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Magnetic hyperfine field at Cr site in $AgCrO_2$ given by perturbed angular correlations

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Abstract This work presents an electric field gradient and magnetic hyperfine field study, in the $AgCrO_2$ multiferroic with triangular spin lattice.

The temperature dependence of the electric field gradient (EFG) and magnetic hyperfine field (MHF) at Cr site was studied at ISOLDE via perturbed angular correlation measurements with the ^{111}In probe, at room temperature and below the Néel temperature (T≤21 K) down to 12 K. The results show the presence of two distinct local environments. One axial symmetric EFG with a very low MHF, and a non axially symmetric EFG with a much higher one. The temperature dependences of MHF magnitude and of the angle between the MHF and the principle component of the EFG are investigated.

Keywords Delafossite structure · Magneto-electric · Triangular lattice · Distortions · Perturbed Angular Correlation

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1 Introduction

Over the last years a large interest has been devoted to materials presenting a coupling between magnetic, electric and/or elastic orders [1, 2]. Among these materials we can find the $AgCrO_2$, of the delafossite family, where recently a magnetoelectric coupling has been ascertained [3]. With this coupling and consequent possibility of manipulation of the magnetic degrees of freedom, electrically or vice-versa, one can open a vast set of applications [4], namely, for new non volatile memories for computers and cellular phones [5].

Delafossite compounds are part of a family of ternary oxides having the general formula ABO_2, with a monovalent metal atom (Ag, Li, Cu, ...) in the A-site and a trivalent transition element (Cr, Fe, Co, ...) at the B-site. In this structure, the A cation is linearly coordinated to two oxygen ions and is occupied by a noble metal cation which normally has a +1 oxidation state. The B cation is located in a slightly distorted edge-shared BO_6 octahedra with a central metal cation having a +3 charge with a twofold linear coordination parallel to the c-axis to the A cation (Fig.1 a) [6]). The delafossite structure crystallizes into the $R\bar{3}m$ space group with the following lattice parameters: $a, b = 2.98$ Å and $c = 18.5$ Å with $\alpha, \beta, \gamma = 90°, 90°, 120°$ [7].

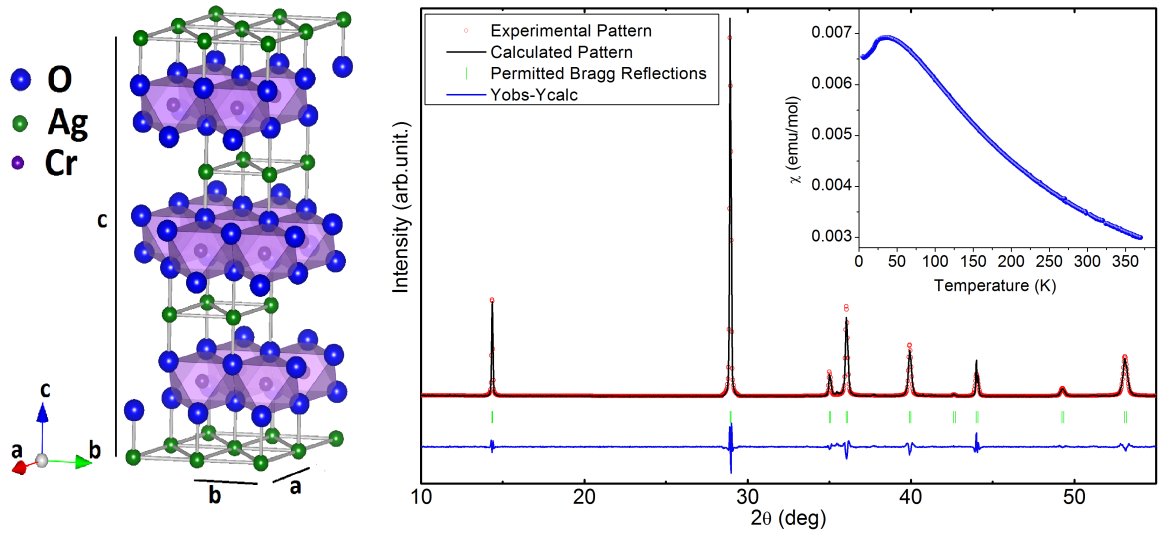

Fig. 1: (a) Ball and stick model representation of the delafossite structure. (b) Rietveld refinement output (single phase) and (inset) magnetic susceptibility data as a function of temperature of the $AgCrO_2$ sample sintered by solid state reaction after a final annealing at 900 °C during 12 hours in O_2 flow.

The magnetic structure of this system has been described as a 120° spin spiral structure, typical for Heisenberg spin exchange on a triangular lattice, with a weak interlayer coupling. At the microscopic scale, the origin of magneto-electric coupling in triangular-lattice antiferromagnet, with geometrically frustrated spin systems is still uncleared and has not a straight forward explanation. In fact, *Seki et al* [3] confirmed recently that the geometrical frustration of the antiferromagnetic interaction in $ACrO_2$ (A=Ag, Cu) favors a 120° spiral spin structure with a modulation vector (0.327 0.327 0) [8] and ferroelectricity emerges upon that spin order [3, 9]. Furthermore, they predicted that many trigonal materials with the same magnetic arrangement can be magnetoelectric multiferroic.

Working forward to study the microscopic origin of this spin arrangement and the origin of the magnetoelectric coupling, we performed a study with the perturbed angular correlation technique (PAC). This technique has already proven to be a suitable technique to study the complex magnetic order in a frustrated spin system [10]. In particular, in this work we study the electric field gradient and

magnetic hyperfine field at the Cr site, and how they evolve below the antiferromagnetic/ferroelectric transition.

2 Experimental and Results

Polycrystalline samples of $AgCrO_2$ were prepared using a standard high temperature solid state reaction where a stoichiometric mixture of $AgNO_3$ and Cr_2O_3 were used as starting materials. The powders were mixed and grinded several times in an agate mortar until a very fine homogeneous powder mixture was obtained. A pellet was formed and submitted to several heat treatments in a rich O_2 flow atmosphere. After a final heat treatment at 900 °C the sample was characterized by x-ray diffraction and magnetically, showing a single crystallographic phase.

Figure 1 b) shows the graphical output of the rietveld refinement fit (using the FULLPROF program [11]) performed in the $AgCrO_2$ sample after the final treatment. With this analysis we were able to match the pattern to a $AgCrO_2$ phase with rombohedric $R\bar{3}m$ space group with the unit cell parameters $a, b = 2.986(3)$ and $c = 18.509(3)$. The values were obtained in the last refinement cycle using 11 refining parameters.

The inset on Figure 1 b) shows the temperature dependence of the magnetic susceptibility measured after field cooling with H=100 Oe. The results show that the sample presents, as expected, a paramagnetic to antiferromagnetic phase transition at 21 K. Also, the effective paramagnetic moment and the Curie Weiss constant are accordingly to the expected ones ($\theta_P = -200$ K and $\mu_{eff} = 3.73\ \mu_B$). This is an indication that, despite of the magnetic frustration commonly observed in this systems (in this case $|\theta_P|/T_N \sim 9$), a 3D magnetic order is present below T_N. Both x-ray and magnetization results are in agreement with literature [7, 12].

The Perturbed Angular Correlation (PAC) measurements were performed after ion implanted radioactive $^{111}In \rightarrow ^{111}Cd$ probe ($I = 5/2$) at ISOLDE and measured at room temperature (RT) and below T_N down to 12 K. Measurements were conducted after a suitable annealing procedure at 973 K for 20 minutes in O_2 flow to remove implantation defects. The spectra were obtained using a setup of 6 BaF_2 scintillation counters. In all temperatures the fits were made considering static electric field gradients (EFG) distributions which were assumed to be Lorentzian-like. Typical R(t) spectra at different temperatures are shown in Figure 2 a).

The R(t) spectrum obtained at RT revealed only one local environment (LE), as one can clearly see from the respective Fourier transform. One frequency triplet corresponding to one electric field gradient EFG^u, is clearly identified. EFG^u is characterized by $V_{zz} = 6.57(4) \times 10^{21}$ V/m^2 and an asymmetry parameter $\eta_1 = 0.0(1)$, characteristic of an EFG with axial symmetry. The EFG parameters obtained here are in agreement with the ones reported in the literature for RT measurements [13]. According to previous works the probe nucleus $^{111}In \rightarrow ^{111}Cd$ goes to a substitutional site on the lattice, the Cr^{3+} trivalent B-site [10, 13].

On decreasing temperature, at and below T_N, visible changes are observed (see Fig.2 a)), a damping of the perturbation function $R(t)$ and a line broadening in the Fourier spectra. This result is consistent with the presence of the expected combined electric and magnetic hyperfine interaction.

In order to perform the low temperature fits, the unique EFG present at RT proved to be insufficient. Several fit models were tried, being the simplest by only considering a unique combined interaction. However this model revealed to be not enough to fully account for the experimental data at low temperature.

A different approach was to consider a model based in recent results obtained in the similar compound $CuCrO_2$ [3] where slight deformations of the Cr triangular lattice where observed below the Néel temperature. With this model the spin arrangement proposed by *Kadowaki*[8] and more recently confirmed by *Seki and coworkers* [3] and *Kan et al.* [9] was considered.

Analyzing this spin arrangement one validates that two nonequivalent probe substitutions in the lattice are possible, see Fig. 2 c). In this magnetic arrangement the spins on the in-plane Cr triangular lattice form a 120° angle with each other. In "Type I" environment the probe replaces the atom with spin nearly along the c-axis direction and in "Type II" the probe replaces one of the spins oriented 120° from the c-axis. In this way and taking into account the above mentioned spin arrangement four combined interactions should be used to perform the fits.

The R(t) spectrum obtained at 21 K was fitted having the previous assumption into consideration, *i.e.* four combined interactions. Two corresponding to an undistorted local environment ($\eta = 0$) and

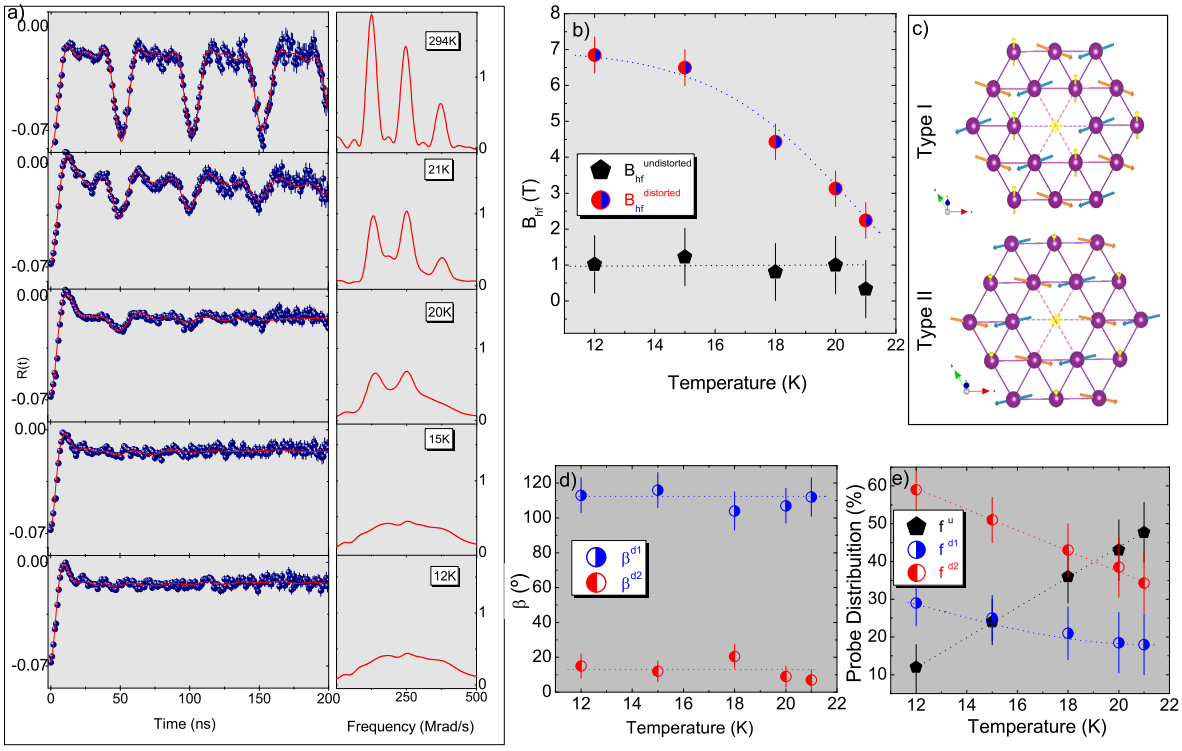

Fig. 2: a) R(t) experimental functions (blue solid points and Y-bar error) and correspondent fits (red line) at T_M=294 K, 21 K, 20 K, 15 K and 12 K. Corresponding Fourier transforms are displayed on the right side. b) Magnetic hyperfine field as a function of temperature. c) Two possible spins directions surrounding the PAC probe in the triangular Cr planes in $AgCrO_2$ depending upon the probes location. d) Angle between the principal component of EFG and B_{HF} as a function of temperature. e) Probe distribution among the different lattice positions as a function of temperature. Dotted lines are guidelines for the eyes.

two corresponding to a distorted one ($\eta \neq 0$). However, it was verified that for the non distorted environment ($\eta = 0$) the magnetic hyperfine field is small and thus we cannot resolve the two distinct orientation of the MHF. Accordingly we performed the fit considering only one fraction (one MHF orientation) and thus the value found for the angle β^u (β, angle between the magnetic hyperfine field and the principal component of the electric field gradient V_{zz}) has not a straightforward physical meaning.

The value found for the magnitude of the MHF for the undistorted local environment was $B^u_{hf} = 0.5(2)$ T with an EFG with principal component $V_{zz} = 6.57(4)\times10^{21}$ V/m^2 and $\beta^u \sim 60°$. The distorted local environment have the same EFGs (that differ from EFG^u) with $V^d_{zz} = 7.3(4) \times 10^{21}$ V/m^2 and $\eta^d \approx 0.5$ (1). The magnetic hyperfine field was considered the same $B^{d1}_{hf} = B^{d2}_{hf} \approx 1.5(5)$ T and $\beta^{d1} \sim 120°$ and $\beta^{d2} \sim 10°$. Fig. 2 d) shows β^{d1} and β^{d2} as a function of temperature. As it can be seen they are nearly temperature independent. Below 21 K the MHF increase reaching $B^u_{hf} \sim 1.0(5)$ T and $B^d_{hf} \sim 7(2)$ T at 12 K (see Fig. 2 b)).

In Figure 2 e) we show the temperature evolution of the probe distribution among the undisturbed (one site - f^u) and the two distorted ones (f^{d1} and f^{d2}). It is possible to see that at 12 K only a small fraction around 10% remain undistorted. Moreover one sees that the temperature dependence of f^{d1} and f^{d2} roughly respects the rule $f^{d1} = 2f^{d2}$, expected by symmetry.

In this work it has been shown that the combined interactions between the electric field gradients and the magnetic hyperfine fields which are observed at and below T_N, are compatible with a scenario

where local distortions are present. In order to relate the observed local scale phenomena with the magneto-elastic properties of this material further research is underway.

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