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Magnetic properties of the magnetoelectric compound Cu_2OSeO_3: Magnetization and ^{77}Se NMR study

M. Belesi[1], T. Philippe[1], I. Rousochatzakis[2], H. C. Wu[3], H. Berger[1], S. Granville[1], I. V. Shvets[3], J. -Ph. Ansermet[1]

[1] Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, Station 3, CH-1015 Lausanne-EPFL, Switzerland
[2] Max Planck Institut für Physik Komplexer Systeme, Nöthnitzer Str. 38, 01187 Dresden, Germany
[3] CRANN and School of Physics, Trinity College, Dublin 2, Ireland

E-mail: `mariaeleni.belesi@epfl.ch`

Abstract. We present magnetization and ^{77}Se Nuclear Magnetic Resonance (NMR) measurements in single crystals of the magneteoelectric compound Cu_2OSeO_3. The temperature and field dependence of the magnetization suggest a ferrimagnetic ordering at $T_c \simeq 60$ K in a 3up-1down configuration. The easy axis of the magnetization is along the [100] crystallographic direction. The ^{77}Se NMR line shape data collected at 14.09 T are consistent with the symmetries imposed by the cubic $P2_13$ space group in the temperature range $20-290$ K and confirm that the magnetic transition is not accompanied by any lowering of the crystal symmetry as has recently been proposed by Bos *et al.* [*Phys. Rev.* B **78** 094416 (2008)].

1. Introduction

Materials that show cross coupling effects between magnetic and electric properties are currently attracting broad experimental and theoretical interest.[1, 2, 3, 4] The control of magnetic order by electric fields and vice versa is important for fundamental research but also for potential technological applications.[5] Even though the research in magnetoelectric materials goes back several decades,[6, 7] a revival of interest has taken place in recent years. This is mainly due to the developments in thin film technology (which have made possible the fabrication of thin films with enhanced magnetoelectric properties as compared to bulk materials[4]), but also due to the discovery of multiferroic compounds such as $TbMnO_3$[8] and $TbMn_2O_5$[9], where the ferroelectricity is driven directly by the spin order. Despite the significant progress over the last years, several problems remain still open in this field. For example, only a relatively small number of magnetoelectric materials exist in nature, or have been synthesized in the lab.[5] Furthermore, the coupling between spontaneous electric polarization P and magnetic moment M in multiferroic materials is weak and high electric (magnetic) fields are needed to switch the magnetization (electrical polarization).

Apart from the multiferroic compounds another interesting class of materials that exhibits magnetoelectric properties exists, such as a change in the dielectric constant at the magnetic ordering temperature or finite magnetocapacitance, but not a spontaneous polarization (in

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contrast to multiferroics). Materials exhibiting the so called magnetodielectric effect are, among others, $SeCuO_3$,[10] $TeCuO_3$,[10] $EuTiO_3$[11], $TmFeO_3$[12], and $Tb_3Fe_5O_12$[13]. Despite the fact that these materials are not ferroelectric, a direct coupling between the electric and magnetic ordering exists. The magnetodielectric effect is commonly accompanied by a distortion of the unit cell which suggests that the magnetoelectric coupling proceeds via lattice deformations. An exception to this behavior has recently been found in polycrystalline samples of Cu_2OSeO_3. [14] In Cu_2OSeO_3 the magnetic ordering is accompanied by a magnetocapacitance signal and an anomaly in the dielectric constant, but the lattice remains metrically cubic down to 10 K according to high resolution powder x-ray diffraction (XRD) data. [14] Motivated by the work of Bos *et al.*, [14] we have performed a magnetization and ^{77}Se NMR study on single crystals of Cu_2OSeO_3. Our results confirm the transition from the high temperature paramagnetic phase to a low-T ferrimagnetic state at $T_c \simeq 60$ K, whereby 3/4 of the Cu^{2+} ions are aligned parallel and 1/4 are aligned antiparallel to some axis. We further show that this magnetic configuration remains stable at least up to 14 T and that the preferential direction (easy axis) of the magnetization is along the [100] crystallographic direction. The transition to the low temperature ferrimagnetic state is probed by ^{77}Se NMR line shape measurements collected at 14.09 T, which show that the transition is not accompanied by any spontaneous lattice distortion in agreement with the high resolution XRD data on powder samples reported previously by Bos *et al.*[14]

2. Synthesis and characterization

We have grown single crystals of Cu_2OSeO_3 by the standard chemical vapor phase method. Mixtures of high purity CuO (Alfa-Aesar, 99.995%) and SeO_2 (Alfa-Aesar, 99.999%) powder in molar ratio 2:1 were sealed in quartz tubes with electronic grade HCl as the transport gas for the crystal growth. The ampoules were then placed horizontally into a tubular two-zone furnaces and heated very slowly by 50°C/h to 600°C. The optimum temperatures at the source and deposition zones for the growth of single crystals have been 610°C and 500°C, respectively. After six weeks, many dark green, almost black Cu_2OSeO_3 crystals with a maximum size of 8x6x3mm were obtained. X-ray powder diffraction analysis was conducted on a Rigaku X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418\mathring{A}$) and the electron microprobe was used for chemical analysis of all solid samples. The diffraction data are similar to previously published data,[15, 14, 16] and show that the material crystallizes in the cubic $P2_13$ space group. The orientations of the crystal axes with respect to the crystal faces were determined by Laue X-ray back-scattering measurements. A detailed description of the crystal structure of this compound can be found in Refs. [15, 14, 16].

3. Experimental results

3.1. Magnetization measurements

For the magnetic measurements we have employed two Quantum Design Physical Properties Measurement Systems (at EPFL and Trinity College). We have measured the field dependence of the magnetization and have carried out zero-field cooled (ZFC) and field cooled (FC) magnetization measurements along various crystallographic directions in the temperature range 2-300 K and for fields of up to 14 T.

The field dependence of the magnetization was measured at 5 K (Fig. 1a) with the magnetic field applied along [111] (circles) and [100] (squares) crystallographic directions. The magnetization saturates at approximately 1 kOe when the magnetic field is applied along [100] axis, while a stronger field is needed (1.5 kOe) in order to saturate the magnetization along [111] direction. No coercive field was measured and the saturation value is 0.53 μ_B/Cu at 5 K, which is the same for both crystallographic directions. This saturation value is half of the full moment of all Cu^{2+} ions and suggests a simple collinear ferrimagnetic alignment where 3/4 of the copper

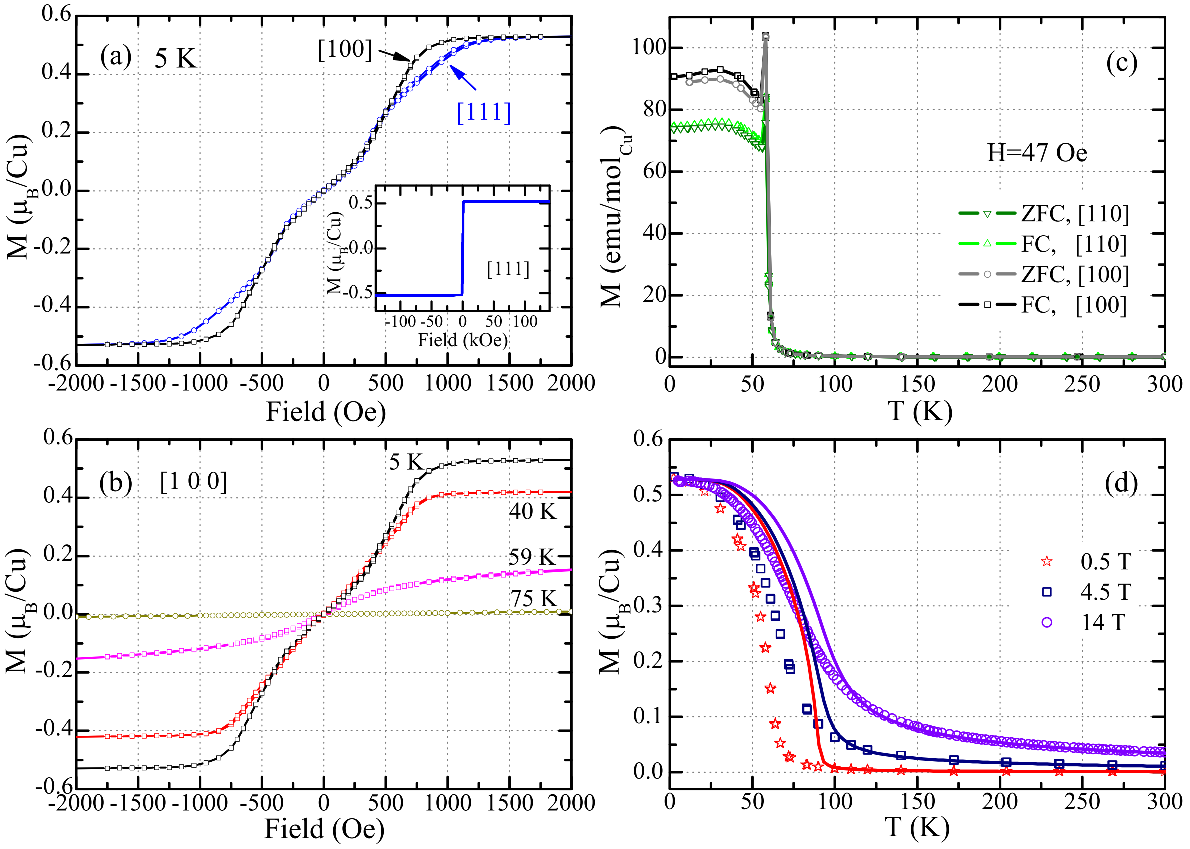

Figure 1. (a) Field dependence of the magnetization measured at 5 K with the magnetic field applied along [111] and [100] crystallographic directions. The inset shows the field dependence of the magnetization along [111] at 5 K where the magnetic field was swept up to 14 T. (b) The field dependence of the magnetization at various temperatures collected with the magnetic field applied along [100]. (c) The temperature dependence of the ZFC and FC magnetization measured in a magnetic field of 47 Oe applied along [110] and [100] direction. (d) The temperature dependence of the FC magnetization measured in applied fields of 0.5 T (stars), 4.5 T (squares) and 14 T (circles). The solid lines are high-T fits based on the mean field solution of a microscopic Heisenberg model introduced in Ref. [17].

ions are aligned parallel (Cu2 ions in 12b sites) and 1/4 are aligned antiparallel (Cu1 ions in 4a sites) to the applied magnetic field. This result is in agreement with the data reported by Bos *et al.*[14] in powder samples. We have extended our measurements to higher magnetic fields (Fig. 1a inset) and we have found that the 1/2 magnetization plateau remains stable at least up to 14 T. At low magnetic fields the magnetization grows linearly and at approximately 400 Oe a magnetization jump with a small amount of magnetic hysteresis is observed, in agreement with Ref. [14]. The field dependence of the magnetization with the magnetic field applied along the easy axis [100] was further measured at 5, 40, 59 and 75 K and the results are presented in Fig. 1b. At 75 K, i.e. in the paramagnetic phase, the typical linear field dependence is observed. In the ordered state we observe a decrease in the saturation value of the magnetization (and an increase in the saturation field) by increasing temperature due to thermal fluctuations.

The temperature dependence of the ZFC and FC magnetization collected at 47 Oe is shown in Fig. 1c. The measurements were performed for two different directions of the magnetic field, one along [110] and the other along the easy axis [100]. The magnetization jumps at 60 K and shows hysteresis between ZFC and FC data in agreement with published data in powder samples.[14] The magnetization measurements collected for magnetic fields higher than the metamagnetic transition are presented in Fig. 1d. The solid lines in Fig. 1d are theoretical fits based on a mean-field solution of a microscopic Heisenberg spin model introduced in Ref. [17]. This model consists of two Heisenberg exchange parameters between nearest-neighbor Cu^{2+} ions, one ferromagnetic J_{fm} between Cu2 sites and one antiferromagnetic J_{afm} between Cu1 and Cu2 sites. The optimal fit to the data with the self-consistent solution of the corresponding mean-field equations provides $g \simeq 2.11$,[16] $J_{\mathrm{afm}} \simeq 68$ K and $J_{\mathrm{fm}} \simeq -50$ K. The fits are quite accurate in a wide high temperature range above 100 K. At lower temperatures the mean-field theory is not accurate since it overestimates the critical temperature $T_c^{\mathrm{MF}} = \frac{1}{2}(\mid J_{fm} \mid + \sqrt{J_{fm}^2 + 3J_{afm}^2}) \simeq 89K$. In addition the mean field theory neglects the quantum fluctuations which reduce the length of the ordered moments.

3.2. Nuclear magnetic resonance

NMR is a powerful local probe which can provide information on both magnetic and structural properties. Here, we have applied pulsed NMR techniques on ^{77}Se nuclei with nuclear spin I = 1/2 and gyromagnetic ratio $\gamma_N/2\pi = 8.1179$ MHz/T. The NMR experiments were performed with a home made spectrometer at an Oxford 14.09 T magnet. The magnet is equipped with a variable temperature insert and the measurements were performed in the temperature range 20-295 K. The NMR spin-echo was produced by a standard Hahn echo pulse sequence with a typical $\pi/2$ pulse length of $6\mu s$. The separation between the two echo generating pulses was kept much shorter than the spin-spin relaxation time T_2. For narrow lines the NMR spectra were measured by a Fourier transform of the half spin-echo signal, while for broad lines they were obtained by plotting the area of the echo as a function of the irradiation frequency (frequency sweep).

The NMR line shapes were found to have strong orientational and temperature dependence. In Fig. 2(a) we show the NMR spectra at a representative high temperature value (220 K) for three different directions of the magnetic field with respect to the crystallographic axes. A comparison between the three directions shows that there are differences with respect to the number of peaks per direction, to the resonance frequency and also to their relative intensities. Two lines of the same integrated area, 4:4, are observed in [100] direction. These two lines split into four peaks when the field is applied along [110] or [111], while the ratio of the relative integrated areas along these directions is 2:2:2:2 and 3:1:3:1 respectively. An explanation of these findings can arise by considering the crystal symmetry but also the 3up-1down magnetic configuration. In $\mathrm{Cu_2OSeO_3}$, there are two crystallographically inequivalent groups of selenium sites containing four selenium ions each.[14] The selenium ions occupy non-cubic sites thus in general more than one line per selenium group is expected. The dipolar contribution to the NMR line shape can be calculated[17] since the positions of the Cu ions are known.[15, 14, 16] It comes out that when the magnetic field is applied along [100] all the eight selenium ions experience the same dipolar field thus only one line should be observed, in contrast to our experimental results which show two lines. Hence apart from the dipolar interactions we must also invoke the transferred hyperfine interactions at the selenium sites. A detailed calculation of the different contributions in the ^{77}Se NMR lines of $\mathrm{Cu_2OSeO_3}$ based on the local symmetry of selenium sites can be found in Ref. [17].

In order to probe the transition to the low temperature ferrimagnetic state we have studied the temperature dependence of the NMR spectra along the [111] axis. As can be seen in Fig. 2b by lowering the temperature the relative shift for each one of the four NMR peaks from the Larmor frequency (dotted line) increases. The temperature dependence of the NMR shifts is related to the spin density at the selenium sites, and the enhancement at low temperatures signals the transition to a magnetically ordered state. Two important observations can be made

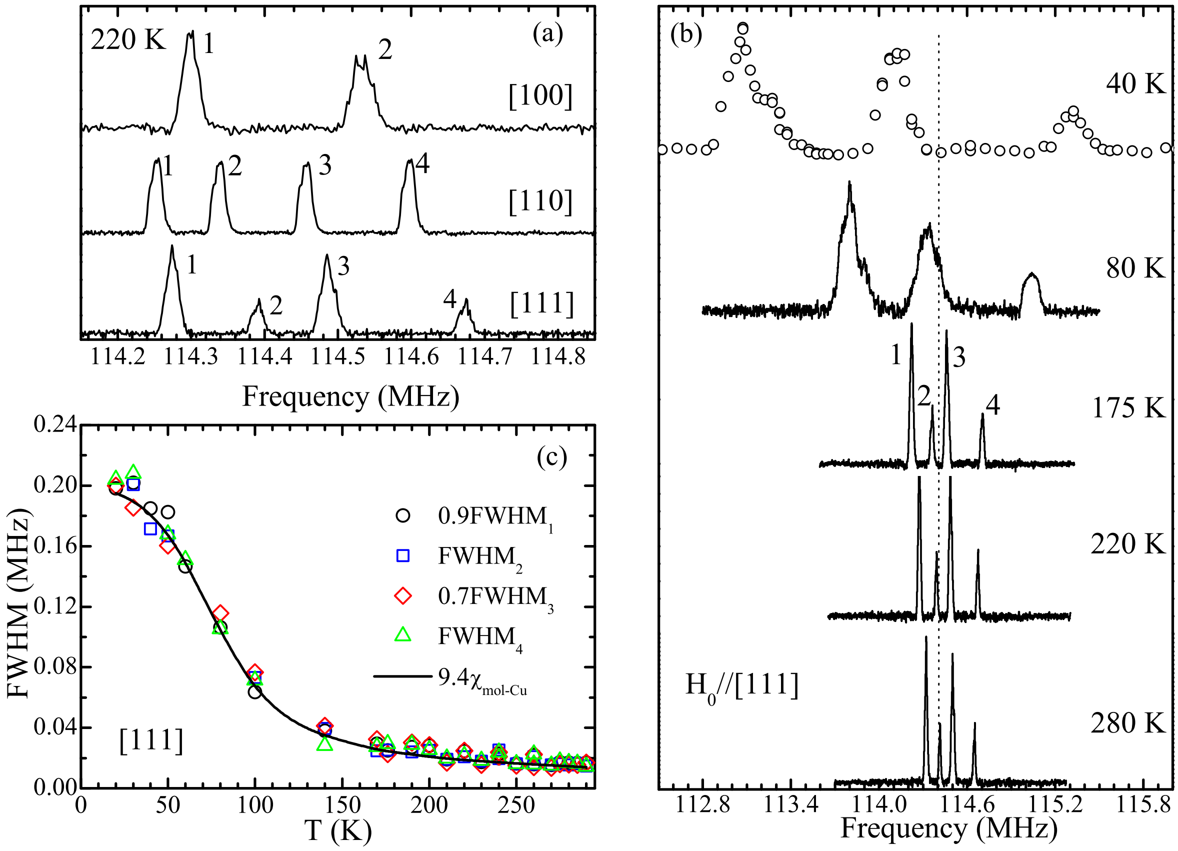

Figure 2. (a) ^{77}Se NMR line shape measurements collected at 220 K with the magnetic field, $H_0 = 14.09$T, applied parallel to three different crystallographic directions i.e., [100], [110] and [111]. (b) The ^{77}Se NMR spectra at representative temperatures obtained with the magnetic field applied along [111]. (c) The temperature dependence of the full width at half maximum (FWHM) for each one of the four ^{77}Se NMR lines shown in (b).

from the NMR spectra. First, no splitting of the NMR lines is observed and the ratio of the relative integrated areas for peaks 1-4 remains 3:1:3:1 down to 20 K, which is much lower than the transition temperature. This result is important since any symmetry lowering from the $P2_13$ crystal structure would result in a partial or full splitting of the 3:1:3:1 pattern observed. Second, the Full Width at Half Maximum (FWHM) for each one of the four spectral lines increases by decreasing temperature (Fig. 2c) and follows the temperature dependence of the bulk magnetization as measured by the magnetometer (solid line in Fig. 2c). This is the typical behavior of inhomogeneous broadening. Both of these results are important since they show that there is no modification of the crystal lattice to a state with symmetry lower than the original cubic $P2_13$ space group.

4. Conclusions

We have presented magnetization and high field ^{77}Se NMR data in single crystals of the magneteoelectric compound Cu_2OSeO_3. The temperature and the field dependence of the magnetization suggest that the high field magnetic state is a simple collinear ferrimagnetic arrangement with three majority and one minority Cu^{2+} magnetic moment. The ferrimagnetic ordering temperature is $T_c \simeq 60$ K and the preferential direction of the magnetization is along the [100] crystal axis. The magnetization data can be understood by a simple mean field model with two nearest neighbor magnetic interactions, one ferromagnetic between Cu2 ions and one antiferromagnetic between Cu1 and Cu2 sites. The values of the exchange parameters ($J_{\rm afm} \simeq 68$ K, $J_{\rm fm} \simeq -50$ K) were obtained by fitting a wide high temperature range of the magnetization data.

The ^{77}Se NMR spectra do not show any splitting or abrupt broadening through the magnetic transition thus there is no reduction in the crystal symmetry from the high temperature $P2_13$ space group. Our results are in agreement with previously published data in polycrystalline samples by Bos *et al.*,[14] and exclude the possibility that the magnetoelectric coupling in Cu_2OSeO_3 proceeds via a spontaneous lattice distortion below T_c. This is also confirmed by far-infrared[18] and Raman[19] studies in single crystals of Cu_2OSeO_3 prepared in the same way as our crystals.

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