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Quasi-one-dimensional antiferromagnetism and multiferroicity in CuCrO_4

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The bulk magnetic properties of the new quasi-one-dimensional Heisenberg antiferromagnet, CuCrO_4 , were characterized by magnetic susceptibility, heat capacity, optical spectroscopy, EPR and dielectric capacitance measurements and density functional evaluations of the intra- and inter-chain spin exchange interactions. We found type-II multiferroicity below the Néel temperature of 8.2(5) K, arising from competing antiferromagnetic nearest-neighbor (J_{nn}) and next-nearest-neighbor (J_{nnn}) intra-chain spin exchange interactions. Experimental and theoretical results indicate that the ratio $J_{\text{nn}}/J_{\text{nnn}}$ is close to 2, putting CuCrO_4 in the vicinity of the Majumdar-Ghosh point.

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I. INTRODUCTION

Ferroelectricity driven by magnetic ordering in so-called type-II multiferroics exhibits a high potential for technological applications.¹ Switching ferroelectric polarization by a magnetic field or magnetization by an electric field offers unprecedented applications in modern energy-effective electronic data storage technology.^{2,3} However, the link of magnetic order and ferroelectricity in type-II multiferroics still remains an intriguing question.⁴⁻⁶ To elucidate this issue, lately much attention has been focused on the magnetic and magnetoelectric (ME) properties of quasi-one-dimensional (1D) antiferromagnetic (afm) quantum chain systems, which exhibit incommensurate cycloidal magnetic ordering.⁷ Such systems lose inversion symmetry and appear to be suitable candidates for multiferroicity. Incommensurate spin-spiral magnetic ordering occurs in magnetic systems consisting of 1D chains when the intra-chain nearest-neighbor (nn) and next-nearest-neighbor (nnn) spin exchange interactions (J_{nn} and J_{nnn} , respectively) are spin-frustrated, as found for compounds with CuX_2 ribbon chains made up of CuX_4 plaquettes, where X is a suitable anion, e.g. oxygen or a halide. Current examples include LiCuVO_4 , NaCu_2O_2 , CuCl_2 .⁸⁻¹⁴ It is typical that the Cu-X-Cu superexchange J_{nn} is ferromagnetic (fm), the Cu-X...X-Cu super-superexchange J_{nnn} is afm and larger in magnitude.^{12,15} A cycloidal spin-spiral along a 1D chain induces a macroscopic electric polarization, $\vec{P} \propto \vec{e}_{ij} \times (\vec{S}_i \times \vec{S}_j)$, where \vec{e}_{ij} is the vector linking the moments residing on adjacent spins \vec{S}_i and \vec{S}_j .¹⁶⁻¹⁸

In an ongoing effort to identify new quantum spin chain systems which potentially exhibit spiral magnetic order and ferroelectric polarization, we recently focused our attention on compounds crystallizing with ribbon chains, mainly those belonging to the CrVO_4 structure-type. The aforementioned structure-type features MO_2 ribbon chains where M is a magnetic $3d$ transition metal. Such compounds were recently shown to exhibit exotic magnetic ground-states.¹⁹⁻²² Here, we report on the magnetic and ME properties of another member of this structure-type, CuCrO_4 . Our density functional calculations indicate J_{nn} to be about twice as strong as J_{nnn} putting CuCrO_4 in the vicinity of the Majumdar-Ghosh point for which the ground state can be exactly solved.²³ This feature makes CuCrO_4 uniquely exceptional since all of the CuX_2 ribbon chain systems investigated so far exhibit fm J_{nn} and afm J_{nnn} spin exchange, where J_{nnn} is considerably larger in magnitude than J_{nn} .^{9,12,15,24} We demonstrate that CuCrO_4 exhibits long-range afm ordering below ~ 8.2 K, which is accompanied by a ME anomaly due to possible spin-spiral ordering in the CuO_2 ribbon chains.

A. Crystal Structure

CuCrO_4 crystallizes in the CrVO_4 structure-type^{25,26} (SG: $Cmcm$, No. 63) with Cu^{2+} (d^9 , $S=1/2$) and Cr^{6+} (d^0) ions. In the crystal structure of CuCrO_4 , the axially-elongated CuO_6 octahedra share edges to form chains running along the c -axis (Fig. 1(a)). These chains are interconnected by CrO_4 tetrahedra such that each CrO_4 tetrahedron is linked to three CuO_4 chains by corner-sharing (Fig. 1(b)). The x^2-y^2 magnetic orbital of each CuO_6 octahedron is contained in the CuO_4 plaquette with four short Cu-O bonds.²⁷ Thus, as far as the magnetic properties are concerned, CuCrO_4 consists of corrugated CuO_2 ribbon chains running along the c -axis (Fig. 1(a)). At room temperature the Cu...Cu distance is 2.945(2) Å and the Cu-O-Cu \angle is 98.1(1)°.

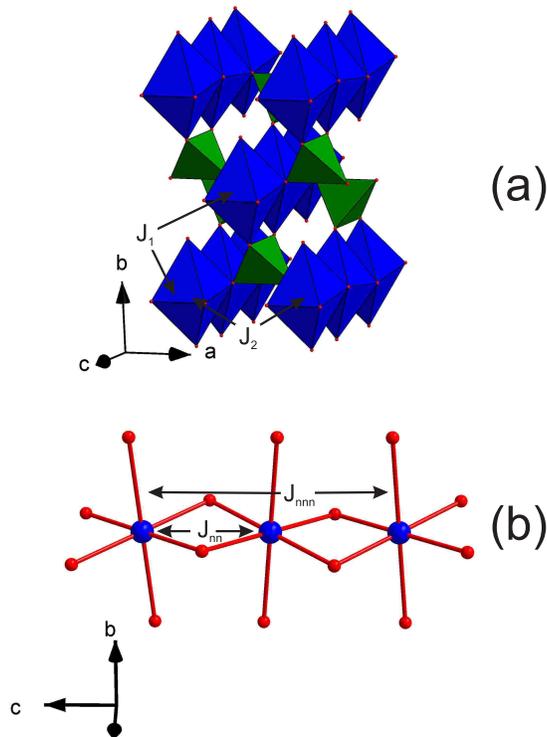


FIG. 1: (Color online)(a): The crystal structure of CuCrO₄. The (blue) octahedra are the CuO₆ units while the (green) tetrahedra are the CrO₄ units. The inter-chain spin exchange pathways J_1 and J_2 are also indicated. (b): A section of the CuO₂ ribbon chain highlighting the edge sharing CuO₄ plaquettes, with the nn J_{nn} and nnn J_{nnn} spin exchange pathways labeled.

II. SPIN EXCHANGE INTERACTIONS

To examine the magnetic properties of CuCrO₄, we consider the four spin exchange paths defined in Fig. 1; the two intra-chain exchanges J_{nn} and J_{nnn} as well as the inter-chain exchanges J_1 and J_2 . To determine the values of J_{nn} , J_{nnn} , J_1 and J_2 , we examine the relative energies of the five ordered spin states depicted in Fig. 2 in terms of the Heisenberg spin Hamiltonian,

$$H = - \sum J_{ij} \vec{S}_i \vec{S}_j, \quad (1)$$

where J_{ij} is the exchange parameter (i.e., J_{nn} , J_{nnn} , J_1 and J_2) for the interaction between the spin sites i and j . Then, by applying the energy expressions obtained for spin dimers with N unpaired spins per spin site (in the present case, $N = 1$),²⁸ the total spin exchange energies of the five ordered spin states, per four formula units (FUs), are given as summarized in Fig. 2. We determine the relative energies of the five ordered spin states of CuCrO₄ on the basis of density functional calculations with the Vienna *ab initio* simulation package, employing the projected augmented-wave method,^{29–31} the generalized gradient approximation (GGA) for the exchange and correlation functional,³² with the plane-wave cut-off energy set to 400 eV, and a set of 64 \mathbf{k} -points for the irreducible Brillouin zone. To account for the strong electron correlation associated with the Cu $3d$ state, we performed GGA plus on-site repulsion (GGA+ U) calculations with $U_{\text{eff}} = 4$ and 6 eV for Cu.³³ The relative energies of the five ordered spin states obtained from our GGA+ U calculations are summarized in Fig. 2. Then, by mapping these relative energies onto the corresponding relative energies from the total spin exchange energies,^{27,34–37} we obtain the values of the spin exchange parameters, J_{nn} , J_{nnn} , J_1 , and J_2 as summarized in Table I.

The intra-chain spin exchanges J_{nn} and J_{nnn} are both afm and constitute the two dominant spin exchanges in CuCrO₄. The inter-chain parameter J_2 , connecting Cu atoms related by a translation along a , is fm and, depending on the onsite repulsion parameter U_{eff} , its magnitude amounts to 15 to 20% of the intra-chain spin exchange J_{nn} . J_1 , which couples adjacent spin moments which are related by a translation along [110], is afm and comparatively small. Therefore, to a first approximation, CuCrO₄ can be described as a quasi 1D Heisenberg magnet with nn and nnn spin

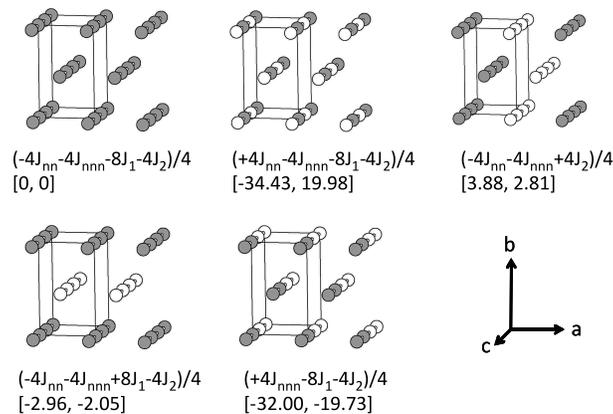


FIG. 2: Five ordered spin states used to extract the values of J_{nn} , J_{nnn} , J_1 , and J_2 , where the Cu^{2+} sites with different spins are denoted by filled and empty circles. For each ordered spin state, the expression for the total spin exchange energy per 4 FUs is given, and the two numbers in square bracket (from left to right) are the relative energies, in meV per 4 FUs, obtained from the GGA+ U calculations with $U_{\text{eff}} = 4$ and 6 eV, respectively.

J_i	$U_{\text{eff}} = 4 \text{ eV}$		$U_{\text{eff}} = 6 \text{ eV}$		experiment
J_{nn}	-199.7(1.0)	-63.8	-115.9(1.0)	-55.4	-54
J_{nnn}	-85.8(0.43)	-27	-56.5(0.49)	-27	-27
J_1	-8.6(0.04)	-2.7	-6.00(0.05)	-2.9	-
J_2	+31.1(0.16)	+9.8	+22.3(0.19)	+10.7	+12
θ_{CW}		-43.2		-38.8	-56/-60

TABLE I: Spin exchange parameters J_{nn} , J_{nnn} , J_1 and J_2 (in K) of CuCrO_4 obtained from GGA+ U calculations with $U_{\text{eff}} = 4$ and 6 eV. The left column for each U_{eff} contains the theoretical results, while the values in the right column are the scaled theoretical results such that J_{nnn} equals the experimental finding, -27 K. The rightmost column summarizes the experimentally found spin exchange values. The final row show the Curie-Weiss temperatures of the scaled GGA+ U spin exchange parameters, calculated using the mean field expression; $\theta_{\text{CW}} = \frac{1}{3} \sum_i z_i J_i S(S+1)$, where z_i is the number of neighbor with which a single atom interacts with the spin exchange J_i , and the experimentally observed values (see below).

exchange interactions, both being afm. Since these 1D chains are connected by weak inter-chain exchanges (J_1 and J_2), long range ordering will eventually take place at low temperatures.

III. EXPERIMENTAL

A polycrystalline sample of CuCrO_4 was prepared by separately dissolving equimolar amounts of anhydrous Copper(II)acetate and Chromium(VI)oxide in distilled water, similar to the recipe given by Arsene *et al.*³⁸. The two solutions were mixed and boiled to dryness. The resulting powder was heat treated in air at a temperature of 150°C for 2 days. The phase purity of the sample was checked by x-ray powder diffraction measurements using a STOE STADI-P diffractometer with monochromated Mo- $K\alpha_1$ radiation. The powder pattern was analyzed using the Rietveld profile refinement method employed within the Fullprof Suite.³⁹ No other reflections besides those of CuCrO_4 were observed.

Powder reflectance spectra of CuCrO_4 were collected at room temperature using a modified CARY 17 spectrophotometer, equipped with an integrating sphere. The spectrometer was operated in the single-beam mode using BaSO_4 as reflectance (white) standard. CuCrO_4 powder was mixed with BaSO_4 in a volumetric ratio $\text{CuCrO}_4:\text{BaSO}_4 \sim 1 : 5$.

Temperature dependent electron paramagnetic resonance (EPR) spectra of a ~ 5 mg polycrystalline sample, contained within an EPR low-background suprasil[®] quartz tube, were collected using ~ 9.5 GHz microwave radiation (Bruker ER040XK microwave X-band spectrometer, Bruker BE25 magnet equipped with a BH15 field controller

atom	Wyckoff site	x	y	z	$B_{\text{iso}} (\text{\AA}^2)$
Cu	4a	0	0	0	0.09(8)
Cr	4c	0	0.3700(3)	0.25	0.90(8)
O1	8f	0	0.2652(5)	0.0320(9)	0.80(12)
O2	8g	0.2326(7)	-0.0198(6)	0.25	0.80(12)

TABLE II: Atomic positional parameters of CuCrO_4 (SG: $Cmcm$) as obtained from a profile refinement of the x-ray powder diffraction pattern, collected at room temperature. The lattice parameters amount to $a = 5.4388(5) \text{ \AA}$, $b = 8.9723(8) \text{ \AA}$ and $c = 5.8904(6) \text{ \AA}$.

calibrated against Diphenylpicrylhydrazyl (DPPH).

The molar magnetic susceptibilities, χ_{mol} , of a polycrystalline sample weighting $\sim 84 \text{ mg}$ were measured with various fields between 2 K and 350 K using a SQUID magnetometer (MPMS, Quantum Design). The raw magnetization data were corrected for the magnetization of the sample container.

The specific heats, C_p , of a powder sample weighting $\sim 2.4 \text{ mg}$ were determined as a function of the temperature and magnetic field with a relaxation-type calorimeter (PPMS, Quantum Design) for the temperature range 0.4 K to 50 K and magnetic fields up to 9 T.

The relative dielectric constant, ϵ_r , was measured at a constant frequency and excitation voltage, 1000 Hz and 15 V, respectively, with an Andeen-Hagerling 2700A capacitance bridge on a compacted powder (thickness: $\sim 0.8 \text{ mm}$, \varnothing : 3.6 mm).

IV. RESULTS AND DISCUSSION

Figure 3 shows the measured and simulated x-ray powder diffraction patterns of the sample of CuCrO_4 used for all subsequent characterization. The refined atomic parameters and the lattice parameters are summarized in Table II and were found to be in good agreement with the previously published single crystal results.²⁶

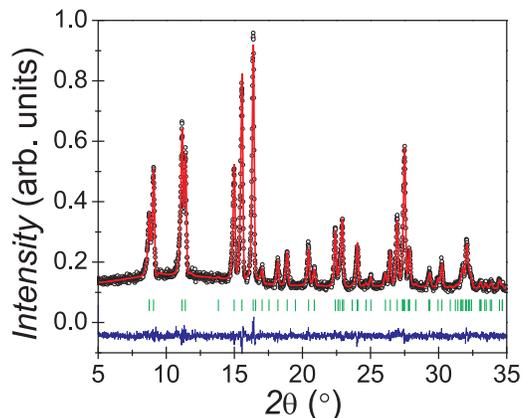


FIG. 3: (Color online) (o): Measured x-ray diffraction pattern of CuCrO_4 (wavelength 0.709 \AA Mo- $K\alpha_1$ radiation). Solid (red) line: Fitted pattern ($R_p = 3.42 \%$, reduced $\chi^2 = 1.15$) using the parameters given in Table II. Solid (blue) line (offset): Difference between measured and calculated patterns. The positions of the Bragg reflections used to calculate the pattern are marked by the (green) vertical bars in the lower part of the figure.

Figure 4 displays the optical spectrum of CuCrO_4 which is consistent with the deep brownish-red color of the CuCrO_4 powder. The spectrum is dominated by a strong absorption band centered at 21500 cm^{-1} (466 nm) which we attribute to an $\text{O}^{2-} \rightarrow \text{Cr}^{6+}$ charge transfer transition, in agreement with observations for other hexavalent chromates.^{40,41} In the near infrared regime (NIR) the spectrum exhibits a maximum at $\tilde{\nu}_3 = 13000 \text{ cm}^{-1}$ with a tail extending down to $\sim 7000 \text{ cm}^{-1}$. Two subsequent faint shoulders are seen within the slope at $\tilde{\nu}_2 = 11000 \text{ cm}^{-1}$ and $\tilde{\nu}_1 \sim 8000 \text{ cm}^{-1}$.

Using ligand-field considerations (see below) the observed absorption bands ($\tilde{\nu}_1$, $\tilde{\nu}_2$ and $\tilde{\nu}_3$) can be assigned to Cu^{2+}

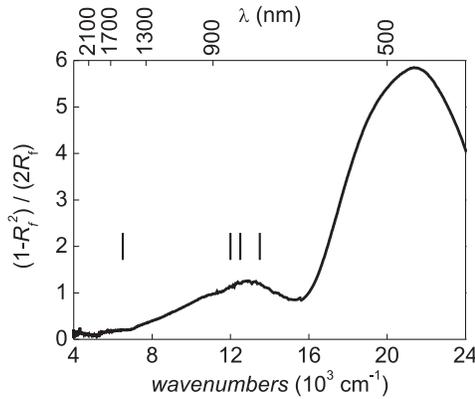


FIG. 4: (Color online) Powder reflectance spectrum of CuCrO_4 . Black vertical bars mark the ligand-field transition energies, for the CuO_6 distorted octahedron, obtained from AOM calculations. We show the Kubelka-Munk relation, $(1-R_f)^2/(2R_f)$, where $R_f = I(\text{CuCrO}_4)/I(\text{BaSO}_4)$ and $I(\text{CuCrO}_4)$ and $I(\text{BaSO}_4)$ are the reflected light intensities of the sample and the BaSO_4 standard, respectively.⁴²

$d-d$ transitions, ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ($z^2 \rightarrow x^2 - y^2$), ${}^2B_{1g} \rightarrow {}^2B_{2g}$ ($xy \rightarrow x^2 - y^2$), and ${}^2B_{1g} \rightarrow {}^2E_g$ ($xz, yz \rightarrow x^2 - y^2$), respectively.⁴³⁻⁴⁶

From $\tilde{\nu}_1$, $\tilde{\nu}_2$, and $\tilde{\nu}_3$ the crystal field splitting, $10Dq$ for CuO_6 , can be calculated using the relation,

$$10Dq = \tilde{\nu}_3 - \left(\frac{\tilde{\nu}_3 - \tilde{\nu}_2}{3}\right) - \left(\frac{\tilde{\nu}_1}{2}\right),$$

which yields a value of $10Dq \sim 8300 \text{ cm}^{-1}$. This value is similar to crystal field splitting values previously reported e.g. for Cu^{2+} aquo-complexes.⁴³

UV/vis spectra for CuCrO_4 have been reported before by Baran and an assignment of the observed transitions has been proposed.⁴⁷ Based on calculations within the framework of the angular overlap model (AOM)⁴³⁻⁴⁶ we argue that this assignment has to be revised.

Within the AOM model the pairwise interactions of the ligands with the d -orbitals are encoded into the parameters, e_σ , $e_{\pi,x}$ and $e_{\pi,y}$ which take care of interaction along and perpendicular to the $\text{Cu} - \text{O}_i$ ($i = 1, \dots, 6$) bond, respectively. The energies of the individual d -orbitals are obtained by summation over all pairwise interactions. The variation of the AOM parameters $e_{\sigma i}$ with the $\text{Cu} - \text{O}_i$ distance has been taken care of by,

$$e_{\sigma i} \propto 1/r_i^n.$$

An exponent of $n \approx 5$ is derived from electrostatic and covalent theoretical bonding considerations.^{42,48,49} Measurements of the pressure dependence of $10Dq$ pointed to a similar exponent $5 \leq n \leq 6$.⁵⁰ For the sake of simplicity we have chosen $e_{\pi,x} = e_{\pi,y} = 1/4e_\sigma$. AOM calculations have been performed using the program CAMMAG.^{51,52} Table III summarizes the parameters which have been used for these calculations. The resulting transition energies marked by vertical bars in Fig. 4 are in good agreement with the centers of the experimentally observed absorption features.

	O_{eq}	O_{ax}
d (Cu-O) (Å)	1.965 (4×)	2.400 (2×)
e_σ (cm^{-1})	5600	2061
$e_{\pi,x}$ (cm^{-1})	1400	515
$e_{\pi,y}$ (cm^{-1})	1400	515

TABLE III: Parameter used in the AOM calculations. The equatorial plane forms a rectangle with the equatorial $\text{O}_{\text{eq}} - \text{Cu} - \text{O}_{\text{eq}}$ bonds enclosing an \angle of 81.92° and 98.08° , respectively. The Racah parameters amounted to $B = 992 \text{ cm}^{-1}$, $C = 3770 \text{ cm}^{-1}$ yielding a ratio $C/B = 3.8$, as given for the free Cu^{2+} ion.⁴³ As for the aquo-complex the nephelauxetic ratio β was chosen to be 0.80, and the spin-orbit coupling parameter $\zeta = 664 \text{ cm}^{-1}$ was reduced by 20% as compared to the free ion value.^{43,53}

In addition to the energy of the excited electronic states of the isolated CuO_6 unit, its magnetic properties are also obtained from the AOM calculations. The parametrization leads to an average $g_{\text{av}} = 2.18$ and a strongly anisotropic

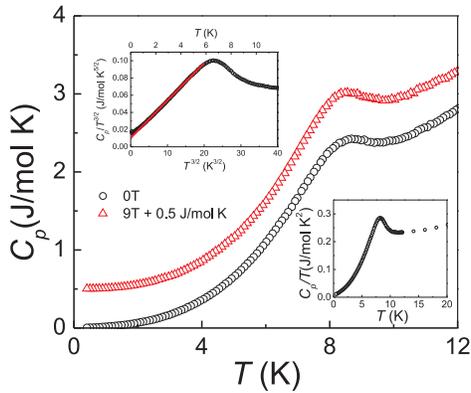


FIG. 5: (Color online) (Black) \circ and (red) \triangle : Heat capacity of CuCrO_4 at 0 T and 9 T, respectively. The latter data have been shifted by $+0.5$ J/mol K. Upper left inset: $C_p/T^{3/2}$ plotted versus $T^{3/2}$ to highlight the low-temperature $T^{3/2}$ power law. The (red) solid line is a fit of the data to eq. (2) with parameters given in the text. Lower right inset: C_p/T depicted against T in the low-temperature regime.

g -tensor with $g_x = 2.07$, $g_y = 2.07$, and $g_z = 2.39$ along the principle axes. The z -direction of the g -tensor lies along the Cu - O_{ax} bond direction.

The results of the specific heat measurements for magnetic fields of 0 T and 9 T are displayed in Fig 5. The 0 T data reveal a rather broad, smeared, λ -type anomaly centered at 8.2(5) K marking the onset of long-range magnetic ordering. Within experimental error the data measured in a magnetic field of 9 T are identical to those obtained at 0 T. The plot of C_p/T versus T given in the low right inset of Fig. 5 enables the estimation of the entropy contained within the anomaly, which equates to ~ 0.6 J/mol K or $\sim 10\%$ of the expected entropy of a $S = 1/2$ system, $R \ln(2)$, where R is the molar gas constant. 90% of the entropy has already been removed by short-range afm ordering above T_N .

At low temperatures, the heat capacity comprises of a phonon and magnon contribution. The temperature dependence of the phonon contributions to the heat capacity can be described by a Debye- T^3 power law. The magnon heat capacity at low temperatures varies with a power law depending on the spin wave dispersion relation and the dimensionality of the lattice. For a three-dimensional (3D) magnetic lattice, one obtains a T^3 power law for afm magnons, and a $T^{3/2}$ power law for fm magnons.⁵⁴ The $C_p/T^{3/2}$ versus $T^{3/2}$ plot shown in the upper left inset of Fig. 5 demonstrates that at low temperatures the heat capacity conforms well to a $T^{3/2}$ power law, with the coefficient of the fm magnon contribution given by the non-zero intercept with the ordinate, γ , according to,

$$C_p/T^{3/2} = \beta T^{3/2} + \gamma, \quad (2)$$

where β is related to the Debye temperature, $\theta_D(0)$ at zero temperature via,

$$\beta = MR \frac{12\pi^4}{5} \left(\frac{1}{\theta_D}\right)^3, \quad (3)$$

with $M = 6$ being the number of atoms per formula unit of CuCrO_4 . By using eq. (3) we ascertain $\theta_D(T \rightarrow 0)$ to be,

$$\theta(T \rightarrow 0) = 138(3) \text{ K},$$

and from the intercept and eq. (2) we obtain γ as

$$\gamma = 1.03(2) \times 10^{-2} \text{ J/molK}^{5/2}.$$

Figure 6 summarizes the results of our EPR measurements. Near 3.4 kOe a single rather broad (peak-to-peak linewidth $\Delta H_{\text{pp}} \approx 0.8 - 1$ kOe) symmetric resonance line was observed. It can be well fitted to the derivative of a single Lorentzian absorption line with a small contribution $|\alpha| \leq 0.04$ of dispersion according to

$$\frac{dP_{\text{abs}}}{dH} \propto \frac{d}{dH} \frac{\Delta H + \alpha(H - H_{\text{res}})}{(H - H_{\text{res}})^2 + \Delta H^2} + \frac{\Delta H + \alpha(H + H_{\text{res}})}{(H + H_{\text{res}})^2 + \Delta H^2}. \quad (4)$$

As the linewidth (half-width at half-maximum (HWHM)), ΔH , is of the same order of magnitude as the resonance field, H_{res} (see Fig. 6(a)), in eq. (4) we took into account both circular components of the exciting linearly polarized microwave field and therefore also included the resonance at negative magnetic fields centered at $-H_{\text{res}}$.

The resonance field of the room temperature powder spectrum corresponds to a g -factor of 2.117(2). Upon cooling a slight increase of the g -factor with saturation to a value of ~ 2.125 below 150 K was observed (Fig. 6(c)). Such a value is somewhat lower than the expected average value g_{av} ascertained from the AOM calculations. The resonance line is too broad to resolve the anisotropic g -factors which range between ~ 2.39 and ~ 2.07 (see above).

The integrated intensity of the EPR resonance, $I(T)$ which is proportional to the spin-susceptibility, increases with decreasing temperature down to ~ 15 K where a hump occurs. Above ~ 150 K, $I(T)$ follows a Curie-Weiss type temperature-dependence,

$$I(T) \propto \frac{1}{T - \theta_{\text{EPR}}}, \quad (5)$$

with

$$\theta_{\text{EPR}} \approx -60(5) \text{ K}.$$

The negative T -axis intercept indicates predominant afm spin exchange interactions. Deviations from the Curie-Weiss type temperature-dependence are ascribed to short-range afm correlations, which start to develop below ~ 150 K, similar to the behavior of the dc magnetic susceptibility (see below). The decrease of the integrated intensity below ~ 15 K signals the onset of long-range ordering.

The magnitude and temperature-dependence of the EPR linewidth, ΔH , are similar to those observed for the inorganic spin-Peierls system CuGeO_3 or the frustrated afm 1D system LiCuVO_4 .^{56,57} The linewidth exhibits a concave temperature dependence with a linear increase at low temperatures and for $T \rightarrow \infty$ one extrapolates a saturation value of ~ 1.4 kOe.

If we assume that the temperature-dependant broadening of the EPR resonance line is due to anisotropic or antisymmetric components in the exchange Hamiltonian, the constant high-temperature value can be estimated from the Kubo-Tomita limit as,⁵⁸

$$\Delta H(T \rightarrow \infty) \approx \frac{1}{g\mu_{\text{B}}} \frac{\delta^2}{J}, \quad (6)$$

where δ indicates the deviations from the symmetric Heisenberg spin exchange and J is the afm symmetric intra-chain exchange. If for CuCrO_4 we associate J with the nn spin exchange, ~ 60 K (see below), we can estimate a δ of ~ 3 K, i.e. 5% of the symmetric exchange.

The linear slope of the linewidth at low temperatures can be explained using the formulism put forth by Oshikawa and Affleck^{59,60} predicting

$$\Delta H(T) \propto \frac{\delta^2}{J^2} T. \quad (7)$$

We find a linear slope, indicative of 1D afm system, of ~ 2.5 Oe/K, similar to that observed for CuGeO_3 (~ 4.5 Oe/K).⁵⁶

The magnetic susceptibility of a polycrystalline sample of CuCrO_4 was measured in magnetic fields of 1, 3, 5 and 7 Tesla. Above ~ 20 K the susceptibilities are independent of the magnetic field indicating negligible ferromagnetic impurities. The susceptibilities, $\chi_{\text{mol}}(T)$, above ~ 150 K follow the modified Curie-Weiss law,

$$\chi_{\text{mol}}(T) = \frac{C}{T - \Theta} + \chi_{\text{dia}} + \chi_{\text{VV}}. \quad (8)$$

C is the Curie constant pertaining to the spin susceptibility of the Cu^{2+} entities, $C = N_{\text{A}} g^2 \mu_{\text{B}}^2 S(S+1)/3k_{\text{B}}$. χ_{dia} refers to the diamagnetic susceptibilities of the electrons in the closed shells, that can be estimated from the increments given by Selwood, which equates to $-62 \times 10^{-6} \text{ cm}^3/\text{mol}$.⁶¹

At high temperatures, $T \geq 150$ K, we fitted the molar susceptibility to the aforementioned modified Curie-Weiss law (eq. 8). We found best agreement with the following parameters:

$$g = 2.17(2) \quad \text{and} \quad \theta = -56(1) \text{ K}$$

and

$$\chi_{\text{dia}} + \chi_{\text{VV}} \approx +20 \times 10^{-6} \text{ cm}^3/\text{mol}.$$

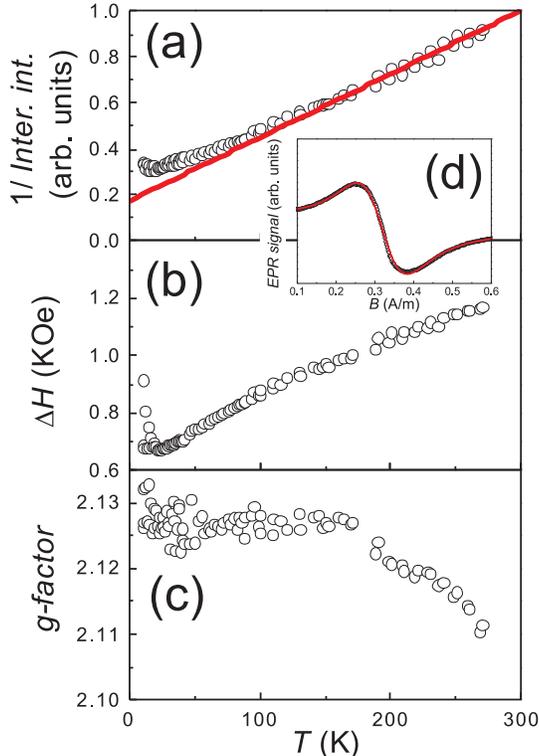


FIG. 6: (Color online) Results of the EPR measurements on a polycrystalline sample of CuCrO_4 . (a) (o) Inverse of the integrated intensity. The (red) solid line is a fit of eq. (5) to the high temperature data ($T \geq 150$ K). (b) (o) The fitted half-width-at-half-maximum (HWHM) versus temperature. (c) (o) g -factor versus temperature. (d) (o) EPR spectrum of CuCrO_4 measured at RT with ~ 9.45 GHz versus applied magnetic field. The (red) solid line represents the fitted derivative of a Lorentzian absorption line (eq. 4) to the measured spectrum.

This puts the Van Vleck contribution to $\approx +80 \times 10^{-6} \text{ cm}^3/\text{mol}$ which is in reasonable agreement with what has been found for other Cu^{2+} compounds (see Ref. 12 and refs. therein). The fitted g -factor is in good agreement with optical spectroscopy and the Curie-Weiss temperature is negative and in accordance with θ_{EPR} .

Below 150 K there are deviations from the Curie-Weiss law attributed to increasing afm short range correlations. The susceptibility passes through a broad shoulder with a subsequent kink at ~ 8 K whereupon it becomes field dependent, with a tendency to diverge for small fields. With increasing fields the divergence is suppressed and the kink becomes more apparent. By 7 T a pronounced rounded hump with a maximum at 14.2(2) K and a subsequent dip at 8.0(5) K become clearly visible.

In general, GGA+ U calculations overestimate the spin exchange constants typically by a factor up to 4, in our case 2.^{34,35,62} By taking this into account and by using a mean field approach one calculates, from the spin exchange parameters summarized in Table II, a (negative) Curie-Weiss temperatures ranging between -38 K to -45 K, consistent with the experimental observations.

Our GGA+ U calculations indicate that CuCrO_4 can be described by a Heisenberg 1D chain with afm nn and afm nnn spin exchanges, with significantly weak inter-chain interactions ($J_2/J_{\text{nn}} < 0.19$). Therefore, we modeled the magnetic susceptibility of CuCrO_4 against exact diagonalization results for the susceptibility $\chi_{\text{chain}}(g, \alpha, J_{\text{nnn}})$ of a single chain provided by Heidrich-Meissner *et al.*,^{63,64} with

$$\alpha = J_{\text{nn}}/J_{\text{nnn}}. \quad (9)$$

Inter-chain spin exchange is treated within a mean-field approach according to,⁶⁵

$$\chi_{\text{mol}}(T) = \frac{\chi_{\text{chain}}(T)}{1 - \lambda \chi_{\text{chain}}(T)} + \chi_0. \quad (10)$$

By using the already known values, $\chi_0 = \chi_{\text{dia}} + \chi_{\text{VV}} = +20 \times 10^{-6} \text{ cm}^3/\text{mol}$ as found from the fit of the high temperature magnetic susceptibility and a g -factor of 2.13 obtained from the EPR measurements, the simulated

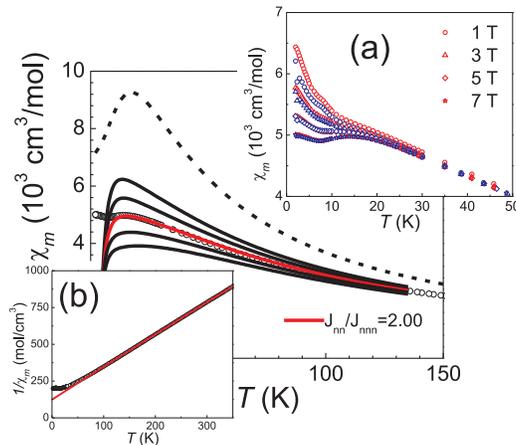


FIG. 7: (Color online) (main panel) (o) Temperature dependence of the molar magnetic susceptibility, χ_m , taken at 7 T. Colored solid lines represent the exact diagonalization results by Heidrich-Meissner *et al.* for various ratios of J_{nn}/J_{nnn} , 1.5, 1.75, 2 (red solid line), 2.25 and 2.5, from top to bottom, respectively. See text for more details. The dashed line is the magnetic susceptibility of a $S=1/2$ Heisenberg chain with afm uniform nn spin exchange of -27 K.⁶⁶ (a) red symbols: heating data, blue symbols: cooling data. χ_{mol} versus temperature for various magnetic field. (b) (o) Reciprocal molar susceptibility versus temperature with a fit ((red) solid line) to a modified Curie-Weiss law (eq. (8)).

results can be compared to experimental data. The mean-field parameter, λ , in eq. (10) can be ascribed to the inter-chain spin exchange interactions according to⁶⁵

$$\lambda = (z_1 J_1 + z_2 J_2)/N_A g^2 \mu_B^2, \quad (11)$$

wherein, $z_1 = 4$ and $z_2 = 2$ count the number of spin moments with which a chain/spin interacts through the inter-chain spin exchange interactions, J_1 and J_2 , respectively. Guided by the GGA+ U results, the ratio α is positive and in the regime of 1.5 to 2.5. Within this range for α we find best agreement of our experimental data with the model calculations for,

$$\alpha \approx 2, \quad \text{implying} \quad J_{nnn} = -27(2) \text{ K},$$

and a positive λ , which amounts to

$$\lambda = 7(1) \text{ mol/cm}^3.$$

Figure 7 shows a comparison of the measured data and the mean-field corrected exact diagonalization results.

$\lambda > 0$ indicates that the dominant inter-chain spin exchange is fm, consistent with our density functional calculations. The DFT calculations indicate $J_1 \approx -1/4 \times J_2$, irrespective of U_{eff} . From eq. (11) using $\lambda = 7(1) \text{ mol/cm}^3$ we derive a value for J_2 which amounts to

$$J_2 = 12(2) \text{ K}.$$

This value is in good agreement with the scaled DFT result, see Table I.

The inter-chain spin exchange can also be estimated from the Néel temperature, T_N , which, according to the heat capacity data, amounts to (see above);

$$T_N \approx 8.2(5) \text{ K}.$$

Yasuda *et al.* calculated the Néel temperature of a quasi 1D Heisenberg antiferromagnet on a cubic lattice with the isotropic inter-chain coupling J_\perp , inducing 3D long-range magnetic ordering at a Néel temperature, T_N ;⁶⁷

$$T_N/|J_\perp| = 0.932 \sqrt{\ln(A) + \frac{1}{2} \ln(\ln(A))}, \quad (12)$$

where $A = 2.6 J_\parallel/T_N$ and J_\parallel is the intra-chain spin exchange constant. If we assume J_\parallel to be our $J_{nn} \sim -60$ K we find the inter-chain coupling to be

$$|J_\perp| \approx 5 \text{ K},$$

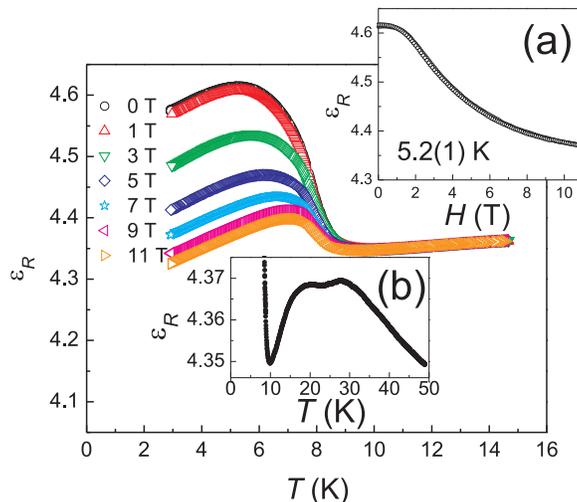


FIG. 8: (Color online) (a) Colored symbols represent the relative dielectric constants, ϵ_r , versus temperature for different applied magnetic fields, as given in the legend. (b) The zero field relative dielectric constant is shown by the solid black line within a greater temperature range. (c) (o) The relative dielectric constant versus applied magnetic field at a temperature of 5.2(1) K.

consistent with the value obtained, from λ . The differences may arise, since our real system has two different inter-chain coupling constants, J_1 and J_2 , as indicated by our density functional calculations. Additionally, CuCrO_4 has a nnn spin exchange J_{nnn} , which is not included in Yasuda's model.

Figure 8 displays the temperature and magnetic field dependence of the relative dielectric constant, ϵ_r , of a compacted polycrystalline sample of CuCrO_4 .

At room temperature, a value of ~ 48 was found for ϵ_r . With decreasing temperature, ϵ_r is seen to decrease in a smooth fashion, until it passes through a shallow double maximum between 35 and 15 K, possibly indicating some magnetostriction induced by short range magnetic ordering processes above T_N (see Fig. 8 inset (b)). At 10 K a value of $\epsilon_r \sim 4.35$ was measured. Long-range magnetic ordering leads to a sizeable ME effect as evidenced in the ϵ_r , however, with a rather broad anomaly extending over the whole temperature range down to 3 K. Indication for a sharp spike near T_N , as is frequently found in multiferroic systems, has not been seen. Similar broad anomalies, originating at T_N , have been seen in CuCl_2 and CuBr_2 .^{68,69} In zero field a steep increase of ϵ_r is seen to occur below ~ 8.5 K with a broad slightly asymmetric hump centered at ~ 5.35 K. In zero field the increase of ϵ_r from the paramagnetic phase to the maximum of the hump amounts to $\sim 6\%$. Applying a magnetic field decreases the ME anomaly and moves the maximum to higher temperatures. The onset of the ME anomaly is not seen to move, in accordance with the aforementioned C_p measurements (see Fig. 8, inset (c)). The decrease of ϵ_r with a magnetic field starts above ~ 1 T and tends to saturation at sufficiently high fields.

V. CONCLUSION

In summary, CuCrO_4 represents a new 1D quantum antiferromagnet with a remarkable pronounced ME anomaly below the Néel temperature of 8.2 K. Our density functional calculations indicate that, to a first approximation, the spin lattice of CuCrO_4 is a 1D Heisenberg chain with the unique situation that both, nn and nnn, spin exchanges are afm. $J_{\text{nn}}/J_{\text{nnn}}$ is found to be close to 2, which places CuCrO_4 in the vicinity of the Majumdar-Ghosh point. There one could expect an incommensurate magnetic structure along the c -axis, with the c -axis magnetic unit cell being approximately $3/2 \times c$. The presence of sizeable ferromagnetic inter-chain spin exchange interaction leads to long-range ferromagnetic ordering between individually antiferromagnetically ordered chains. The occurrence of the rather large ME anomaly below the Néel temperature is taken as evidence for non-collinear, possibly helicoidal, spin ordering in the 1D chains. CuCrO_4 therefore represents a new interesting example for an unusual type-II multiferroicity system. Neutron scattering investigations are scheduled to clarify the exact nature of the magnetic ground state of CuCrO_4 .

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