Thermal contraction at the spin-Peierls transition in $CuGeO_3$

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We report the results of an x-ray-scattering study of the b-axis lattice constant of the quasi-one-dimensional spin-$\frac{1}{2}$ antiferromagnetic chain system $CuGeO_3$ as a function of temperature and magnetic field. A spontaneous thermal contraction Δb along the b axis perpendicular to the chain direction is observed below the spin-Peierls transition temperature T_c near 14 K. The contraction, Δb, is well described by a simple power law, $\Delta b \propto (1-T/T_c)^x$, where the exponent x is found to be close to 0.5. Below the transition temperature, Δb scales with the intensity of the superlattice reflections with indices $(h/2,k,l/2)(h,l$: odd, k: nonzero integer) measured by neutron scattering. The shift of the transition temperature, $\Delta T_c \equiv T_c(0)-T_c(H)$, is found to scale as H^2 in quantitative agreement with the results of magnetic susceptibility measurements and with theory. A small increase in the a-axis lattice constant is observed below T_c.

The cooperative behavior of lower-dimensional quantum spin systems is a subject of continuing research. One particularly interesting phenomenon is the so-called spin-Peierls transition, which is a structural phase transition driven by the magnetic interaction in one-dimensional (1D) $S=\frac{1}{2}$ chain compounds. By analogy with the well-known Peierls instability in a 1D metal,[1] it can be shown[2] that a uniform antiferromagnetic chain is unstable with respect to a lattice distortion, which dimerizes the chain into an alternating antiferromagnet, thereby introducing a gap into the chain spin-excitation spectrum. Until about a year ago, spin-Peierls transitions had only been observed in a few organic compounds such as TTF-$CuS_4C_4(CF_3)_4$ (Refs. 3 and 4) and (MEM)-$(TCNQ)_2$ (Ref. 5). In each case the transition was well described by mean-field theory.[6]

Recently, a structurally simple, inorganic chain compound copper germanium trioxide [$CuGeO_3$] has attracted wide-spread attention. This material appears to be a good realization of a 1D $S=\frac{1}{2}$ system, although there are non-negligible 2D interactions. $CuGeO_3$ exhibits the behavior predicted for a spin-Peierls system in several respects. First, Hase, Terasaki, and Uchinokura[7] discovered that the magnetic susceptibilities in all directions drop exponentially to small constant values below a transition temperature (T_c) of 14 K. Second, T_c shifts to lower values with increasing magnetic field. Third, Nishi, Fujita, and Akimitsu[8] confirmed the formation of a gap in the spin-excitation spectrum below the transition temperature using inelastic neutron-scattering techniques. Using the same experimental technique, Fujita *et al.*[8] characterized the nature of this gap mode to be a triplet by observing the splitting of the gap mode into three distinct modes under the application of a magnetic field. Fourth, the superlattice reflections resulting from the lattice dimerization below the transition temperature have recently been observed by electron diffraction,[9] x-ray, and elastic neutron diffraction.[10,11]

The crystal structure of $CuGeO_3$ is orthorhombic, space group $P_{bmm}(D^5_{2h})$, with a unit cell (Fig. 1) of dimensions $a=4.81$ Å, $b=8.47$ Å, and $c=2.94$ Å at room temperature. Each Ge atom is tetrahedrally coordinated to four neighboring oxygens, and each distorted tetrahedron shares oxygens at the corners with two other tetrahedra to form a GeO_3 chain along the c axis. The Cu atoms are octahedrally coordinated to the neighboring oxygens, and each distorted octahedron shares edges with two neighboring octahedra to form a CuO_4 chain parallel to the GeO_3 chain. The two chains are linked together through the oxygen atoms.

In a recent neutron-scattering study, Lorenzo *et al.*[12] observed an anomalous softening of the longitudinal acoustic phonons propagating along the b axis perpendicular to the chain direction. They also observed a spontaneous lattice contraction in the same direction below the transition temperature of 14 K, which coincides with the transition temperature observed in the magnetic susceptibility measurements.[7,13] The motivation of the

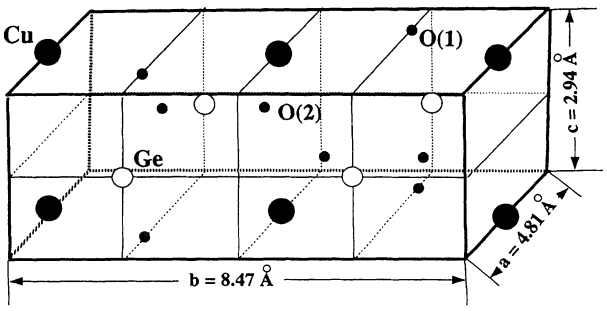

FIG. 1. Unit cell of $CuGeO_3$; the space group is P_{bmm}. The atomic positions are Cu in 2(d) at $\frac{1}{2}$,0,0; Ge in 2(e) at $x,\frac{1}{4},\frac{1}{2}$ ($x=0.0743$); O(1) in 2(f) at $x,\frac{1}{4}$,0 ($x=0.8700$), and O(2) in 4(i) at $x,y,\frac{1}{2}$ ($x=0.2813$, $y=0.0838$).

present experiment was to understand the nature of this thermal contraction.

In this paper, we present an x-ray-scattering measurement of the lattice constant b as a function of temperature under various external magnetic fields. The experiment was carried out on MIT/IBM beamline X20B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The white x-ray beam from a bending magnet was monochromatized by a single Si(111) crystal. The energy of the incident x-ray photons was fixed at 17.4 keV. Scattering was in the horizontal plane and a flat Si(111) crystal was utilized as the analyzer. A single crystal of $CuGeO_3$ grown by the floating zone method was used in the experiment. The sample was mounted with wave vectors ($0kl$) in the scattering plane in an x-ray-compatible split pair superconducting magnet manufactured by Oxford Instruments Ltd. The measurements were carried out around the (080) reciprocal lattice position, since in this experimental configuration, the ratio of $\Delta q/q$, where Δq is the half-width-at-half-maximum (HWHM), at (080) was the smallest among those at (020), (040), (060), and (080). The longitudinal HWHM at (080) was ~ 0.0013 Å^{-1}, while the in-plane transverse resolution was controlled by the sample mosaic of $\sim 0.009°$ HWHM. A variable temperature insert of the liquid-He flow type was used. Hence, stable and reproducible experimental conditions could only be obtained for $T > 7$ K, where all the experiments were performed.

The experimental results at zero field are shown in Fig. 2(a). The lattice contraction appears below a T_c of ~ 14.2 K. The data are well described by the simple form

$$b(T)=b_0(1+BT^4)-\Delta b \ , \tag{1}$$

where the first term on the right-hand side of the equation is the conventional thermal expansion of the lattice derived from $\alpha \equiv (1/b)(\partial b/\partial T) \propto T^3$ for small T.[14] The second term Δb is well represented by the single power-law form:

$$\Delta b = \begin{cases} 0 \ , & T > T_c \\ A(1-T/T_c)^x \ , & T \le T_c \ , \end{cases} \tag{2}$$

where the exponent x is found to be close to 0.5. The solid line in Fig. 2(a) is the result of a least-squares fit of Eq. (1) to the data with x fixed at 0.5.

In order to probe further the connection of this thermal contraction along the b axis to the magnetic transition observed by Hase and co-workers,[7,13] we repeated the measurement of the lattice constant as a function of temperature in several fields up to 6 T. The magnetic field was applied in the vertical direction, that is, the a-axis direction. Results similar to those found at zero field were obtained for a series of fields up to 6T. Shown in Figs. 2(b) and 2(c) are the results of the lattice constant measurements under $H=2$ T and $H=5$ T, respectively. While applying magnetic fields, the sample position moved slightly compared with that at zero field; this necessitated realigning the spectrometer, thence causing a slight difference in the arm-zero position in different magnetic fields; this subsequently led to a small difference in the apparent absolute value of the lattice constant. Accordingly, in Fig. 2 we have normalized the lattice constants in different magnetic fields at 25 K.

In Fig. 2, the solid curves are the best fits of the data to

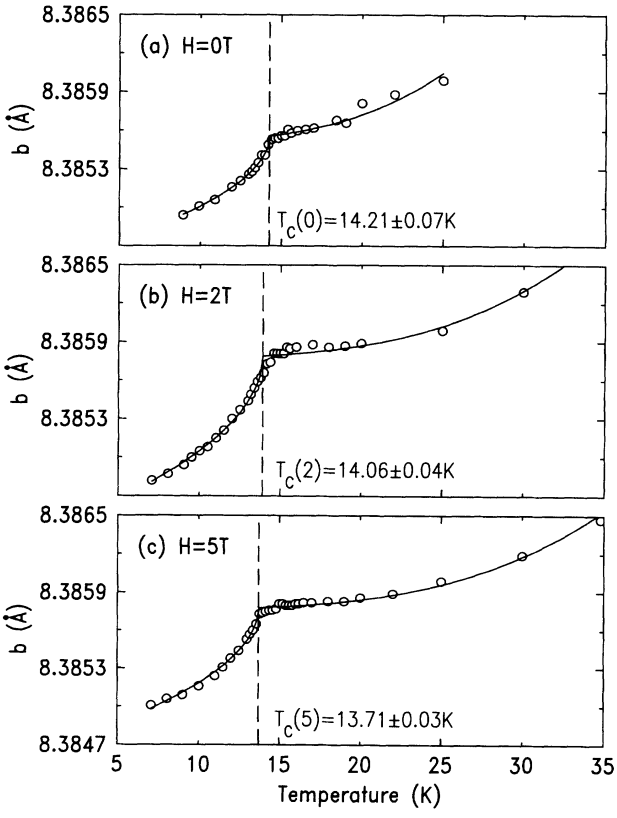

FIG. 2. The lattice constant b of $CuGeO_3$ as a function of temperature and magnetic field. A spontaneous contraction along the b axis is observed below $T_c \sim 14$ K; the solid lines are the best fits to Eq. (1) with exponent $x=0.5$. The fitted error bars are smaller than the symbols shown in the figure, though the absolute error bars are larger. (a) $H=0$ T, $T_c=14.21\pm0.07$ K. (b) $H=2$ T, $T_c=14.06\pm0.04$ K. (c) $H=5$ T, $T_c=13.71\pm0.03$ K. The lattice constants in different magnetic fields are normalized at 25 K; see text.

Eq. (1) with $x=0.5$; one can clearly see that T_c shifts to lower values with increasing magnetic field. Figure 3 shows the magnetic field dependence of T_c. The solid line in the figure is the best fit to

$$T_c(H)=T_c(0)\left[1-\alpha\left[\frac{g\mu_B H}{2k_B T_c(0)}\right]^2\right], \quad (3)$$

where μ_B is the Bohr magneton and k_B is the Boltzmann constant.[15,16] The g factors observed by electron spin resonance (ESR) along the a, b, and c axes are $g_a=2.15$, $g_b=2.23$, and $g_c=2.05$, respectively.[17] The fitted value for α is 0.45 ± 0.09 in very good agreement with the value $\alpha=0.40$ deduced from magnetic susceptibility measurements[7] on a polycrystalline sample of $CuGeO_3$. These two values for α in turn also agree well with the theoretical values of 0.44 calculated in the Hartree-Fock approximation[15] and 0.36 in a theory based on the Luther-Peschel-type treatment of the spin-correlation functions.[16] We note that the approximation of Eq. (3), $g\mu_B H/k_B T_c(0)\ll 1$, is only moderately well satisfied, since $g\mu_B H/k_B T_c(0)\sim 0.1$ and 0.6 for $H=1$ T and 6 T, respectively.

We also fitted all of the b-axis lattice-constant data simultaneously to the following equation:

$$b(H,T)=b_0(1+BT^4)-\Delta b(H,T), \quad (4)$$

where

$$\Delta b(H,T)=\begin{cases}0, & T>T_c(H)\\ A(H)\left[1-\dfrac{T}{T_c(H)}\right]^x, & T\le T_c(H)\end{cases} \quad (5)$$

with b_0, B, $A(H)$, $T_c(H)$, and x as adjustable parameters. The best fit gives $x=0.53\pm0.02$. This value for x provides satisfactory fits to the temperature dependence of Δb at all magnetic fields studied.

Very recently, the superlattice reflections with indices $(h/2,k,l/2)$ (h,l: odd, k: nonzero integer) have been observed in electron,[9] x-ray, and neutron diffraction.[10,11] Hirota *et al.*, based on their neutron-diffraction measurement of the intensity of the superlattice reflections, have proposed a lattice dimerization model of $CuGeO_3$ below the transition temperature with oxygens O(2) displacing in the ab plane by about 0.01 Å, accompanied by a comparable shift of the Cu ions along the c axis.[11] The intensity (I) of the superlattice reflections from the neutron-diffraction measurements[11] turns out to be well described by a simple power law, $I\propto(1-T/T_c)^{2\beta}$. In Fig. 4 we show a comparison of the measured lattice contraction Δb from our x-ray studies together with the intensity I of the superlattice reflection at (0.5, 5, 0.5) from the neutron measurements.[11] The agreement is clearly quite good; this can be understood simply as originating in the coupling between the lattice contraction and the order parameter in a Landau free-energy formalism. We also note that both Δb and the intensity I (0.5, 5, 0.5) are well described by a single power law $[1-T/T_c(0)]^{0.53}$.

The appearance of the superlattice reflections is the result of the Cu dimerization and oxygen displacement below the spin-Peierls transition temperature. If we let δ denote a generalized lattice distortion amplitude, then the intensity of the superlattice reflections I is simply proportional to δ^2. We can write down the extended Landau free-energy F after integrating out the spin degrees of freedom:[18]

$$F=F_0+\tfrac{1}{2}a(T-T_c)\delta^2+\tfrac{1}{4}u_4\delta^4+\tfrac{1}{6}u_6\delta^6 +\tfrac{1}{2}K(\Delta b)^2+\gamma\Delta b\delta^2, \quad (6)$$

where $\frac{1}{2}K(\Delta b)^2$ is the elastic energy contribution of the

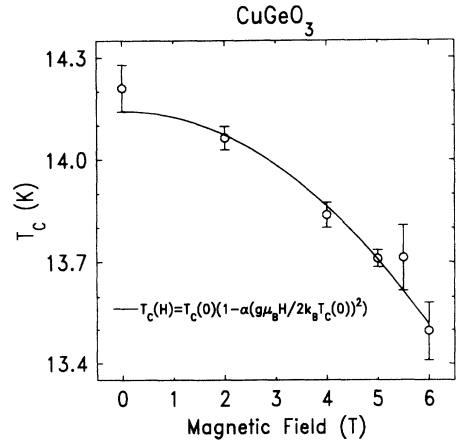

FIG. 3. The transition temperature T_c as a function of applied magnetic field H. The solid line is the result of a least-squares fit to the form $T_c(H)=T_c(0)[1-\alpha(g\mu_B H/2k_B T_c(0))^2]$, where the fitted value of α is 0.45 ± 0.09. The magnetic-field dependence of the transition temperature $T_c(H)$ agrees quantitatively with the results from magnetic susceptibility measurements (Ref. 7).

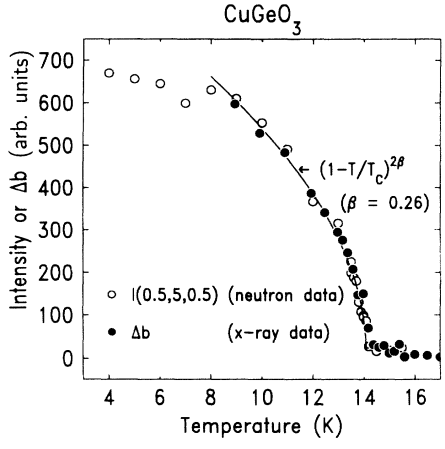

FIG. 4. Δb together with the intensity I of the superlattice reflections measured using neutron-diffraction techniques (Ref. 11). The empty circles are the intensity of the superlattice reflection at (0.5, 5, 0.5) measured by neutron scattering (Ref. 11). The solid line is the result of a fit of the superlattice reflection intensity to a simple power law $I\propto(1-T/T_c)^{2\beta}$, where the fitted value of β is 0.26 ± 0.03. The filled circles are the lattice contraction Δb data from the x-ray measurements reported here.

lattice contraction (K is the corresponding elastic constant), and the $\gamma\Delta b\delta^2$ term represents the lowest-order nonvanishing coupling between the distortion amplitude δ and the contraction Δb. From the condition that the sample is stress free, one has $\partial F/\partial(\Delta b)=0$, which gives

$$\Delta b=-\frac{\gamma}{K}\delta^2 . \tag{7}$$

Combining Eq. (7) with $I\propto\delta^2$, we have $\Delta b\sim I$, which is exactly the result displayed in Fig. 4.

By inserting Eq. (7) back into the free-energy expression Eq. (6), we can see some indication why β might be close to the tricritical value of 0.25. Combining Eqs. (6) and (7), one has

$$F=F_0+\tfrac{1}{2}a(T-T_c)\delta^2+\tfrac{1}{4}\left[u_4-\frac{2\gamma^2}{K}\right]\delta^4+\tfrac{1}{6}u_6\delta^6 . \tag{8}$$

Since $u_4'\equiv(u_4-2\gamma^2/K)<u_4$, the system is closer to a tricritical point ($u_4=0$ at the tricritical point) than the noncoupling situation ($\gamma=0$). The magnetoelastic interaction between the 1D antiferromagnetic chains and the 3D phonon field in the lattice drives the system $CuGeO_3$ through a spin-Peierls transition and opens up a finite energy gap in the spin-excitation spectrum[8] by dimerizing the lattice.[9-11] The atomic shifts induce the lattice contraction Δb and the coupling between the contraction and the lattice distortion in turn puts the system near the tricritical point. A similar argument might be made for the organic spin-Peierls system TTF-$CuS_4C_4(CF_3)_4$, which instead has $\beta=0.5$. However, in that case, there is a precursive 3D soft-phonon mode at the superlattice position, which persists to very high temperatures.[6] Cross and Fisher[19] argue that this soft-phonon mode causes the mean-field $\beta=\frac{1}{2}$ behavior in the TTF salt. No such soft phonon has been observed in $CuGeO_3$ so far.

We also observed a small increase of the lattice constant a in the a-axis direction below the transition temperature T_c (Fig. 5). The change of the lattice constant a between 10 and 15 K is about 0.002%, which is to be compared with the 0.0065% change along the b-axis direction.

Finally the theory of Cross and Fisher[19] predicts that the spin gap Δ varies as $\delta^{2/3}$ or equivalently $\Delta\sim I^{1/3}\sim(\Delta b)^{1/3}$. We show in Fig. 6 the data of Nishi, Fujita, and Akimitsu[8] for the spin gap together with the power law of Fig. 4 raised to the power $\frac{1}{3}$ and the low-temperature superlattice intensity data of Hirota *et al.*[11] also raised to the power $\frac{1}{3}$ normalized at 4 K. Clearly the agreement is quite satisfactory given the combined uncertainties. Thus, once more we see the consistency between the theory for the spin-Peierls transition and the experimental data of $CuGeO_3$. The small gap exponent of 0.093 suggested in the paper of Nishi, Fujita, and Akimitsu[8] is the result of fitting the gap data far away from the transition temperature to a power law. Clearly, in order to draw a definitive conclusion on the scaling of the spin gap with the atomic displacements, additional data on the gap energy, especially close to the transition temperature, are needed.

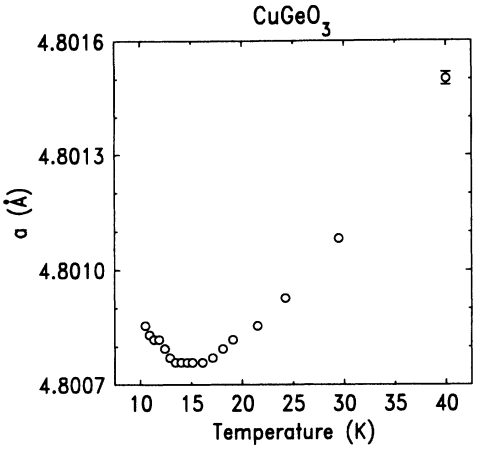

FIG. 5. The lattice constant along the a axis as a function of temperature. The fitted error bars are smaller than the symbols (except the last point), although the absolute error bars are larger.

In summary, we have accurately measured the lattice constant b as a function of temperature and magnetic field in $CuGeO_3$. A spontaneous thermal contraction Δb is observed below the transition temperature T_c of about 14 K, which coincides with the spin-Peierls transition temperature. The quadratic magnetic-field dependence of T_c agrees quantitatively with the results from the magnetic susceptibility measurements,[7] which in turn agrees with theory.[15,16] Δb is well described by a simple power law, with an exponent x close to 0.5. Δb is also found to

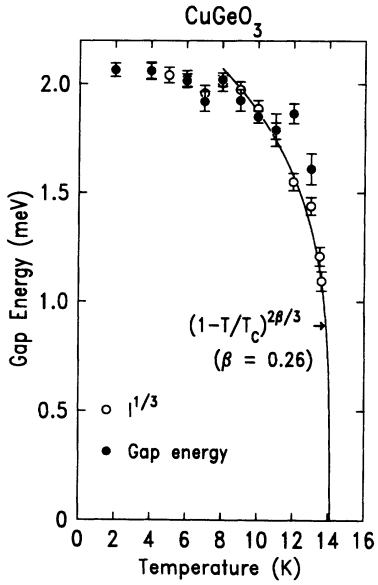

FIG. 6. Gap energy (Ref. 8) together with $I^{1/3}$ and the power law in Fig. 4 raised to the power $\frac{1}{3}$. The empty circles are the intensity of the superlattice reflection at (5, 0.5, 5) (Ref. 11) raised to the power $\frac{1}{3}$. The solid line is the power law $(1-T/T_c)^{2\beta}$ of Fig. 4 raised to the power $\frac{1}{3}$. The solid circles are the gap energy (Ref. 8).

scale with the intensity of the superlattice reflections, which is explained through a simple coupling term between the contraction and the order parameter in the Landau free-energy formalism. It is noted that the transition may be close to a tricritical point. Future, more precise experiments on the heat capacity, the critical fluctuations above T_c, and the order parameter below T_c should serve to distinguish between tricritical behavior and the expected asymptotic 3D Ising behavior at the spin-Peierls transition.

Although, in many aspects, $CuGeO_3$ has demonstrated itself to be a model spin-Peierls system, there are still some remaining questions yet to be answered. Among them, the most significant is how important the interchain couplings are, that is, whether $CuGeO_3$ is best described as a *one*-dimensional antiferromagnetic chain system or a spatially anisotropic *two*-dimensional system. Specifically, Nishi, Fujita, and Akimitsu[8] find significant dispersion of the magnetic excitations along both the *b* and *c* axes, with zone-boundary energies of ~ 6 meV and ~ 16 meV, respectively, while the dispersion along the *a* axis is negligible. The atomic displacements below the transition temperature as determined by Hirota *et al.*[11] are also more complicated than the simple dimerization along the chain direction as expected from an idealized spin-Peierls transition. The atomic displacements of Cu and O(2) may not only dimerize the intrachain interaction but may also modify the interchain interactions, suggesting that spin-ladder gap effects could also play a role.[20,21] Finally, the temperature dependence of the magnetic susceptibility above the transition temperature departs significantly from the Bonner-Fisher[22] curve for the linear spin-$\frac{1}{2}$ antiferromagnetic chain.[7] It is clear, therefore, that in order to understand fully the interesting behavior of $CuGeO_3$, much more experimental and theoretical work is needed.

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[1]R. E. Peierls, *Quantum Theory of Solids* (Oxford University, London, 1955).

[2]G. Beni and P. Pincus, J. Chem. Phys. **57**, 3531 (1972).

[3]J. W. Bray, H. R. Hart, Jr., L. V. Interrante, I. S. Jacobs, J. S. Kasper, G. D. Watkins, S. H. Wee, and J. C. Bonner, Phys. Rev. Lett. **35**, 744 (1975).

[4]I. S. Jacobs, J. W. Bray, H. R. Hart, Jr., L. V. Interrante, J. S. Kasper, G. D. Watkins, D. E. Prober, and J. C. Bonner, Phys. Rev. B **14**, 3036 (1976).

[5]S. Huizinga, J. Kommandeur, G. A. Sawatzky, B. T. Thole, K. Kopenga, W. J. M. de Jonge, and D. Roos, Phys. Rev. B **19**, 4723 (1979).

[6]D. E. Moncton, R. J. Birgeneau, L. V. Interrante, and F. Wudl, Phys. Rev. Lett. **39**, 507 (1977).

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

[8]M. Nishi, O. Fujita, and J. Akimitsu (unpublished); O. Fujita, J. Akimitsu, M. Nishi, and K. Kakurai (private communication).

[9]O. Kamimura, M. Terauchi, M. Tanaka, O. Fujita, and J. Akimitsu (unpublished).

[10]J. P. Pouget, L. P. Regnault, M. Ain, B. Hennion, J. P. Renard, P. Veillet, G. Dhalenne, and A. Revcolevschi, Phys. Rev. Lett. **72**, 4037 (1994).

[11]K. Hirota, D. E. Cox, J. E. Lorenzo, G. Shirane, J. M. Tranquada, M. Hase, K. Uchinokura, H. Kojima, Y. Shibuya, and I. Tanaka, Phys. Rev. Lett. **73**, 736 (1994).

[12]J. E. Lorenzo, K. Hirota, G. Shirane, J. M. Tranquada, M. Hase, K. Uchinokura, H. Kojima, I. Tanaka, and Y. Shibuya, Phys. Rev. B **50**, 1278 (1994).

[13]M. Hase, I. Terasaki, K. Uchinokura, M. Tokunaga, N. Miura, and H. Obara, Phys. Rev. B **48**, 9616 (1993).

[14]N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976).

[15]L. N. Bulaevskii, A. I. Buzdin, and D. I. Khomskii, Solid State Commun. **27**, 5 (1978).

[16]M. C. Cross, Phys. Rev. B **20**, 4606 (1979).

[17]K. Kindo *et al.* (unpublished).

[18]A. D. Bruce and R. A. Cowley, *Structural Phase Transitions* (Taylor & Francis, London, 1981).

[19]M. C. Cross and D. S. Fisher, Phys. Rev. B **19**, 402 (1979).

[20]T. Barnes, E. Dagotto, J. Riera, and E. S. Swanson, Phys. Rev. B **47**, 3196 (1993).

[21]T. M. Rice, S. Gopalan, M. Sigrist, and F. C. Zhang (unpublished).

[22]J. C. Bonner and M. E. Fisher, Phys. Rev. **135**, A640 (1964).