delta=27$ K using a theoretical relation of $\Delta=0.2J_1$ for $\alpha=0.9$, as well.[1,12] This is in good agreement with the value estimated from the low-temperature data mentioned above.

C. High-field magnetization

Figure 4 shows the magnetization curve taken at 1.3 K in a pulsed magnetic field. Below 15 T a Brillouin-function-like behavior owing to the free spins was seen, while above 18 T the magnetization began to increase again almost linearly. The gap between the singlet ground state and the first triplet excitation in the presence of magnetic field is given as $\Delta(H)=\Delta-g\mu_BH$. If the gap is assumed to close at 18 T based on the field dependence of the magnetization, Δ is estimated to be about 23 K. This value seems considerably smaller than that estimated from the susceptibility data, but magnetization data tends to give smaller values in comparison with other methods.[15] The magnetization increased almost linearly up to 60 T without showing such a secondary anomaly as found for the AP phase. It is reasonable to attribute this difference to the multiplicity of the chains: The AP phase has two kinds of chains with single, different gaps while the HP phase has a unique kind of chain with a single gap.

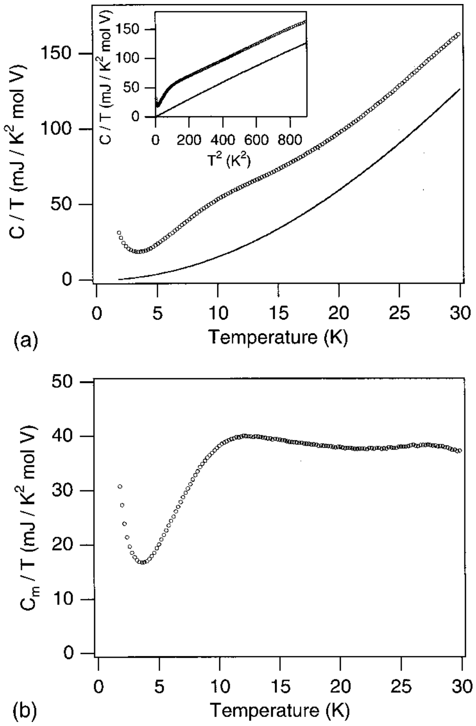

FIG. 5. Total specific heat divided by temperature C_p/T vs T and vs T^2 (inset) (a). The solid line stands for the lattice contribution. The magnetic specific heat divided by temperature (C_m/T) is also plotted against T (b).

D. Specific heat

The specific heat of the HP phase divided by temperature is plotted against temperature in Fig. 5(a). Above 20 K, the data could be well fitted to $Cp=\gamma T+\beta_1T^3+\beta_2T^5$ ($\gamma=38$ mJ/K^2 mol V, $\beta_1=1.5\times10^{-1}$ mJ/K^4 mol V, $\beta^2=-1.5\times10^{-5}$ mJ/K^6 mol V) as seen in the linear C/T vs T^2 behavior shown in the inset. Since this compound is an insulator, it is reasonable to assign the $\beta_1T^3+\beta_2T^5$ term to the lattice contribution and the γT term to the magnetic contribution. This β_1 value gives a Debye temperature of 438 K. The lattice contribution is shown with the solid line in Fig. 5(a). As seen in Fig. 5(b) the magnetic specific heat divided by temperature is almost constant above 20 K. Such a linear temperature dependence is characteristic of a uniform 1D AF chain, for which $\gamma=2Nk_B/3J$.[20] Applying $J=137$ K as estimated from the susceptibility data to this equation, $\gamma=41$ mJ/K^2 mol V was obtained, which is in good agreement with the experimental value of 38 mJ/K^2. Below 20 K, the specific heat divided by temperature showed a broad maximum centered at around 12 K and then decreased rapidly toward zero. The upturn below 3 K should be attributed to the free spins observed in the susceptibility and the magnetization data. The magnetic specific heat thus seems to be vanishing at the lowest temperature because of the spin gap. The broad maximum seems to be of the Shottky type reflecting the presence of the energy gap in the spin excitation spectrum. The specific heat of the HP phase thus seems to change from the ‘‘dimer’’ type to the ‘‘uniform chain’’ type above 20 K. Unfortunately, however, reliable theoretical calculations to be compared with these experimental data are not available at present.

IV. CONCLUSIONS

$(VO)_2P_2O_7$ was found to undergo a structural transition when treated at 2 GPa and 700 °C. The HP phase was found to comprise a unique kind of spin-1/2 alternating AF chain, not multiple chains as the AP phase does. According to magnetic measurements, $J_1 = 137$ K, $\alpha = 0.9$, and $\Delta = 23$ (magnetization) ~ 27 (susceptibility) K. The magnetic specific heat seemed to change from the Shottky type to the uniform chain type around 20 K. This HP phase must be a good example of spin-1/2 Heisenberg AF chain with a weak alternation. The two step increase of the magnetization found for the AP phase was not observed. This result confirms the recent assertion based on magnetization and NMR measurements that the two kinds of alternating chains of the AP phase have single independent spin gaps.

ACKNOWLEDGMENTS

The authors express their thanks to Professor S. Maekawa, Professor H. Yokoyama, Professor H. Takagi, Dr. Y. Mizuno, and Dr. M. Nohara for fruitful discussions.

---

*Current address: Institute for Solid State Physics, University of Tokyo 7-22-1, Roppongi, Minato-ku, Tokyo 106-8666, Japan.

[1] J. C. Bonner and M. E. Fisher, Phys. Rev. **135**, A640 (1964); J. C. Bonner, H. W. J. Blöte, J. W. Bray, and I. S. Jacobs, J. Appl. Phys. **50**, 1810 (1979); J. C. Bonner and H. W. J. Blöte, Phys. Rev. B **25**, 6959 (1982).

[2] For review, see E. Dagotto and T. M. Rice, Science **271**, 618 (1996).

[3] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).

[4] J. Darriet and L. P. Regnault, Solid State Commun. **86**, 409 (1993).

[5] Z. Hiroi, M. Azuma, M. Takano, and Y. Bando, J. Solid State Chem. **95**, 230 (1991); M. Azuma, Z. Hiroi, M. Takano, K. Ishida, and Y. Kitaoka, Phys. Rev. Lett. **73**, 3463 (1994); M. Azuma, M. Takano, and R. S. Eccleston, J. Phys. Soc. Jpn. **67**, 740 (1998).

[6] R. S. Eccleston, M. Uehara, J. Akimitsu, H. Eisaki, N. Motoyama, and S. Uchida, Phys. Rev. Lett. **81**, 1702 (1998).

[7] D. C. Johnston, J. W. Johnson, D. P. Goshorn, and A. J. Jacobson, Phys. Rev. B **35**, 219 (1987).

[8] E. Dagotto, J. Riera, and D. Scalapino, Phys. Rev. B **45**, 5744 (1992).

[9] T. Barnes and J. Riera, Phys. Rev. B **50**, 6817 (1994).

[10] R. S. Eccleston, T. Barnes, J. Brody, and J. W. Johnson, Phys. Rev. Lett. **73**, 2626 (1994).

[11] A. W. Garrett, S. E. Nagler, D. A. Tennant, B. C. Sales, and T. Barns, Phys. Rev. Lett. **79**, 745 (1997).

[12] G. S. Uhrig and H. J. Schulz, Phys. Rev. B **54**, R9624 (1996).

[13] P. T. Nguyen, R. D. Hoffman, and A. W. Sleight, Mater. Res. Bull. **30**, 1055 (1995).

[14] Z. Hiroi, M. Azuma, Y. Fujishiro, T. Saito, M. Takano, F. Izumi, T. Kamiyama, and T. Ikeda, J. Solid State Chem. (to be published).

[15] T. Yamauchi, Y. Ueda, Y. Narumi, K. Tatani, T. Kobayashi, K. Kindo, J. Kikuchi, and K. Motoya (unpublished); J. Kikuchi, K. Motoya, T. Yamauchi, and Y. Ueda, Phys. Rev. B **60**, 6731 (1999).

[16] F. Izumi, in *The Rietveld Method*, edited by R. A. Young (Oxford University Press, New York, 1993), p. 236.

[17] I. D. Brown and D. Altermatt, Acta Crystallogr., Sect. B: Struct. Sci. **41**, 244 (1985).

[18] M. Troyer, H. Tsunetsugu, and D. Würtz, Phys. Rev. B **50**, 13 515 (1994).

[19] J. W. Hall, W. E. Marsh, R. R. Weller, and W. E. Hatfield, Inorg. Chem. **20**, 1033 (1981); W. E. Hatfield, J. Appl. Phys. **52**, 1985 (1981).

[20] T. Wei, A. J. Heeger, M. B. Salamon, and G. E. Delker, Solid State Commun. **21**, 595 (1977).