PAPER

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A detailed study of the magnetic phase transition in $CuCrO_2$

G Ehlers[1], A A Podlesnyak[1], M Frontzek[2], R S Freitas[3], L Ghivelder[4], J S Gardner[5,6,7], S V Shiryaev[8] and S Barilo[8]

[1] Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6475, USA
[2] Laboratory for Neutron Scattering, Paul Scherrer Institute, CH-5232 Villigen, Switzerland
[3] Instituto de Física, Universidade de São Paulo, CP 66318, 05314-970 São Paulo, SP, Brazil
[4] Instituto de Física, Universidade Federal do Rio de Janeiro, CP 68528, 21941-972 Rio de Janeiro, RJ, Brazil
[5] Physics Department, Indiana University, Bloomington, IN 47408, USA
[6] NCNR, NIST, Gaithersburg, MD 20899-6102, USA
[7] Neutron Group, National Synchrotron Radiation Research Center, Hsinchu, 30077, Taiwan
[8] Institute of Solid State and Semiconductor Physics, Minsk 220 072, Belarus

E-mail: ehlersg@ornl.gov

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Abstract
The phase transition in $CuCrO_2$ to an ordered magnetic state is studied with bulk measurements and elastic and inelastic neutron scattering techniques. The reported onset of spontaneous electric polarization at $T = 23.5$ K coincides with the appearance, on cooling, of elastic magnetic scattering. At higher temperatures long range magnetic correlations gradually develop but they are dynamic. The ground state is characterized by three-dimensional long range magnetic ordering but along the c direction the correlation length remains limited to ~200 Å.

(Some figures may appear in colour only in the online journal)

1. Introduction

The basic paramagnetic properties of $CuCrO_2$ and related systems with the delafossite structure were established many years ago with measurements of mean-field parameters such as the Curie–Weiss temperature, $\theta_{CW} \sim -200$ K, and the effective paramagnetic Cr^{+3} moment, $\mu_{eff} \sim 3.7$–3.9 μ_B [1, 2]. Later, Kadowaki *et al* [3] were the first to publish neutron scattering results on this material. Using a powder sample they found magnetic ordering with a propagation vector $(1/3, 1/3, 0)$ below a Néel temperature of $T_N \sim 25 \pm 0.5$ K. Magnetic powder diffraction peaks appeared broadened, and spatial magnetic correlations were also found in the paramagnetic phase above T_N. Therefore the authors concluded that the magnetic order was two-dimensional (with a short correlation length along the c direction) and that the ordered spins were confined to the ac plane and made a '120° structure' in that plane. The sizable degree of magnetic frustration, as indicated by the $|\theta_{CW}/T_N| \sim 8$ ratio, and the discovery that $CuCrO_2$ is multiferroic [4] are the main reasons why more detailed studies have been published in recent years [5–15].

Neutron diffraction experiments [9–11] revealed that magnetic order in $CuCrO_2$ is in the form of an incommensurate proper-screw spiral, with a propagation vector of the moments of $(\tau, \tau, 0)$, where $\tau = 0.329$, very close to the value originally assigned by Kadowaki *et al* [3]. Individual spins rotate in the $(HH0)$ plane. Consequently, it is generally agreed that the microscopic origin for ferroelectric polarization can be explained following Arima's original idea of d–p hybridization due to spin–orbit coupling, because the spiral does not propagate along the threefold symmetry axis (the c axis) [16].

When flux-grown single-crystal specimens of $CuCrO_2$ became available, two phase transitions at $T_{N1} = 23.6$ K and $T_{N2} = 24.2$ K were reported for the first time by Kimura

et al [6]. Ferroelectric polarization was found below the lower transition, $T_{N1} = 23.6$ K. These transitions were observed as two separate peaks in the specific heat, and were reproduced for different samples, but until now not by other groups (see below). Kimura *et al* speculated that the intermediate phase between the two transition temperatures features a collinear spin structure, which would not lead to macroscopic electric polarization.

In two single-crystal diffraction studies with polarized neutrons [10, 11] the Arima model was confirmed, demonstrating how the incommensurate proper-screw magnetic structure of $CuCrO_2$ induces electric polarization. In these studies the c axis was perpendicular to the scattering plane, thus only ($HK0$) reflections were measured and the question of long or short range order along c was not addressed. A neutron powder diffraction study by Poienar *et al* [9] concluded, based on an observed broadening of magnetic peaks in the ordered phase, that the magnetic correlations along the c axis are of short range, not exceeding 200 Å. A later measurement by the same group of the spin dynamics, using inelastic neutron scattering on a small crystal [12], confirmed that the magnetic interactions are of 'essentially two-dimensional character', based on the observation of weak dispersion along the c direction.

A general consensus has not been reached to date about how exactly the transition to an ordered state unfolds in $CuCrO_2$, and in particular whether there are two successive phase transitions or only one. Looking over the published literature, subtle differences in the sample quality/makeup, depending on the preparation method, seem to cause inconsistencies in the measurements. For example, Poienar *et al* published two studies with remarkably different specific heat curves [9, 15]. In an earlier study using powder samples prepared by a solid state reaction in air [9], a well developed single peak was observed in specific heat at $T = 24$ K. Later, measurements of single-crystal specimens [15] grown by a flux technique similar to ours [14] and that of [6] produced a basically featureless specific heat curve, which barely showed even a single local maximum around $T \sim 23$ K, and which was ∼20% lower at the transition. The same measurement apparatus and protocol were used in these two studies. In their conclusions the authors make the point that the sample properties depend on the nature and density of defects, which in turn depend critically on the details of the sample growing process [15]. Okuda *et al* [5] published a measurement of a powder sample prepared by a solid state reaction which showed a single well developed peak of the specific heat at 24.2 K.

In this paper we take a closer look at the phase transition in $CuCrO_2$, by re-measuring the specific heat and dielectric constant of single-crystal specimens, and by means of high resolution neutron spectroscopy. Another question we address is about the influence of a short correlation length along the c direction on the development of the electric polarization. Arima's explanation requires incommensurate magnetic order with a propagation vector perpendicular to the c axis, but does not require long range correlations along that axis. Incommensurate spirals in the ($HH0$) plane suffice, they do not have to be 'in phase' with each other along the threefold axis. Our own previous study showed that spatial magnetic correlations do already exist in the ab plane *above* $T_{N1} = 23.6$ K with the same propagation vector [14]. Since the $\boldsymbol{k}$ vector is the same above and below T_{N1}, it is not intuitive to assume, as Kimura *et al* did, that the spin structure in the plane is collinear above T_{N1}. Our conclusions will provide a simple alternative explanation of why electric polarization was observed only below $T_{N1} = 23.6$ K by Kimura *et al* [6].

2. Experimental methods

Sample preparation and characterization were reported elsewhere [14]. Dielectric measurements were made with an AH 2700A ultra-precision capacitance bridge operating at 1 kHz. The temperature and field dependent dielectric measurements were made using a Quantum Design PPMS commercial cryostat, and the same equipment was used for high resolution specific heat measurements. For the dielectric measurements electrodes made with silver paint were used in a 240 μm thick sample along the c direction and the magnetic field was applied parallel to the ab plane. Dielectric measurements along the c direction in the presence of a magnetic field are being reported here for the first time.

Specific heat data were collected with careful control of the measurement protocol. The goal was to see how much the result may be affected by the choice of the amount of heat applied on the sample from point to point, and in particular whether there are truly two maxima which can be perceived as one if the temperature resolution of the measurement is not fine enough. It was found that two maxima in the specific heat could be resolved within less than 1 K when the sample temperature was raised by less than 1% from point to point.

An array of co-aligned crystals, with a total mass of about ∼0.6 g, was used in the neutron scattering experiments described here. Elastic scattering was recorded at the cold neutron chopper spectrometer (CNCS) at the spallation neutron source (SNS) in Oak Ridge [17]. For this measurement a neutron energy of $E_i = 3.3$ meV was used ($\lambda_i = 5.0$ Å). The energy was chosen to provide good enough Q resolution to address the question of short magnetic correlation length raised earlier [3, 9], while giving still enough coverage of reciprocal space to access a fair number of magnetic peaks. This measurement used optimized conditions to analyze the magnetic correlation length through the width of the magnetic Bragg peaks, in contrast to the one published earlier as figure 1 in [14], which was obtained using 12 meV neutrons resulting in coarser Q resolution. The crystal array was orientated with the (HHL) plane in the horizontal scattering plane. The sample was rotated during the measurement around the vertical axis. The instrument was operated in the 'high flux' setting with an energy resolution at the elastic line of 0.5 meV full width at half maximum (fwhm). The Q resolution translated to ∼0.17 fwhm relative lattice units (r.l.u.) in the relevant crystallographic direction. A reference measurement at higher temperature, ∼200 K, was used to correct for instrument background.

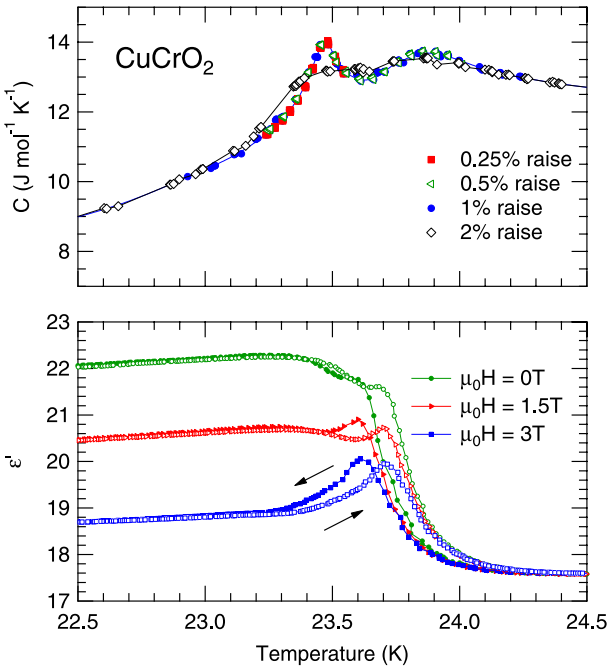

Figure 1. Measurements of the specific heat (upper panel) at increasing temperature and the field dependent real part of the dielectric constant (lower panel) at both increasing and decreasing temperature, showing hysteresis. The various measurements of the specific heat differ in how much heat was applied for each individual point—no difference in the peak amplitude and position can be observed for heat pulses below 1%.

Neutron spin echo (NSE) measurements were performed at the NG5 instrument at the NIST Center for Neutron Research (NCNR), National Institute of Standards and Technology [18], using the same sample. A neutron wavelength $\lambda_i = 6.0$ Å was used and the instrument aligned to detect scattering at the incommensurate wavevector $Q = (\tau, \tau, 0)$, $\tau = 0.329$ r.l.u., where the first magnetic Bragg peak occurs. In the chosen instrument setting, a Fourier time range of $\sim 10^{-2}$ to $\sim 10^{+1}$ ns could be accessed, which corresponds to an energy resolution better than ~ 0.1 μeV [19].

3. Experimental results

Bulk measurements can be seen in figure 1. The top panel shows the temperature dependent specific heat, the lower panel shows the real part of the dielectric constant at various applied magnetic fields.

Our measurement of the specific heat shows two separate maxima in a very narrow temperature interval, at $T = 23.5$ and 23.9 K. The higher temperature peak appears to be somewhat broader than the lower temperature peak. In order to clearly detect both peaks in the specific heat, a fine temperature control in the measurement protocol is needed. The data in the top panel of figure 1 were measured with a fine temperature interval, $\Delta T \approx 0.05$ K, close to the phase transition. Care must also be taken in the amount of heat supplied to the sample during the measurement. We find that if the sample temperature is raised by more than 1% from point to point during the heat capacity measurement, both peaks merge into a single broad maximum around 23.7 K. Only if the temperature rise is limited to 1% or less between points are the two maxima clearly resolved.

Even though we have thus demonstrated that the measurement protocol can make a difference, by looking at the various published specific heat data [5, 6, 9, 15] it should be concluded that the most likely reason for the discrepancies lies in the sample preparation. Polycrystalline samples prepared by a solid state reaction of the oxides in air at high temperature will show one peak whereas flux-grown crystals will show two peaks. Whether the sample is single-crystalline or polycrystalline, on the other hand, should not matter because no magnetic field is present. The one study that disagrees with this conclusion is that of [15], but here the specific heat in the transition region is overall much lower, around 12 J K^{-1} mol^{-1}, while all other studies consistently show $\sim$14 J K^{-1} mol^{-1}. The stated peak temperatures do agree within the variation one should allow for thermometer calibration and thermal contact with the apparatus during the measurements.

Both in this work and in the study of Kimura *et al* [6], the higher temperature peak of the specific heat is *broader*. Below we will argue that this is a relevant observation, reflecting a *gradual* building up of magnetic correlations on cooling. First of all we note that a broad 'hump' in specific heat commonly occurs in geometrically frustrated magnets that do not show—due to frustration effects—a true thermodynamic phase transition to an ordered phase [20]. One would certainly expect some degree of geometric frustration in $CuCrO_2$, as indicated by the $|\theta_{CW}/T_N| \sim 8$ ratio. However, the occurrence of two maxima in the specific heat of an anisotropic Heisenberg antiferromagnet, near the transition from a correlated two-dimensional regime to a fully three-dimensionally ordered state, has also been predicted in Monte Carlo simulations [21] which showed that the expected ordering transition peak may be accompanied by a broader 'precursor' peak at higher temperature reflecting two-dimensional (planar) correlations that exist above the transition.

Turning to the measurements of the dielectric constant, these are shown in the lower panel of figure 1. The steepest slope of the dielectric constant is at $T = 23.7$ K (cooling) and at $T = 23.8$ K (warming), respectively. The observed hysteresis in this measurement can be interpreted as a clear indication of the first order nature of the transition. The steepest slope is exactly in the 'valley' between the two peaks of the specific heat. Below that temperature, there is 'structure' in the measured curve and saturation is reached below 23.3 K. The saturation level decreases by $\sim$15% when the applied magnetic field is increased to 3 T. Since the measurement of the dielectric constant is along the crystallographic c direction and the polarization is limited to the *ab* plane, the magneto-electric coupling response to an applied magnetic field is probed without the need to consider domain effects. Regarding the magnetic structure, a magnetic field below the flop field (see [11]) of 5.3 T applied in the *ab* plane has two effects. First, the domains will be re-populated in respect of their spiral axes to the magnetic

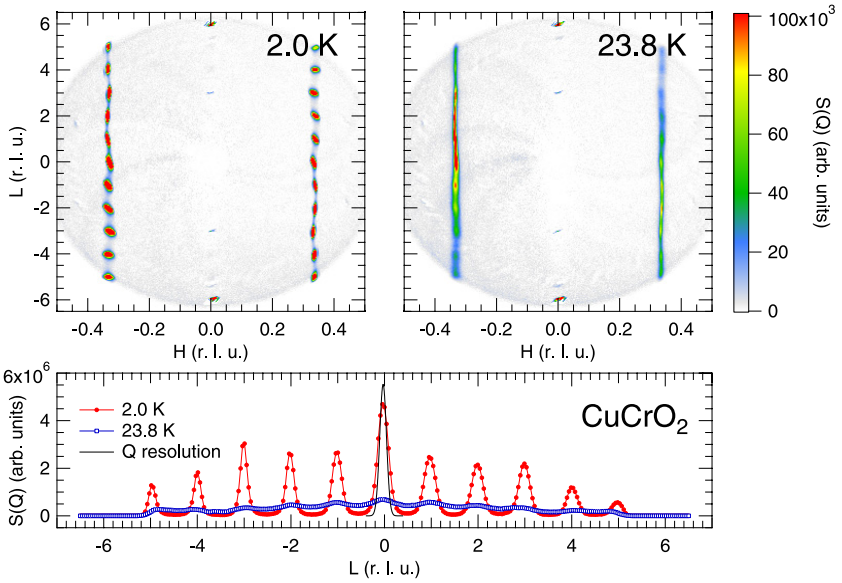

Figure 2. Elastic scattering measured at the CNCS at two temperatures. The lower panel shows a cut through the scattering plane at $H = -0.329$ r.l.u. The instrumental Q resolution is indicated for the central peak at $L = 0$ in the lower panel.

field vector. This will have no effect on the dielectric function measured along the c direction. Second, the magnetic spirals will be slightly deformed with an incline of the magnetic moments towards the magnetic field direction. This reduces the dielectric response and therefore indicates the strong correlation of the antiferromagnetic spiral to the spontaneous polarization.

Elastic neutron scattering results are summarized in figure 2. At low temperature, $T \sim 2$ K, a series of Bragg peaks running along the L direction confirms true three-dimensional long range magnetic order. The Bragg peaks do not all have the same shape, which is due to the instrumental resolution [17]. As the sample is rotated, which itself is a linear array of small crystals, it intercepts the beam in a non-uniform way which leads to a dependence of the effective Q resolution on both sample rotation angle and scattering angle. As a previous study of the temperature dependence of this order has shown, on warming long range correlations are first lost along the L direction (figure 7 in [14]). At $T = 23.8$ K the series of Bragg peaks has transformed into a ridge running along L, with long range correlations still present in the ab plane (the ridge is still narrow in the H direction).

A closer look at the 2 K dataset reveals two further subtle features: there is diffuse scattering between the Bragg peaks clearly observed above background, and the widths of the Bragg peaks are not resolution limited but broadened. Both of these features suggest that the long range order is not perfect along L. No diffuse scattering can be seen above background at positions $H \neq \pm 0.329$ r.l.u. A four-circle diffraction measurement performed on the same sample has not revealed any deficiencies in the crystal structure [14]. The magnetic Bragg peaks can be directly compared to the nuclear (003) and (006) peaks which are also seen in the figure. The actual Q resolution of the experiment was calculated from the neutron chopper opening times [17]. It corresponded to $\sim$0.17 r.l.u. fwhm in the L direction. Since the instrumental line shape is nearly Gaussian, the broadening of the magnetic peaks was analyzed using a convolution of a Lorentzian component to the line width with the instrumental Gaussian profile whose width was fixed in the analysis. The result for the width of the Lorentzian component was $\sim$0.1 r.l.u., that is, the correlation length along the L direction can be estimated to about 170 Å. Thus a similar conclusion is reached as in the diffraction study of Poienar *et al* [9] using powder samples, which also found a limited correlation length along L.

Turning to the measurements of the spin dynamics with the exquisite energy resolution of the spin echo technique (figure 3), one notices first a sharp transition from a 'completely static' to a 'completely inelastic' scenario, within a few tenths of a degree K, at 23.5 K. Therefore we identify this transition with the *lower* of the two transitions seen in specific heat. This measurement is self-normalized to the elastic magnetic scattering intensity. At low temperature one measures an elastic echo signal near 1, which is expected since the detector is at the Bragg peak position. As the temperature is raised, the normalized echo signal becomes smaller, which is attributed to the presence of diffuse scattering (see above) in the detector near the Bragg peak which is not elastic and gains spectral weight on warming. As the temperature is further raised (lower panel of figure 3), a sharp transition is then observed to a completely inelastic situation at $T = 23.5$ K. The time-of-flight measurement at the CNCS with much coarser energy resolution confirms this observation. Whereas at low temperature one can see strong elastic scattering and the low energy part of the spin wave dispersion (figure 4 in [13]) on the neutron energy loss side, at 24 K the magnetic scattering has become very broad and centered at zero energy transfer, which is expected for a paramagnet. Taking the dynamics measurements together, the transition from an ordered to a paramagnetic state thus looks very conventional.

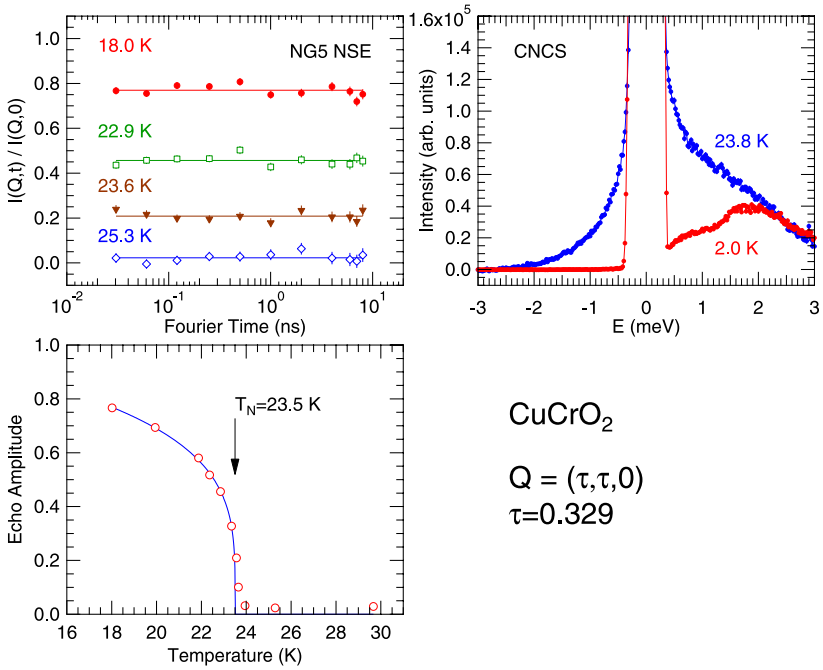

Figure 3. Quasi-elastic neutron scattering results. Error bars (top left) represent $\pm 1\sigma$ from counting statistics. Lines are guides to the eye. Top left: neutron spin echo measurements. There is no spin relaxation but a temperature dependent superposition of truly elastic and fully inelastic (on a $\sim$0.1 μeV energy scale) scattering which results in time-independent $I(Q, t)$ curves. Bottom: order parameter resulting from the spin echo measurements. Top right: energy dependence spectra on the Bragg peak at two temperatures.

The apparent phase transition temperature deduced from specific heat and neutron spin echo, $T_N = 23.5$ K, is similar to other published values, which range from 23.6 K (lower transition in [6]) to 24.2 K [5]. As was mentioned above, this result agrees with previous work, because one should take into account possible variations in thermometer calibration and thermal contact with the apparatus between various measurements.

4. Conclusions

Looking at the magnetic phase transition in $CuCrO_2$ with high resolution neutron spectroscopy, one concludes that only one true phase transition takes place at $T_N = 23.5$ K. Two measurements, specific heat and neutron spin echo spectroscopy, independently lead to the exact same result for T_N. On cooling, two-dimensional long range spatial correlations gradually build up at higher temperatures in the (HH0) plane. These are observed directly with neutron scattering (figure 7 in [14]) and as a broad contribution of the magnetic specific heat (high temperature maximum in figure 1). However these correlations are just a precursor to the ordering at lower temperature and no order parameter onset around $T = 24.2$ K can be seen that is associated with them. For the general scenario—a three-dimensional system of Heisenberg spins with strong in-plane coupling $J_\parallel$ and considerably weaker inter-plane coupling $J_\perp$—Monte Carlo simulations have shown that one can expect a double-peak feature in the specific heat where the lower peak corresponds to the true three-dimensional ordering transition and the upper peak represents two-dimensional correlations in the planes, if the ratio $J_\perp/J_\parallel$ falls in the right range [21]. The Monte Carlo study was for a cubic lattice but it is natural to expect a similar effect to occur in a different lattice geometry as well, though probably in a different $J_\perp/J_\parallel$ range. Our earlier work [13] indicated $J_\perp/J_\parallel \sim 0.007$ for $CuCrO_2$, whereas the simulations on a cubic lattice showed the effect was most pronounced when this ratio was 4–10 times higher [21].

Just above T_N one may thus characterize $CuCrO_2$ as a 'correlated paramagnet', and the magnetic correlations are dynamic on the energy/time scale of the spin echo measurement (faster than 10^{-11} s). The reason why no electric polarization can be observed above the ordering transition then appears to be simple—the system is a paramagnet and the correlations are too short-lived for the spin–charge coupling mechanism to establish itself.

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