Anisotropic Spin Freezing in the $S = 1/2$ Zigzag Chain Compound $SrCuO_2$

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We characterize an unusual magnetic phase in orthorhombic $SrCuO_2$ using neutron scattering. $SrCuO_2$ contains zigzag spin chains formed by pairs of linear $S = 1/2$ chains ($J = 180$ meV) coupled through a frustrated interaction ($|J'| \lesssim 0.1J$). For $T < T_{c1} = 5.0(4)$ K, an elastic peak develops in a gapless spectrum indicating spin freezing on a time scale $\delta t > 2 \cdot 10^{-10}$ s. While the frozen state has long range order along chains ($\xi_c > 200c$) and a substantial correlation length, $\xi_a = 60(25)a$, perpendicular to zigzag planes, the correlation length is only $\xi_b = 2.2(3)b$ in the direction of frustrated interactions. We argue that slow dynamics of stripelike cooperative magnetic defects yield this anisotropic frozen state.

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Reduced dimensionality [1,2], geometrical frustration [3], and band formation [4] can suppress the critical temperature of magnets far below a cooperative energy scale such as the Curie-Weiss temperature. The resulting low temperature ordered phases have unconventional features that challenge conventional theories of magnetism. They include strongly reduced sublattice magnetization, abnormal sensitivity to low levels of disorder, and mean-field-like critical behavior.

Quasi-one-dimensional magnetic dielectrics are excellent model systems in which to explore weakly ordered phases because a quantitative connection between the dynamic properties of the one-dimensional units and critical phenomena in the coupled system can be established [5–7]. Haldane spin-1 chains and other spin systems with a gap have a critical value for the interchain coupling $zJ_\perp \approx \Delta$ below which they remain disordered down to $T = 0$. Spin-1/2 chains, on the other hand, are believed to order even for vanishingly small nonfrustrated interchain interactions. This is consistent with the low temperature long range order (LRO) among weakly coupled spin-1/2 chains found in Sr_2CuO_3 and Ca_2CuO_3 [8].

In this Letter we describe a different low temperature phase in closely related $SrCuO_2$, which contains linear spin-1/2 chains assembled pairwise in an array of weakly interacting zigzag chains [9–15]. Though weak static sublattice magnetization does develop for $T < 5.0(4)$ K $\approx 2.8 \cdot 10^{-3} J/k_B$, three-dimensional long range order is absent for $T \gtrsim 10^{-4} J/k_B$. Specifically, we find a low temperature correlation length of only two lattice spacings along the direction of frustrated intra-zigzag-chain interactions. We argue that slow dynamics of stripelike defects in quasi-two-dimensional antiferromagnetic (AFM) layers yields "spin freezing" to a static disordered structure rather than static LRO.

Zigzag chains in $SrCuO_2$ are built from corner-sharing Cu-O chains with an AFM exchange constant $J \approx 181(17)$ meV [13] stacked pairwise in edge-sharing geometry (see Fig. 3). The frustrating interaction between chains proceeds through $\approx 87.7°$ Cu-O-Cu bonds [10,16] and is expected to be weak and ferromagnetic $|J'| \lesssim 0.1J$. Field theory [17–19] and numeric simulations [19–21] predict that weak AFM interchain coupling in such a system induces incommensurate correlations and a gap $\Delta \sim J \exp(-\alpha J/J')$. For ferromagnetic J' the zigzag chain should remain gapless [18,19].

$SrCuO_2$ is centered orthorhombic (space group $Cmcm$) [11] with low T lattice parameters $a = 3.556(2)$ Å, $b = 16.27(4)$ Å, $c = 3.904(2)$ Å. We index wave vector transfer in the corresponding simple orthorhombic reciprocal lattice. Nuclear Bragg reflections (h,k,l) are allowed for even $h + k$ and even l when $k = 0$. While there is no direct information about the magnitude of interactions between zigzag chains, the structural features that determine them are similar to those in Sr_2CuO_3. Application of quantum chain mean field (CMF) theory [7] to Sr_2CuO_3 yields an estimate for interchain interactions of $\overline{J_\perp} \approx k_B T_N / (1.28\sqrt{\ln[5.8J/k_B T_N)}] \approx 0.13$ meV, while according to classical [5] CMF $\overline{J_\perp} = 3(k_B T_N)^2/[8JS^2(S+1)^2] \approx 8 \times 10^{-4}$ meV.

Neutron scattering experiments were performed at the NIST Center for Neutron Research using cold and thermal neutron spectrometers. PG(002) reflections were used for monochromator and analyzer, supplemented by Be or PG (pyrolytic graphite) filters. Our sample is a cylindrical rod, $\ell \approx 46$ mm, $D \approx 5$ mm, and $m = 3.875(5)$ g, grown by the traveling solvent floating zone (TSFZ) technique. Rocking curves about the **b** axis showed two roughly equal intensity peaks separated by $\approx 0.5°$ and each with a full width at half maximum (FWHM) $\approx 0.25°$. Experiments were performed with wave vector transfer in the $(h,0,l)$ and (h,k,h) reciprocal lattice planes. We used incoherent scattering from vanadium to normalize the magnetic scattering intensity.

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The defining feature of a quasi-one-dimensional spin system is an anisotropic dynamic correlation volume, which can be probed by inelastic magnetic neutron scattering. Figure 1 shows scans with constant energy transfers $0.5\ \text{meV} < \hbar\omega < 14\ \text{meV}$ along two perpendicular directions in the $(h, 0, l)$ plane. Scans along the chain direction [Figs. 1(d)–1(f)] reveal a resolution limited peak centered at $l = \frac{1}{2}$. The data yield an upper limit $\delta q \lesssim 0.01\mathbf{c}^*$ on any intrinsic FWHM of the peak (the observed peak width $\approx 0.03\mathbf{c}^*$ is consistent with the instrumental resolution). For comparison, the FWHM of the des Cloizeaux-Pearson continuum for each AFM spin-1/2 chain is $\delta q/c^* = 2\hbar\omega/\pi^2 J = (1.1 \times 10^{-3}\ \text{meV}^{-1})\hbar\omega$ and hence it is unresolved in our measurement. Figures 1(a)–1(c) show scans along the $\mathbf{a}$ direction which is normal to the plane of the zigzag chains. There we find broad peaks centered at $|h| \approx \frac{1}{2}$ whose FWHM increase rapidly with $\hbar\omega$. For $\hbar\omega \gtrsim 2$ meV the peaks span the Brillouin zone and the modulation is less than 20% of the magnetic signal. This provides evidence for short range, low energy AFM correlations perpendicular to zigzag chains. The correlation anisotropy between the two directions probed is $\delta q_a/\delta q_c > 10 a^*/c^*$.

Muon spin rotation (μSR) measurements show that $SrCuO_2$ has static magnetic order below $T = 2$ K [12]. Figure 2 shows the corresponding elastic magnetic neutron scattering, which we found at $\mathbf{Q} = \tau \pm \mathbf{Q}_m$ where τ is a reciprocal lattice vector, $\mathbf{Q}_m = (\frac{1}{2} + \epsilon, k, \frac{1}{2})$, $\epsilon = 0.006(1)$, and k is an integer. Rather than being concentrated in a resolution limited Bragg peak characteristic of 3D order, the scattering is distributed in reciprocal space. The peak is sharpest in the $\mathbf{c}^*$ direction, wider and incommensurate along $\mathbf{a}^*$, and very broad along $\mathbf{b}^*$. Figure 2(a) also reveals a rod of elastic magnetic scattering along $\mathbf{b}^*$. Energy scans through this magnetic scattering yield an upper limit of $\delta E \lesssim 0.02$ meV on the half width at half maximum of the peak. Based on this information we conclude that on a time scale $\delta t \gtrsim \hbar/\delta E = 2 \times 10^{-10}$ s there is static short range magnetic order in $SrCuO_2$ that can be described as follows. Spins in each $\mathbf{a}$-$\mathbf{c}$ plane are aligned antiferromagnetically with a superposed long wavelength modulation or defect structure along $\mathbf{a}$. Such planes are stacked with a correlation length of order b.

By fitting the data in Fig. 2 to Lorentzians convoluted with the instrumental resolution function, the magnetic correlation lengths in the $\mathbf{a}$-$\mathbf{c}$ plane were determined to be $\xi_a = 60(25)a$ and $\xi_c \gtrsim 200c$. The peak position refined to $\mathbf{Q}_m = (0.506(1), 0.00(1), 0.500(1))$. Note that the incommensurability along $\mathbf{a}^*$ was reproduced in several independent experiments. Moreover, we found an equivalent magnetic satellite from $\tau = (202)$ at $\mathbf{Q} = (1.494(3), 0.00(1), 1.500(1)) \approx \tau - \mathbf{Q}_m$.

The extremely short correlation length along $\mathbf{b}$ suggests analysis of scans in that direction in terms of a Fourier series:

$$\bar{S}^{\alpha\alpha}(\mathbf{Q}) = \frac{\langle S \rangle^2}{3}\left(1 + \frac{1}{N_\parallel}\sum_{j \neq j'} C_{j,j'} \cos \mathbf{Q} \cdot (\mathbf{d}_j - \mathbf{d}_{j'})\right), \tag{1}$$

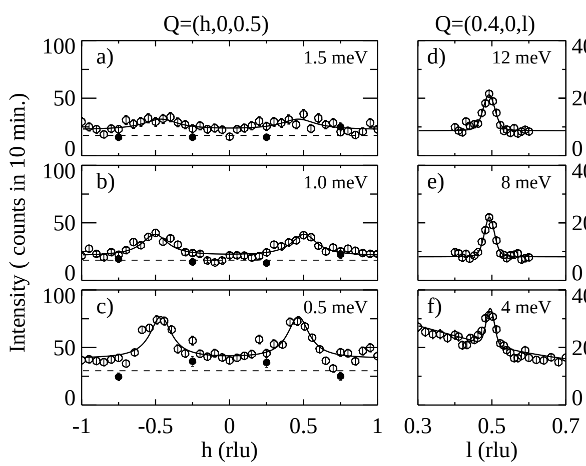

FIG. 1. Wave-vector dependence of inelastic magnetic scattering from $SrCuO_2$. (a)–(c) Scans along $\mathbf{a}^*$, which is perpendicular to the zigzag chains, collected on SPINS at $T = 0.35$ K with $E_f = 5.1$ meV and collimations 80′-80′-240′. (d)–(f) Scans along the chains measured on BT2 at $T = 12.5(5)$ K with $E_f = 14.7$ meV and collimations 60′-60′-80′-120′. Increasing background in (f) comes from the direct beam.

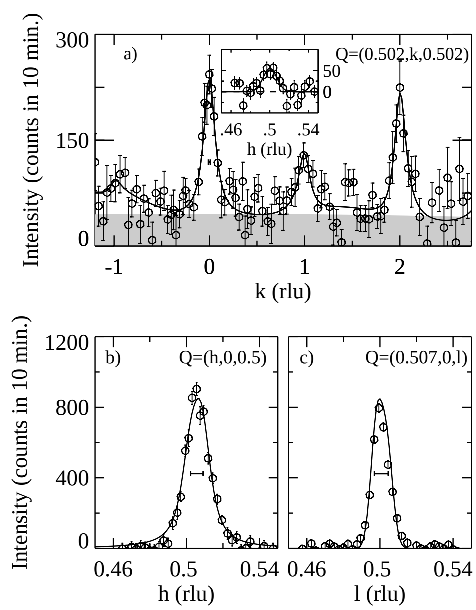

FIG. 2. (a)–(c) Wave-vector dependence of the net elastic magnetic intensity around $\mathbf{Q} \approx (0.5, 0, 0.5)$ at $T = 0.35$ K along $\mathbf{b}^*$, $\mathbf{a}^*$, and $\mathbf{c}^*$ directions, respectively. The background was measured at $T = 8$ K. Horizontal bars show calculated FWHM of the instrument resolution function. (a) BT2 and BT9 measurements with $E_f = 14.7$ meV and collimations 60′-40′-40′-120′. The shaded area shows k-independent "magnetic rod" intensity. The solid line shows Eq. (1) with optimized Fourier coefficients and multiplied by the squared magnetic form factor for Cu^{2+}. The inset shows a scan across the rod at $k = 0.35$. (b), (c) SPINS data with $E_f = 3.7$ meV and collimations 80′-40′-240′. Solid lines are fits to resolution convoluted Lorentzians.

where j, j' index consecutive **a**-**c** spin planes and $C_{j,j'} = (2/N_{\|}) \sum_m \langle S_{\mathbf{d}_{j+2m}} \rangle \langle S_{\mathbf{d}_{j'+2m}} \rangle / \langle S \rangle^2$. We assume that the frozen spin configuration is isotropic in spin space, and that correlations between planes separated by distances of $2b$ and beyond decay exponentially. The line through the data in Fig. 2(a) shows the result of this fit. The correlation length extracted is $\xi_b = 2.2(3)b$. The correlation parameters $C_{jj'}$ are listed in Table I.

As shown in the inset to Fig. 3, $SrCuO_2$ is built from copper bilayers. Equivalent spins within a bilayer are displaced by $\mathbf{d}_1 - \mathbf{d}_0 = (0\delta\frac{1}{2})$ to form zigzag chains. Neighboring bilayers are separated by $\mathbf{d}_2 - \mathbf{d}_0 = (\frac{1}{2}\frac{1}{2}0)$. Table I shows that despite the proximity of planes in a bilayer, correlations between them are weak, pointing to an effective decoupling between the two sides of zigzag chains. Looking beyond a bilayer we see AFM correlations between planes in neighboring bilayers ($C_{0\bar{1}}, C_{03}, C_{0\bar{5}}, C_{07} < 0$) and ferromagnetic correlations between spins in bilayers separated by multiples of **b** ($C_{0\bar{3}}, C_{0\pm4}, C_{05}, C_{0\bar{7}} > 0$). The fit yields a reliable value for the frozen moment at $T = 0.3$ K which is only a fraction of the full moment: $\mu = 0.033(7)\ \mu_B$ per Cu.

The temperature dependence of the squared frozen moment and the in-plane correlation parameters are shown in Fig. 3. Staggered magnetization first appears below $T_{c1} = 5.0(4)$ K. μ^2 initially increases in proportion to $(T_{c1} - T)^{2\beta}$ where $\beta = 0.46(12)$, but below an inflection point at $T_{c2} = 1.5(3)$ K it increases faster before saturating for $T \lesssim 0.5$ K. While ZF μSR does not detect static magnetization until $T \approx 2\ \mathrm{K} \approx T_{c2}$, specific heat and susceptibility data show anomalies close to both T_{c1} and T_{c2} [12]. These data corroborate our evidence for two magnetic phase transitions. Transitions between incommensurate phases are not uncommon for magnets with competing interactions [22] and Figs. 3(b) and 3(c) actually do provide evidence for a modification in the magnetic structure below T_{c2}. The incommensurability, ϵ, and the FWHM along $\mathbf{a}^*$, $\kappa_h = a/(\pi\xi_a)$, decrease by roughly a factor of 2 while peaks in scans along $\mathbf{c}^*$ are resolution limited and near commensurate at all temperatures. Combining our results with those of Matsuda *et al.* [12], we conclude that T_{c1} marks the onset of sublattice magnetization that is static on a time scale $\delta t > 2 \times 10^{-10}$ s, yet fails to produce zero field muon spin relaxation. T_{c2} brings rearrangement of the magnetic structure and magnetization on the μSR time scale.

It is useful to compare our results to those for Sr_2CuO_3 [8]. The critical temperature ($T_N = 5$ K) and intrachain exchange constant ($J = 220$ meV) are similar for the two materials. Nonetheless, the moment in $SrCuO_2$ is almost twice smaller than in Sr_2CuO_3. There is also a qualitative distinction between ordering in these materials; the frozen phase in $SrCuO_2$ is incommensurate along **a**, while Sr_2CuO_3 has commensurate order [8]. Magnetic disorder along **b** also appears to be unique to $SrCuO_2$. Because $\xi_b = 2.2(3)b$ is easily an order of magnitude smaller than

TABLE I. Correlations between spins in **a**-**c** planes displaced by $\mathbf{d}_{j'} - \mathbf{d}_0$ with respect to each other. Coordinates are given in units of orthorhombic cell parameters. $\delta = 0.122$ [11] is the transverse width of a zigzag chain in units of b. Error bars define intervals wherein χ^2 is statistically indistinguishable from its minimum value. "?" indicates correlations whose contributions to Eq. (1) cancel in a $(\frac{1}{2}k\frac{1}{2})$ scan.

j'	$\mathbf{d}_{j'} - \mathbf{d}_0$	$C_{0,j'}$
1	$[0\delta\frac{1}{2}]$	−0.09(6)
−1	$[\frac{1}{2}\delta - \frac{1}{2}\frac{1}{2}]$	−0.09(5)
±2	$[\frac{1}{2} \pm \frac{1}{2}0]$	?
3	$[\frac{1}{2}\frac{1}{2} + \delta\frac{1}{2}]$	−0.19(5)
−3	$[0\delta - 1\frac{1}{2}]$	0.06(5)
±4	$[0 \pm 10]$	0.23(3)
5	$[01 + \delta\frac{1}{2}]$	0.09(4)
−5	$[\frac{1}{2}\delta - \frac{3}{2}\frac{1}{2}]$	−0.18(4)
±6	$[\frac{1}{2} \pm \frac{3}{2}0]$	?
7	$[\frac{1}{2}\frac{3}{2} + \delta\frac{1}{2}]$	−0.11(4)
−7	$[0\delta - 2\frac{1}{2}]$	0.06(4)

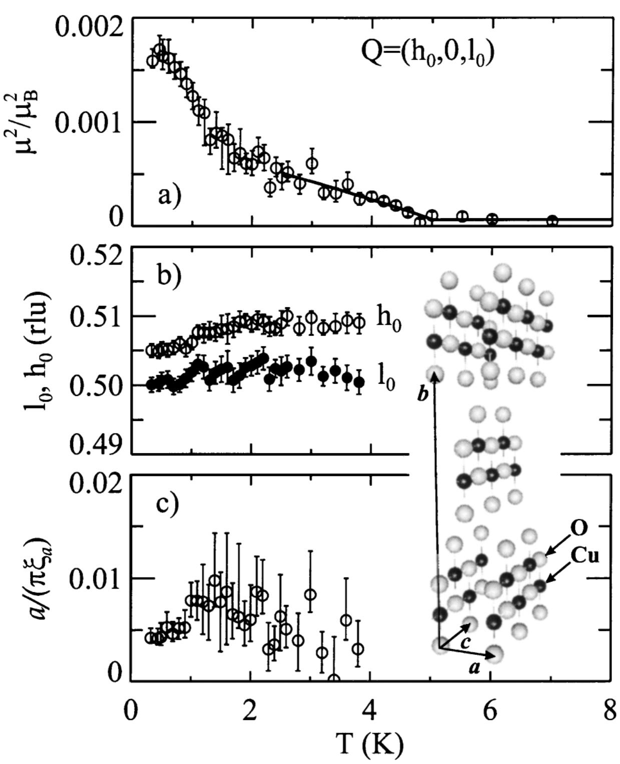

FIG. 3. Temperature dependencies of (a) the frozen sublattice magnetization squared, (b) the in-plane wave vector, $\mathbf{Q} = (h_0.0.l_0)$, and (c) the inverse correlation length along **a**. Data derived from h and l scans through the $(\frac{1}{2} + \epsilon 0\frac{1}{2})$ elastic magnetic peak on SPINS using $E_f = 4.47$ meV and collimations 80′-80′-240′. The frozen moment in (a) is within error bars of our global average. Inset shows copper and oxygen atoms in the $SrCuO_2$ crystal.

the average defect spacing in our sample, we conclude that the low T magnetic state of $SrCuO_2$ is either intrinsically disordered or displays an extreme sensitivity to low levels of quenched disorder. We shall argue that highly frustrated intra- and inter-zigzag-chain interactions are central to understanding these differences between Sr_2CuO_3 and $SrCuO_2$, and the anisotropic frozen state in general.

The main contribution to inter-zigzag-chain interactions along **a** comes from weak superexchange along Cu-O-O-Cu paths with two $\approx 90°$ bonds. For each spin there are 12 such equivalent Cu-O-O-Cu paths to neighbors in the same **a**-**c** plane. Four connect it to nearest neighbors along **a**, denote the corresponding exchange constant $J_a' > 0$, and one to each next nearest neighbor in diagonal $[1, 0, \pm 1]$ directions, $J_a'' > 0$. As a consequence we expect that $J_a'' \sim J_a'/4$ corresponding to a highly frustrated point for this lattice. Similar interactions exist in the $[1, \delta, \pm\frac{1}{2}]$ directions between nearest neighbors in adjacent **a**-**c** planes. In fact, it is evident that these interactions as well as the interbilayer interactions all share the same frustrating zigzag geometry and cancel at the mean-field level. Experimental evidence for competing interactions in $SrCuO_2$ lies in the incommensurability of the magnetic peaks along the $\mathbf{a}^*$ direction. We note that the shift of the magnetic peak along $\mathbf{a}^*$ equals its FWHM not only at the lowest T but also as a function of $T \lesssim T_{c2}$. This indicates that we are dealing not with a periodic modulation superimposed on otherwise AFM **a**-**c** planes but a disordered or even random sequence of *frozen* stripe defects induced by competing interactions.

Recent theoretical studies [6,23] have established that coupled $S = 1/2$ chain systems can remain disordered at $T = 0$ if interchain interactions are sufficiently frustrated. In the quasi-two-dimensional case, which given the small value of ξ_b may be a good first approximation for $SrCuO_2$, disorder at $T = 0$ could result from *instanton* topological defects created through quantum tunneling [23]. For *half-integer* or *odd* integer spin systems the disordered ground state is predicted to be degenerate and gapless, while *even* integer spin systems should be gapfull. Our experimental results support a gapless phase for $S = 1/2$.

For $T > 0$ topological disorder is enhanced through thermal creation of defects. In the coupled $S = 1/2$ chain system we expect these defects to be strongly anisotropic, taking the form of stripes extending along **c** between bands of phase shifted AFM domains. For order to develop in a stack of **a**-**c** planes, stripe defects in neighboring planes must move into registry. However, residual interactions favoring such order could be exceedingly weak or cancel at the mean field level. Thus it is plausible that pinning or intrinsically slow dynamics of stripe defects might lead to a static disordered state, i.e., *spin freezing,* instead of LRO.

In summary, we have found an anisotropic spatially disordered spin configuration among interacting zigzag spin-$1/2$ chains in $SrCuO_2$. The magnetic correlation length along the short direction of the zigzag chain is far less than any impurity spacing. Highly frustrated interactions both within the zigzag spin-$1/2$ chains and between chains, as well as slow dynamics and pinning of order-destroying stripe defects are likely reasons that $SrCuO_2$ behaves differently from the closely related linear chain system Sr_2CuO_3. Previous theoretical work on coupled $S = 1/2$ chains has shown the possibility of an intrinsic disordered phase [6,21,23]. Given our data it would be interesting to further explore this possibility with competing interactions of the specific type found in $SrCuO_2$.

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[1] M. Steiner, J. Villain, and C. G. Windsor, Adv. Phys. **25**, 87 (1976).
[2] L. J. DeJongh and A. R. Miedema, Adv. Phys. **23**, 1 (1974).
[3] A. P. Ramirez, Annu. Rev. Mater. Sci. **24**, 453 (1994).
[4] G. Aeppli and C. Broholm, in *Handbook on the Physics and Chemistry of Rare Earths* (Elsevier, New York, 1994), Vol. 19, Chap. 131, pp. 123–175.
[5] D. Scalapino, J. Imry, and P. Pincus, Phys. Rev. B **11**, 2042 (1975).
[6] I. Affleck, M. Gelfand, and R. P. Singh, J. Phys. A **27**, 7313 (1994); I. Affleck and B. I. Halperin, J. Phys. A **29**, 2627 (1996).
[7] H. J. Schulz, Phys. Rev. Lett. **77**, 2790 (1996).
[8] K. M. Kojima *et al.,* Phys. Rev. Lett. **78**, 1787 (1997).
[9] K. Ishida *et al.,* Phys. Rev. B **53**, 2827 (1996).
[10] M. Matsuda and K. Katsumata, J. Magn. Magn. Mater. **140–145**, 1671 (1995).
[11] Chr. L. Teske and Hk. Müller-Buschbaum, Z. Anorg. Allg. Chem. **371**, 325 (1969).
[12] M. Matsuda *et al.,* Phys. Rev. B **55**, R11 953 (1997).
[13] N. Motoyama *et al.,* Phys. Rev. Lett. **76**, 3212 (1996).
[14] M. Tanaka *et al.,* Physica (Amsterdam) **261C**, 309 (1996).
[15] H. Ohta *et al.,* J. Phys. Soc. Jpn. **61**, 3370 (1992).
[16] S. Gopalan *et al.,* Phys. Rev. B **49**, 8901 (1994); E. Dagotto and T. M. Rice, Science **271**, 618 (1996).
[17] F. D. M. Haldane, Phys. Rev. B **25**, 4925 (1982).
[18] D. Allen and D. Sénéchal, Phys. Rev. B **55**, 299 (1997).
[19] S. R. White and I. Affleck, Phys. Rev. B **54**, 9862 (1996).
[20] R. Chitra *et al.,* Phys. Rev. B **52**, 6581 (1995).
[21] B. Normand *et al.,* Phys. Rev. B **56**, 5736 (1997).
[22] O. Vogt and K. Mattenberger, in *Handbook of the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneidner, Jr. and L. Eyring (Elsevier, Amsterdam, 1993), Vol. 17.
[23] F. D. M. Haldane, Phys. Rev. Lett. **61**, 1029 (1988).