Structural Evidence for a Spin Peierls Ground State in the Quasi-One-Dimensional Compound $CuGeO_3$

J. P. Pouget,[1] L. P. Regnault,[2] M. Ain,[3] B. Hennion,[3] J. P. Renard,[4] P. Veillet,[4] G. Dhalenne,[5] and A. Revcolevschi[5]
[1]*Laboratoire de Physique des Solides, Université de Paris Sud, Bâtiment 510, 91405 Orsay, France*
[2]*Commissariat à l'Energie Atomique, Département de Recherche Fondamentale sur la Matière Condensée SPSMS/MDN, Centre d'Etudes Nucléaires, 38054 Grenoble Cedex 9, France*
[3]*Laboratoire Léon Brillouin, Centre d'Etudes Nucléaires Saclay, 91191 Gif Sur Yvette, France*
[4]*Institut d'Electronique Fondamentale, Université de Paris Sud, Bâtiment 220, 91405 Orsay, France*
[5]*Laboratoire de Chimie des Solides, Université de Paris Sud, Bâtiment 414, 91405 Orsay, France*
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X-ray and elastic neutron scattering measurements reveal that the quasi-one-dimensional $Cu^{2+}(S = 1/2)$ antiferromagnet $CuGeO_3$ undergoes a second order structural transition towards a dimerized ground state at the same temperature, $T_{SP} = 14$ K, at which the magnetic susceptibility abruptly decreases. X-ray diffuse scattering measurements show that the critical fluctuations are quasi one dimensional on a large temperature range above T_{SP}. These results show unambiguously that $CuGeO_3$ undergoes a true spin-Peierls transition triggered by the magnetic chains.

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In recent years it was found that low-dimensional materials exhibit many original phenomena, such as, in metals, the electron-phonon coupling driven Peierls instability and, in magnetic systems, quantum effects and nonlinear excitations [1]. In these magnetic materials special attention has been devoted to chains of quantum spins with antiferromagnetic (AF) interactions. In particular it has been conjectured [2] and observed [1,3] that the excitation spectrum of uniform AF chains with half integer spin values is gapless unlike the case of AF chains with integer spin values which display a gap. However, in presence of an important magnetoelastic coupling a gap can separate a singlet ground state from the continuum of excited states if the $S = 1/2$ AF chains dimerize [4]. Such a dimerization can be achieved by a structural phase transition. When the lattice instability is driven by the AF chain itself this transition, called spin Peierls (SP), is the magnetic analog of the Peierls transition observed in one-dimensional (1D) conductors [5,6]. While many 1D conductors undergo a Peierls transition, there are very few examples of SP transitions in 1D magnetic systems. Nearly all of them are found among the organic compounds such as TTF-CuBDT [7] and $MEM(TCNQ)_2$ [8] or the cation radical salts derived of the tetramethyltetrathiafulvalene (TMTTF) donor [9]. However, only the latter class of compounds exhibits a lattice instability with the quasi-1D anisotropy of the magnetic chain array [10]. Very recently it was shown that the magnetic susceptibility of the inorganic insulator $CuGeO_3$ exhibits below $T_{SP} = 14$ K the characteristic drop [11] and the magnetic field dependence [12] expected for a SP transition.

The cuprate $CuGeO_3$ has an anisotropic structure made of Cu-O and Ge-O chains running along the c direction. The AF chains consist of $S = 1/2$ Cu^{2+} ions located at the center of edge sharing squares of oxygen atoms. These chains are separated by rigid chains of GeO_4 tetrahedra. $CuGeO_3$ crystallizes in the orthorhombic *Pbmm* [13] space group with two formula units per unit cell related by the b glide plane.

In this Letter we report combined x-ray, neutron, and magnetic measurements which directly show that the cuprate $CuGeO_3$ undergoes a second order structural transition at the same temperature $T_{SP} = 14$ K at which the spin susceptibility drops. These findings together with the observation of a doubling of lattice periodicity in the AF chain direction prove unambiguously that a SP ground state is really stabilized in this quasi-1D inorganic material.

The $CuGeO_3$ single crystals used in this study were grown from the melt by a floating zone method associated with an image furnace [14]. Such a crucible free technique is particularly well adapted to the growth of oxide single crystals [15].

The magnetic susceptibility of a single crystal of about 12 mm^3, from which was cleaved the thin slab used for the x-ray measurements, has been measured using a home-made SQUID magnetometer operating in the temperature range 2–300 K. The experiments were performed in a field of 1 kOe for different orientations parallel to the three crystal axes a, b, and c. Our results are fully consistent with those previously reported [11]. For all field orientations, the susceptibility exhibits a flat maximum around 60 K and an abrupt decrease below 14.5 K indicating the occurrence of a nonmagnetic ground state (Fig. 1). Accurate measurements of $d\chi_b/dT$ near the transition temperature (see inset of Fig. 1) show a lambda type behavior with a maximum at 14.3 ± 0.1 K. The jump of $d\chi_b/dT$ occurs in a relatively narrow temperature range $\Delta T \approx 0.2$ K around 14.4 K without thermal hysteresis.

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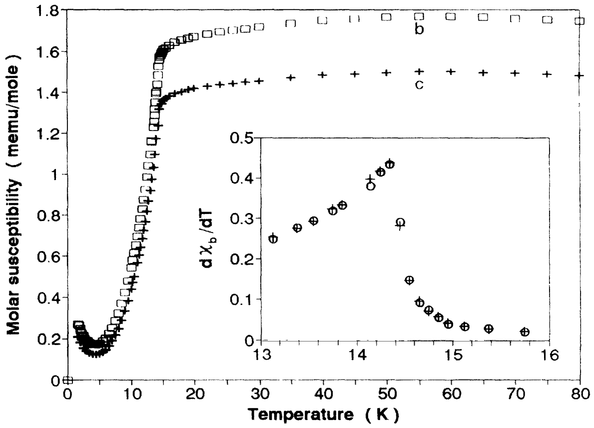

FIG. 1. Molar magnetic susceptibility of $CuGeO_3$ in 10^{-3} cgs emu versus temperature for field orientations along b and c. The inset shows $d\chi_b/dt$ in 10^{-3} cgs emu per K for increasing (crosses) and decreasing (circles) temperatures.

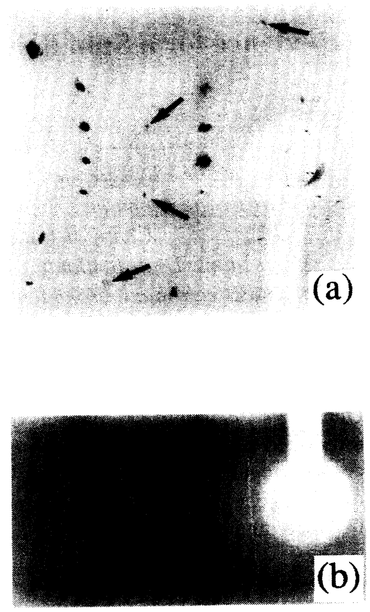

FIG. 2. X-ray patterns from $CuGeO_3$ taken at 10.6 K (a) and 19.5 K (b) and showing (black arrows) in (a) the satellite reflections and in (b) their broadening into an anisotropic diffuse scattering. The b and c crystallographic directions are vertical and horizontal, respectively.

The x-ray study was carried out with the so-called fixed-film, fixed-crystal method [16] which allows performing a large survey of the reciprocal space. The sample ($0.03 \times 4 \times 3$ mm^3) was mounted in a helium filled container, where the temperature could be precisely regulated (± 0.05 K) and measured. Temperatures between 290 and 10 K were achieved on the cold finger of a cryocooler. The Cu $K\alpha(\lambda = 1.542$ Å) radiation was selected after (002) reflection on a doubly bent pyrolithic graphite (PG) monochromator. Several x-ray patterns were taken with the x-ray generator operating at 15 kV to avoid the $\lambda/2$ contamination from the continuous spectrum of the x-ray source. Figure 2(a) shows such an x-ray pattern taken at 10.6 K in an orientation where the (b^*, c^*) reciprocal plane is directly projected on the film. Several weak and sharp satellite reflections located midway between successive layers of main Bragg reflections perpendicular to the c direction [arrows in Fig. 2(a)] can be clearly distinguished. Only satellite reflections with odd integer b^* components have been detected. With the (a^*, b^*) projection of the reciprocal space on the x-ray film, the satellite reflections were found midway between layers of main Bragg reflections perpendicular to the a direction. The x-ray satellite can be indexed by the reduced wave vector $\mathbf{k}_{SP} = (1/2,$"1"$,1/2)$, where "1" accounts for the observation of odd integer b^* components reflections.

The wave vector $\mathbf{k}_{SP}$ has been further confirmed by a neutron scattering investigation performed on the three-axis spectrometer 1 T installed at the reactor Orphée of the LLB. In this experiment, the neutron wave vector was fixed at 2.662 Å^{-1} as a given by a vertically bent PG monochromator in (002) reflection whereas the PG analyzer was set to its elastic position [energy resolution of about 1 meV (FWHM)]. Two PG filters were used in order to reduce the second order contamination. The sample, of about 0.3 cm^3, was oriented in all cases with the c axis lying in the equatorial plane and tilted in such a manner to survey the $(1/2,3,1/2)$, $(1/2,5,1/2)$, and $(1/2,3,3/2)$ satellite reflections. The two former satellite reflections were the strongest whereas the latter one is 1 order of magnitude smaller in intensity. The thermal dependence of the satellite intensity was measured (see Fig. 3) through elastic scans across the $(1/2,3,1/2)$ reflection (a typical transverse scan is shown in the inset). Upon heating above about 9 K this intensity drops rapidly and vanishes at $T_{SP} = 14.3 \pm 0.2$ K. No hysteresis was observed between the cooling and heating curves. The same continuous drop was observed from the $(1/2,1,3/2)$ x-ray satellite reflection, allowing us to determine a critical temperature $T_{SP} 14.0 \pm 0.2$ K. Within experimental errors these T_{SP} coincide with the temperature at which $d\chi_b/dt$ exhibits a maximum.

No elastic critical fluctuations are detected above T_{SP} by neutron scattering (Fig. 3). However, sizable critical fluctuations, probably of inelastic origin, are detected until about 40 K by x-ray diffuse scattering. In this experiment the $\mathbf{k}_{SP}$ satellite reflections were found to spread into a diffuse scattering which broadens very rapidly in an anisotropic manner upon heating above T_{SP}, as illustrated in Fig. 2(b) by the x-ray pattern taken at 19.5 K. The correlation lengths, ξ, of the critical fluctuations were determined from the reciprocal of the half width at half maximum (corrected from the experimental resolution) of the diffuse scattering. Figure 4 gives the thermal dependence of ξ_c^{-1} in the chain direction. Within experimental

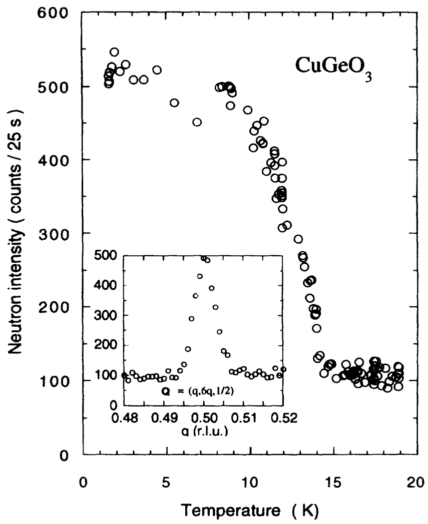

FIG. 3. Temperature dependence of the (1/2, 3, 1/2) satellite reflection measured upon cooling. A transverse scan $(q, 6q, 1/2)$ through this satellite reflection at 1.4 K is shown in the inset.

errors ξ_c^{-1} behaves as $\sqrt{T - T_{SP}}$ with $T_{SP} = 14.1 \pm 0.2$ K (solid line of Fig. 4). ξ_c decreases very rapidly upon heating [typically $\xi_c = 12$ Å (i.e., $4 \times c$) at 19.5 K and $\xi_c \sim 4.5$ Å at 40 K]. The anisotropy ratio of the correlation lengths determined in the vicinity of T_{SP} is $\xi_c : \xi_b : \xi_a \sim 5.5 : 1.8 : 1$. It shows that above about 15 K (where $\xi_a < a = 4.8$ Å) and above about 19 K (where $\xi_b < b/2 = 4.25$ Å) the pretransitional fluctuations are successively decoupled along the a and b directions.

Our study shows unambiguously that the rapid drop of spin susceptibility (Fig. 1) observed below T_{SP}, and associated with the opening of a gap in the magnetic

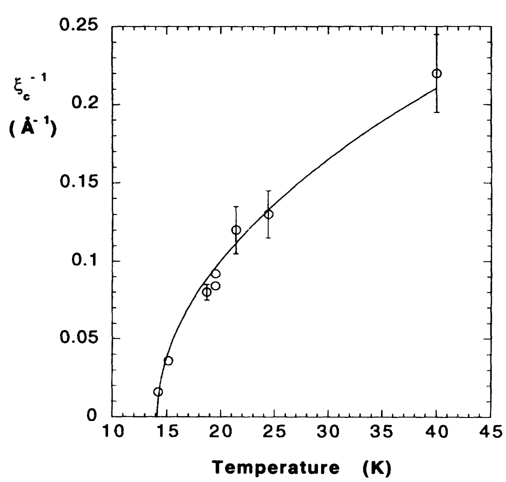

FIG. 4. Inverse of the correlation length of the critical fluctuations at $\mathbf{k}_{SP}$ in the c direction, ξ_c^{-1}, as a function of the temperature. The solid line is the best fit of these data to a $\sqrt{T - T_{SP}}$ law.

excitation spectrum, as recently observed by inelastic neutron scattering measurements [17, 18], corresponds to a progressive dimerization of the $CuGeO_3$ chain structure. The thermal behavior of the satellite intensity (Fig. 3) and of the critical fluctuations (Fig. 4) show that this transition is very likely of second order. All these features are expected for a SP transition.

Both the x-ray and neutron investigations show that the satellite intensity at saturation amounts to about 10^{-3} times the intensity of an average main Bragg reflection of $CuGeO_3$. This relative intensity is comparable to that of the (0, 0, 1/2) satellite reflections observed below the SP transition of MEM-(TCNQ) [19] and for which a structural refinement [20] gives an amplitude of dimerization of $\sim$0.01 Å.

The $1/2\, a^*$ and odd b^* components of $\mathbf{k}_{SP}$ can be simply understood assuming an out-of-phase ordering of the lattice distortions between first neighboring magnetic chains whose Cu atoms dominate the x-ray scattering. A similar out-of-phase order of SP distortions occurs in the organic compounds $(TMTTF)_2PF_6$ [21] and $(BCPTTF)_2AsF_6$ [10] where, because of the presence of a single chain per unit cell, the SP critical wave vector is $\mathbf{k}_{SP} = (1/2, 1/2, 1/2)$. Such an out-of-phase order minimizes the interchain Coulomb repulsions induced by the dimerization [22]. The interchain interactions could also induce the spontaneous strain along b which accompanies the SP distortion of $CuGeO_3$ [23].

Recently another neutron scattering investigation has claimed [24] to have detected below 3.8 K SP satellite reflections at the reduced wave vector (0, 1, 1/2), which differs from our $\mathbf{k}_{SP}$ by its a^* component. We have been unable to detect by neutron scattering such reflections in our $CuGeO_3$ sample which presents a well defined SP transition. However, these reflections were observed by neutron diffraction, and found to have a magnetic origin, in other samples where the SP transition could not be identified by magnetic measurements.

The quasi-1D x-ray fluctuations observed above 19 K shows that the structural transition is triggered by the magnetic chains as expected for a true SP transition like those previously observed in the organic slats $(TMTTF)_2X$ [21, 25] and $(BCPTTF)_2X$ [10] (X = PF_6 and AsF_6). In this respect, $CuGeO_3$ contrasts with TTF-CuBDT [26] and $MEM(TNCQ)_2$ [10, 19] which exhibit quasi-isotropic critical fluctuations.

The critical structural fluctuations induce a local dimerization on ξ_c and thus a spin pairing on this length scale. The observation of dimerized domains until at least 40 K in $CuGeO_3$ could explain the drop of spin susceptibility occurring in that temperature range (see Fig. 1 and Ref. [11]). Here again $CuGeO_3$ resembles $(TMTTF)_2X$ [27] $(BCPTTF)_2X$ [10] where the rate of decrease of spin susceptibility is enhanced by the onset of critical fluctuations. But $CuGeO_3$ contrasts with $MEM(TCNQ)_2$ [8] and TTF-CuBDT [7] where the spin susceptibility, which follows the Bonner and Fisher dependence of the uniform $S = 1/2$ AF Heisenberg chain down to T_{SP}, is apparently insensitive to the growth of structural critical fluctuations.

By analogy with the Peierls transition, where the structural fluctuations create a pseudo-gap in the one electron density of states [28], the SP fluctuations of $CuGeO_3$ will develop a pseudogap in the magnetic excitation spectrum. The formation of such a pseudogap has been detected by inelastic neutron scattering [18] and by two magnon Raman scattering below about 50 K [29]. Theoretical treatments going beyond the mean field treatment of the lattice instability [30] are thus required to describe these features. Additional neutron studies will be essential to determine the critical dynamics of the structural fluctuations and its coupling to the spin degrees of freedom.

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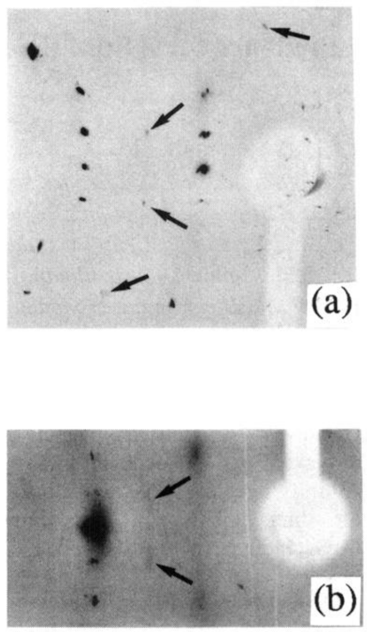

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