Journal of the Physical Society of Japan
Vol. 71, No. 6, June, 2002, pp. 1423–1426

Novel Phase Transition in Spin-1/2 Linear Chain Systems: $NaTiSi_2O_6$ and $LiTiSi_2O_6$

Masahiko ISOBE*, Emi NINOMIYA[1], Alexander N. VASIL'EV[2] and Yutaka UEDA

Materials Design and Characterization Laboratory, Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581
[1]*Deaprtment of Physics, Faculty of Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522*
[2]*Low Temperature Physics Department, Moscow State University, 119899 Moscow, Russia*

(Received February 8, 2002)

We synthesized a well-characterized powder sample of $NaTiSi_2O_6$, which had been missing as a spin-1/2 compound in one-dimensional (1D) magnets of the pyroxene family, and measured the magnetic susceptibility, lattice parameters and specific heat as functions of temperature. We observed a typical behavior of magnetic susceptibility in a spin-1/2 1D magnet, followed by a spin-Peierls-like transition at 210 K. The most significant feature of the transition is that it occurs at a temperature higher than that at the maximum point of the Bonner–Fisher curve. This means that the short-range magnetic correlations within the chain are not fully developed and intrinsic magnetoelastic instability of a 1D system cannot be considered as a driving force for the transition. We propose an important role of the orbital degree of freedom, that is, the orbital order, based on the structural feature that the 1D chain is made up of *skew* edge-sharing $Ti^{3+}O_6$ octahedra. A similar transition was observed at 230 K in $LiTiSi_2O_6$.

KEYWORDS: $NaTiSi_2O_6$, $LiTiSi_2O_6$, quasi-1D system, magnetic susceptibility, structural transition, spin-gap behavior
DOI: 10.1143/JPSJ.71.1423

In the last decade, many quantum spin systems, *e.g.*, spin dimer,[1] spin-Peierls,[2] spin-ladder,[3] and spin-plaquette[4] systems have been discovered and extensively studied both experimentally and theoretically. Since the quantum spin phenomena of interest appear in low-dimensional magnets, many efforts have been made to synthesize new low-dimensional materials and much attention has been paid to already known compounds, particularly minerals, from the viewpoint of the arrangement of magnetic ions in them.

The alkali metal pyroxene family denoted as $AM^{3+}B_2O_6$ (A=alkali metal; B=Si, Ge; M=cations with valence state of 3+) was previously studied from a mineralogical standpoint. The compound $NaAlSi_2O_6$, named jadeite or ''hisui'' in Japanese, has been considered as a very precious stone since ancient times, and $LiAlSi_2O_6$ is called ''kunzite'' after the mineralogist Dr. G. F. Kunz. Recently, the pyroxene compounds with transition metal ions M^{3+} have drawn great attention as low-dimensional magnets. In the crystal structure of pyroxene, shown in Fig. 1, the $M^{3+}O_6$-octahedra form one-dimensional (1D) chains along the c-axis by sharing edges. Since each chain is bridged by SiO_4- or GeO_4-tetrahedra, the magnetic interchain interaction is considered to be much weaker than the intrachain interaction: a typical 1D magnet. Alkali metal ions A^+ occupy the tunnel sites in the framework formed by $M^{3+}O_6$-octahedra and BO_4-tetrahedra. Many transition metal compounds of the pyroxene family have been reported, i.e., $AM^{3+}B_2O_6$ with Ti^{3+} (d^1),[5] V^{3+} (d^2),[6,7] Cr^{3+} (d^3),[8,9] Mn^{3+} (d^4)[10] and Fe^{3+} (d^5)[11,12] as M^{3+} in an ascending order of the number of d-electrons. Almost each compound mentioned exhibits a Néel ordered state as the ground state at low temperatures. In $LiVGe_2O_6$ (d^2), Millet *et al.*[13] first proposed the presence of biquadratic interaction and spin-Peierls transition in the spin-1 ($S = 1$) chain, but subsequently, the antiferromagnetic ordered state as the ground state was confirmed.[14] It is well known that the quantum effects on spin fluctuation and spin-lattice coupling are the most enhanced in the 1D chain system with $S = 1/2$ (d^1). A compound in which such quantum effects can be expected is $AM^{3+}B_2O_6$ with Ti^{3+} (d^1) as M^{3+}.

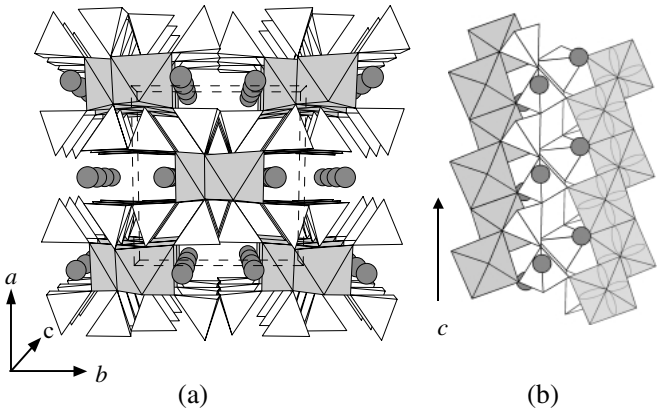

Fig. 1. (a) Schematic crystal structure of monoclinic $NaTiSi_2O_6$ viewed from c-direction. The gray and white polyhedra represent $Ti^{3+}O_6$-octahedra and SiO_4-tetrahedra, respectively. Na^+ ions (filled circles) occupy the tunnel sites surrounded by the polyhedra. (b) Schematic illustrations of the 1D chain made up of *skew* edge-sharing TiO_6 octahedra and of orbital ordering in the chain (see text).

$NaTiSi_2O_6$ was previously synthesized by a solid-state reaction under high pressure and the structure was analyzed by Ohashi *et al.*[5] It crystallizes in a monoclinic unit cell with the space group C2/c, which is similar to other members of the pyroxene family. The lattice constants are $a = 0.9692$ nm, $b = 0.8874$ nm, $c = 0.5301$ nm and $\beta = 106.85^\circ$ at room temperature.[5] The structure includes isolated zigzag chains made up of edge-sharing TiO_6 octahedra, as shown in Fig. 1(b). Since the crystallographic

*E-mail: isobe@issp.u-tokyo.ac.jp

titanium site is unique in structure, the chains can be regarded as uniform linear chains with $S = 1/2$. However, the magnetic properties of $NaTiSi_2O_6$ have been left unsettled and there is no report on the synthesis of $LiTiSi_2O_6$.

Recently, we succeeded in preparing powder samples of $NaTiSi_2O_6$ with high quality and new $LiTiSi_2O_6$ by a solid-state reaction under ambient pressure, and we observed a spin-Peierls-like transition in both compounds. In this letter, we report the structural, thermal and magnetic properties of $S = 1/2$ 1D magnets, $NaTiSi_2O_6$ and $LiTiSi_2O_6$.

Powder samples were prepared by a solid-state reaction of mixtures with an appropriate molar ratio of $Na_2TiSi_4O_{11}$, Ti and TiO_2 for $NaTiSi_2O_6$ (Li_2TiO_3, Ti, TiO_2 and SiO_2 for $LiTiSi_2O_6$). The weighed mixtures were pressed into pellets and heated at 1050°C in an evacuated silica tube for several days. Dark green products were obtained. $Na_2TiSi_4O_{11}$ (Li_2TiO_3) powder samples were prepared by heating mixtures of $NaCO_3$, TiO_2 and SiO_2 (Li_2CO_3 and TiO_2) at 800°C in air. A sample of $NaTiSi_2O_6$ thus prepared was checked by powder X-ray diffraction and was found to be almost of a single phase. The lattice parameters agree well with the previous data. The sample of $LiTiSi_2O_6$, on the other hand, included a significant amount of unknown impurity phases. The X-ray diffraction pattern for $LiTiSi_2O_6$ was similar to that for $NaTiSi_2O_6$. The lattice constants are $a = 0.966$ nm, $b = 0.873$ nm, $c = 0.530$ nm and $\beta = 109.8°$ at room temperature.

Magnetic susceptibility (χ) was measured in the temperature range from 5 K to 700 K using a quantum design SQUID magnetometer. The raw data of χ at $H = 1$ T for $NaTiSi_2O_6$ are shown in Fig. 2 as a function of temperature (T). The most significant feature of the χ–T curve is a gaplike behavior. The $\chi(T)$ shows a Curie–Weiss behavior in a higher temperature region and reveals a sharp decrease below 210 K. The $\chi(T)$ increases again below 60 K and obeys the Curie law, indicating that the raw data of χ can be well expressed as $\chi = \chi_m + \chi_i$, where χ_m and $\chi_i = C/T$ are the magnetic susceptibilities of the title compound and impurity, respectively. By assuming an impurity with $S = 1/2$, the concentration of the impurity can be estimated to be less than 0.5 mol%. The inset in Fig. 2 shows χ_m after the subtraction of the Curie contribution χ_i from the χ raw data. The χ_m starts to decrease at approximately 210 K and becomes temperature-independent below 60 K. The constant value of $\chi_m = 6 \times 10^{-5}$ emu/mol at low temperatures is comparable to the magnetic susceptibility at the ground state in spin-gap systems with $S = 1/2$: NaV_2O_5,[15] MgV_2O_5,[16] CaV_2O_5[17] and CsV_2O_5.[18] Therefore, the ground state of $NaTiSi_2O_6$ can be considered to be a spin-singlet.

The rough estimate for the spin-gap value was obtained by fitting χ_m in a low temperature range to the following equation:

$$\chi_m = \alpha \exp(-\Delta/k_B T) + \chi_0,$$

where α is a constant value corresponding to the dispersion of excitation energy, Δ is the magnitude of the spin gap, and χ_0 ($= 6 \times 10^{-5}$ emu/mol) is the constant term caused by diamagnetism of core electron shells and Van Vleck paramagnetism. The solid line in the inset in Fig. 2 shows the best fit. The parameters obtained from the fitting were $\alpha = 5.4 \times 10^{-3}$ and $\Delta/k_B \sim 500$ K.

In a higher temperature region, the $\chi(T)$ exhibits a Curie–Weiss behavior but it deviates from the Curie–Weiss law at a higher temperature of about 400 K (see the dotted line in Fig. 3). A better fit of the experimental data was obtained using the Bonner–Fisher equation[19] for the $S = 1/2$ antiferromagnetic Heisenberg linear chain. The solid line in Fig. 3 shows the best fit with $g = 2$ and $J/k_B = 295$ K, where g is the powder-averaged g-factor and J the intrachain exchange integral. As can be seen in Fig. 3, χ is well fitted to

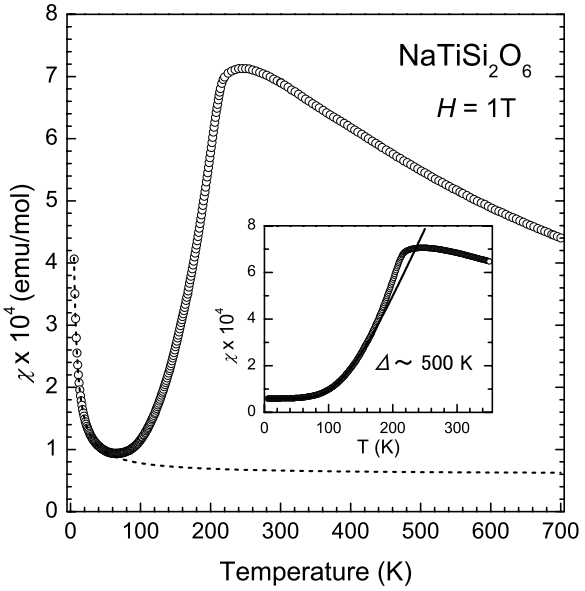

Fig. 2. Temperature dependence of magnetic susceptibility of $NaTiSi_2O_6$. The dotted line shows a Curie law fitting. The inset shows the magnetic susceptibility derived by subtracting the Curie term from the raw data (see text). The solid line in the inset is a fitting curve for the rough estimate of the spin gap (see text).

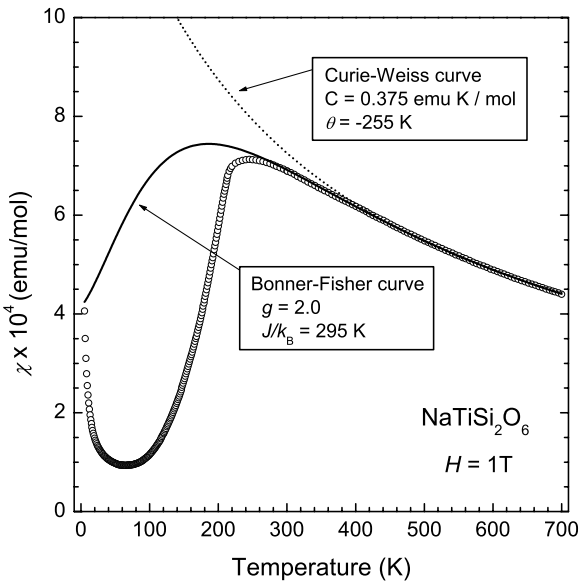

Fig. 3. Temperature dependence of magnetic susceptibility of $NaTiSi_2O_6$. The dotted line shows a Curie–Weiss law fitting in a high-temperature region and the solid line shows a better fit obtained using the Bonner–Fisher equation (see text).

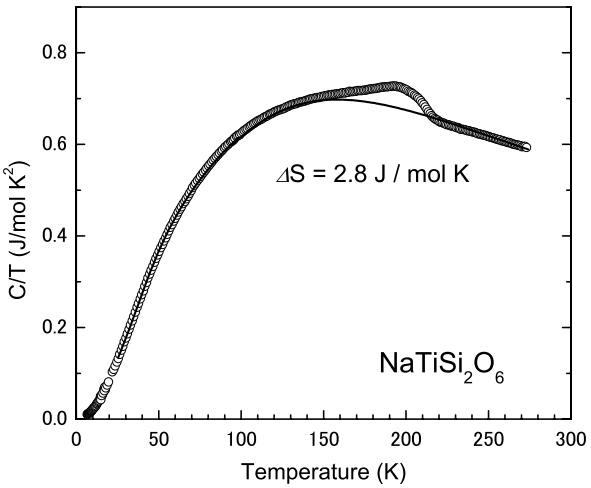

Fig. 4. Temperature dependence of specific heat of $NaTiSi_2O_6$.

the Bonner–Fisher equation above 250 K. This indicates that $NaTiSi_2O_6$ is a typical $S = 1/2$ 1D magnet, as expected from its structure. However, χ begins to deviate from the Bonner–Fisher curve below 250 K and sharply decreases with decreasing temperature below 210 K which is higher by about 30 K than that ($\sim$180 K) at the maximum point of the Bonner–Fisher curve.

In order to investigate the nature of the phase transition, we measured specific heat in the temperature range from 5 K to 280 K using an adiabatic microcalorimeter. The results are shown in Fig. 4. The broad peak of specific heat was observed at the temperature roughly corresponding to that of the spin-gap opening in $NaTiSi_2O_6$. The entropy change was estimated to be $\Delta S = 2.8$ J/mol K and the Debye temperature $\Theta_D = 450$ K. This entropy change cannot be separated into lattice and magnetic subsystem parts, but it is equal to about one-half of the theoretical estimate for the magnetic entropy released at a purely magnetic phase transition $R\ln(2S+1) = 5.76$ J/mol K. Typically, the low-dimensional magnetic systems exhibit much of this entropy above the critical temperature.

Next we measured the X-ray diffraction as a function of temperature in order to check any structural transition. As shown in Fig. 5, some diffraction peaks split into two peaks below 210 K, suggesting the lowering of the crystal symmetry from monoclinic to triclinic. The splitting of the peak developed gradually below 210 K and no coexistence of the two phases (high- and low-temperature phases) was recognized in the X-ray diffraction pattern. These results suggest a second-order phase transition. The X-ray diffraction pattern of the low-temperature phase can be well indexed to a triclinic structure, and the lattice parameters at 10 K are $a = 0.663$ nm, $b = 0.883$ nm, $c = 0.529$ nm, $\alpha = 90.2^\circ$, $\beta = 102.3^\circ$, and $\gamma = 47.1^\circ$.

We also observed a similar transition at 230 K in $LiTiSi_2O_6$, as shown in Fig. 6. The χ–T curve of $LiTiSi_2O_6$ shows some extra anomalies, which may be due to impurity phases. The analyses of the χ similar to those in the case of $NaTiSi_2O_6$ were not carried out in $LiTiSi_2O_6$ because the samples of $LiTiSi_2O_6$ contained a significant amount of impurity phases.

We discovered a phase transition at approximately 210 K

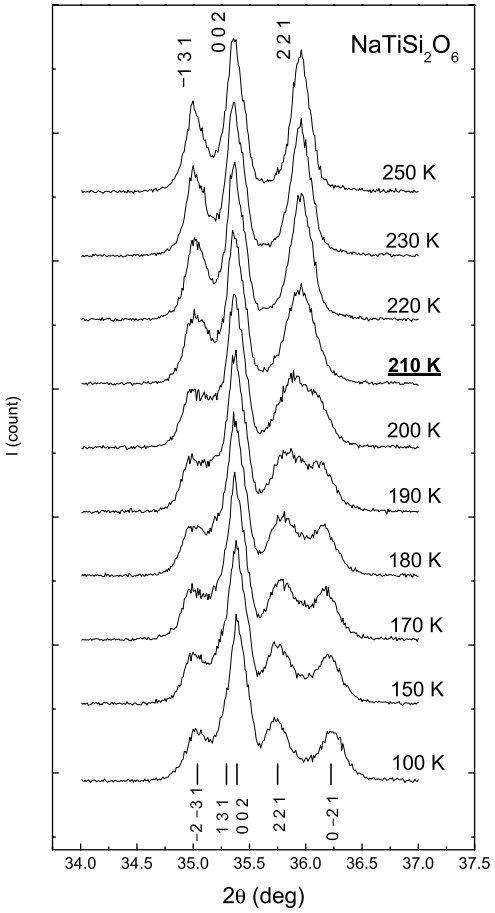

Fig. 5. Temperature dependence of X-ray reflections (−1 3 1), (0 0 2) and (2 2 1) of $NaTiSi_2O_6$.

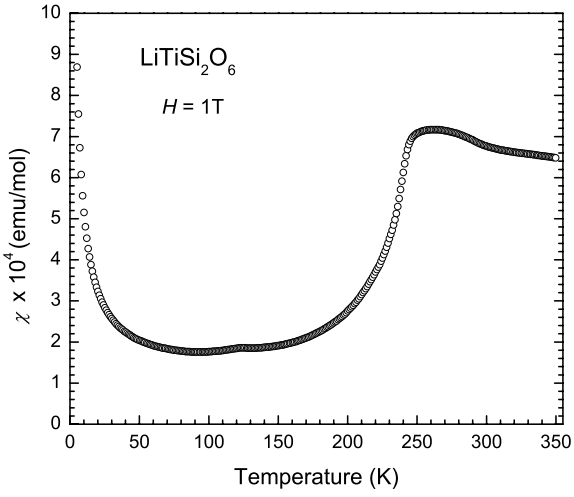

Fig. 6. Temperature dependence of magnetic susceptibility of $LiTiSi_2O_6$.

(230 K) in $NaTiSi_2O_6$ ($LiTiSi_2O_6$). The transition is accompanied by the decrease of magnetic susceptibility, thermal change and structural change. The ground state is a spin-singlet, and above the transition temperature, χ of $NaTiSi_2O_6$ obeys a Bonner–Fisher equation for the $S = 1/2$ antiferromagnetic Heisenberg linear chain. The most well-known quantum phenomenon in an $S = 1/2$ 1D chain system is the spin-Peierls transition. The properties of $NaTiSi_2O_6$ satisfy some features of the spin-Peierls system,

such as the $S = 1/2$ 1D chain, spin-singlet ground state and lattice deformation. However, some different points exist. The value $2\Delta/k_BT_{SP} = 4.8$ for $NaTiSi_2O_6$, where Δ is the gap energy ($\sim$500 K) and T_{SP} the spin-Peierls transition temperature (210 K), is much larger than the theoretical estimate 3.53[20] derived using the BCS formula in a weak coupling regime. The transition occurs at a temperature higher than that at the maximum point of the Bonner–Fisher curve. This means that the short-range magnetic correlations within the chain are not fully developed and intrinsic magnetoelastic instability of the 1D system cannot be considered as a driving force for the transition at 210 K. Moreover, a complex and striking crystal deformation is definitely seen by X-ray diffraction. These significant differences suggest another origin of the transition of $NaTiSi_2O_6$. We can see an example of such exotic transition in the case of NaV_2O_5.[15] Previously, the transition of NaV_2O_5 was regarded as a spin-Peierls transition because the transition satisfied many characteristics of the spin-Peierls transition, except $2\Delta/k_BT_{SP} = 6.4$.[21] However, the transition of NaV_2O_5 was finally established to be a charge order transition; the charge degree of freedom was the origin of such transition.[22–25]

To determine another origin of the transition of $NaTiSi_2O_6$, we shall review again the structural characteristics of $NaTiSi_2O_6$. In $NaTiSi_2O_6$, the TiO_6 octahedra form chains by sharing edges. Here, it should be noted that the chain is not made up of *trans* edge-sharing but of *skew* edge-sharing TiO_6 octahedra, as shown in Fig. 1(b). Therefore, the chain looks like a zigzag chain formed by Ti_2O_{10} dimers, although the crystallographic site of Ti atom is unique. With Ti^{3+} (d^1) octahedrally coordinated by oxygen atoms, the d-electron occupies the three-degenerated t_{2g} orbital, in which case the chain made up of *skew* edge-sharing TiO_6 octahedra is a uniform linear chain. If the d-electron selectively occupies the d_{xy} (or d_{yz} or d_{zx}) orbital as shown in Fig. 1(b), namely, an orbital ordering exists, the chain made up of *skew* edge-sharing TiO_6 octahedra can be regarded as a dimer chain, differing from the case of *trans* edge-sharing TiO_6 octahedra. Such a dimer chain is responsible for spin-singlet formation within the Ti^{3+} (d^1)–Ti^{3+} (d^1) pairs, similar to the case of V^{4+} (d^1)–V^{4+} (d^1) pairs of VO_2.[26]

In summary, we synthesized a well-characterized powder sample of $NaTiSi_2O_6$ ($LiTiSi_2O_6$), which had been missing as an $S = 1/2$ compound in 1D magnets of the pyroxene family, and measured the magnetic susceptibility, lattice parameters and specific heat as functions of temperature. At 210 K (230 K) in $NaTiSi_2O_6$ ($LiTiSi_2O_6$), we found an exotic transition accompanied by a gradual decrease of magnetic susceptibility and structural change. The ground state is a spin-singlet. The transition is similar to the spin-Peierls transition in certain characteristics but is different in some properties. The most significant feature is that the transition occurs at a temperature higher than that at the maximum point of the Bonner–Fisher curve. This means that the short-range magnetic correlations within the chain are not fully developed and intrinsic magnetoelastic instability of a 1D system cannot be considered as a driving force for the transition. We propose an important role of the orbital degree of freedom, that is, a spin-Peierls-like transition driven by the orbital order. In order to investigate the transition in detail, it is necessary to perform microscopic measurements such as neutron diffraction and NMR, which are now in progress. Furthermore, we are now attempting the growth of a single crystal.

The authors thank T. Yamauchi, H. Kageyama and T. N. Voloshok for valuable discussions. This study is partly supported by a Grant-in-Aid for Scientific Research (No. 758) and for Creative Scientific Research (No. 13NP0201) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

1) H. Kageyama, K. Yoshimura, R. Stern, N. V. Mushinikov, K. Onizuka, M. Kato, K. Kosuge, C. P. Slichter, T. Goto and Y. Ueda: Phys. Rev. Lett. **82** (1999) 3168.
2) See for a review, J. P. Boucher and L. P. Regnault: J. Phys. I (France) **6** (1996) 1939.
3) See for a review, E. Dagotto and T. M. Rice: Science **271** (1996) 618 and references therein.
4) K. Kodama, H. Harashina, H. Sasaki, Y. Kobayashi, M. Kasai, S. Taniguchi, Y. Yasui, M. Sato, K. Kakurai, T. Mori and M. Nishi: J. Phys. Soc. Jpn. **66** (1997) 793 and references therein.
5) H. Ohashi, T. Fujita and T. Osawa: J. Jpn. Assoc. Mineral. Petrol. Econ. Geol. **77** (1982) 305.
6) H. Ohashi, T. Osawa and A. Sato: Acta Crystallogr. C **50** (1994) 1652.
7) C. Satto, P. Millet and J. Galy: Acta Crystallogr. C **53** (1997) 1727.
8) J. R. Clark, D. E. Applemen and J. J. Papike: Mineral. Soc. Am. Spec. Pap. **2** (1969) 31.
9) M. Behruzi, Th. Hahn, C. T. Prewitt and K. Baldwin: Acta Crystallogr. A **40** (1984) Suppl. S., C247.
10) H. Ohashi and T. Osawa: Acta Crystallogr. C **43** (1987) 605.
11) E. Baum, W. Treutmann, M. Behruzi, W. Lottermoser and G. Amthauser: Z. Crystallogr. **183** (1988) 273.
12) W. Lottermoser, G. Redhammer, K. Forcher, G. Amthauer, W. Paulus, G. Andre and W. Treutmann: Z. Crystallogr. **213** (1998) 101.
13) P. Millet, F. Mila, F. C. Zhang, M. Mambrini, A. B. Van Oosten, V. A. Pashchenko, A. Sulpice and A. Stepanov: Phys. Rev. Lett. **83** (1999) 4176.
14) M. D. Lumsden, G. E. Granroth, D. Mandrus, S. E. Nagler, J. R. Thompson, J. P. Castellan and B. D. Gaulin: Phys. Rev. B **62** (2000) R9244.
15) M. Isobe and Y. Ueda: J. Phys. Soc. Jpn. **65** (1996) 1178.
16) M. Isobe, Y. Ueda, K. Takizawa and T. Goto: J. Phys. Soc. Jpn. **67** (1998) 755.
17) H. Iwase, M. Isobe, Y. Ueda and H. Yasuoka: J. Phys. Soc. Jpn. **65** (1996) 2397.
18) M. Isobe and Y. Ueda: J. Phys. Soc. Jpn. **65** (1996) 3142.
19) J. C. Bonner and M. E. Fisher: Phys. Rev. **135** (1964) A640.
20) J. W. Bray, L. V. Interrante, I. S. Jacobs and J. C. Bonner: *Extended Linear Chains Compounds*, ed. J. S. Miller (Plenum Press, New York and London, 1983) Vol. 3, p. 353.
21) Y. Fujii, H. Nakano, T. Yoshihama, M. Nishi, K. Nakajima, K. Kakurai, M. Isobe, Y. Ueda and H. Sawa: J. Phys. Soc. Jpn. **66** (1997) 326.
22) T. Ohama, H. Yasuoka, M. Isobe and Y. Ueda: Phys. Rev. B **59** (1999) 3299.
23) H. Seo and H. Fukuyama: J. Phys. Soc. Jpn. **67** (1998) 2602.
24) K. Ohwada, Y. Fujii, N. Takesue, M. Isobe, Y. Ueda, H. Nakao, Y. Wakabayashi, Y. Murakami, K. Ito, Y. Amemiya, H. Fujihisa, K. Aoki, T. Shobu, Y. Noda and N. Ikeda: Phys. Rev. Lett. **87** (2001) 086402.
25) H. Sawa, E. Ninomiya, T. Ohama, H. Nakao, K. Ohwada, Y. Murakami, Y. Fujii, Y. Noda, M. Isobe and Y. Ueda: J. Phys. Soc. Jpn. **71** (2002) 385.
26) See for reviews, J. B. Goodenough: *Progress in Solid State Chemistry* (Pergamon Press, New York, 1971) Vol. 5, p. 145; N. F. Mott: *Metal–Insulator Transition* (Taylar and Francis, London, 1974).