63,65Cu NMR study of the antiferromagnet CuCrO2

A Smolnikov1, I Arapova1, V Ogloblichev1, Y Piskunov1, A Sadykov1, K Mikhalev1, Y Furukawa2, S Barilo3 and S Shiryaev3

1 M.N. Mikheev Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, Yekaterinburg 620108, Russia
2 Ames Laboratory; Department of Physics and Astronomy, Iowa State University; Ames, Iowa 50011, USA
3 Institute of Solid State Physics and Semiconductors, National Academy of Sciences of Belarus, Minsk 220072, Belarus

E-mail: arapova@imp.uran.ru

Abstract. The 63,65Cu NMR and NQR spectra have been obtained in single crystal sample of CuCrO2 in the magnetically ordered phase. The components of the electric field gradient tensor (EFG) characterizing the structure of the nearest environment of copper ions are determined from the analysis of the spectra. Comparative analysis obtained data with similar data of paramagnetic phase showed that the local charge environment of copper nuclei does not change during the magnetic phase transition.

1. Introduction

Interest in oxides with delafossite structure is caused by their multiferroic behavior [1, 2]. The macroscopic electric polarization arises in CuCrO2 simultaneously with incommensurate proper-screw magnetic ordering of the Cr3+ ions below TN ≈ 24 K [3, 4]. A microscopic origin of the electric polarization, as well as its connection with the incommensurate long-range magnetic order remains yet under debate for this compound. A possible change of structural symmetry (R3m→C/2m) at TN is discussed in connection with the magnetic transition [4, 5]. The result of numerous studies of magnetic ordering in delafossites with different monovalent ions [6, 7] indicates on a significant role of the Cu+1 ions in the exchange interactions of magnetic ions Cr3+(S=3/2) and in a possible appearance of the electric polarization in CuCrO2. The 63,65Cu nuclei with spin I = 3/2 and significant quadrupole moments (63eQ = 0.220•10−24 cm2, 65eQ = 0.204•10−24 cm2) are sensitive local NMR probes of the charge distribution changes that may occur nearby copper in the magnetic ordered CuCrO2.

2. Samples and experimental procedure

The CuCrO2 sample was a single crystal with dimensions of 3×2×1 mm. Its preparation, structural and magnetic characterization are described in detail in [8]. Neutron scattering studies and bulk magnetization measurements were carried out on the single-crystalline samples [3, 8] taken from the same patch as the NMR crystal. NMR study was carried out on a homemade spectrometer equipped with a receiver produced by Thamway company and with a superconducting magnet of "Oxford Instruments" allowing to scan magnetic field from zero up to 90 kOe. The 63,65Cu NMR spectra were obtained using the standard spin echo technique τπ/2 - τdel - τπ - τdel - echo in the magnetic-field-scan mode at several irradiation frequencies 36.8 MHz and 49 MHz. The first pulse duration was τπ/2 = 1 µs, the RF amplifier power was N = 150 - 250 W. The 63,65Cu NQR spectra (H = 0) were obtained in
the frequency-scan mode at temperatures of liquid nitrogen and helium in two crystal orientations \( \mathbf{H} \parallel \mathbf{a} \) and \( \mathbf{H} \parallel \mathbf{c} \). The measurements were performed with a delay between RF pulses \( t_{\text{del}} = 15 \, \mu\text{s} \). A special simulation program Simul [9, 10] was used to calculate the shape of NMR and NQR spectra obtained in the magnetically ordered state. The program calculates the energy levels and probabilities of the corresponding \( \Delta m_I = 1 \) transitions obtained as a result of numerical diagonalization of the Hamiltonian taking into account the Zeeman, quadrupole, dipole and hyperfine interactions.

### 3. Experimental results and discussion

The components of the EFG tensors \( \{V_{ii}\} \) expressed through an asymmetry parameter \( \eta = (V_{XX} - V_{YY})/V_{ZZ} \approx 0 \) and quadrupole frequencies \( 63\nu_Q = V_{ZZ}63Q/2h = 27.0(4) \, \text{MHz} \), \( 65\nu_Q = V_{ZZ}65Q/2h = 25.0(4) \, \text{MHz} \) are reported in [9], where the \( ^{63,65}\text{Cu} \) NQR and NMR spectra were measured in the paramagnetic phase of the same sample. The main axis of the EFG tensor \( Z_\| \) is directed along the \( \text{O} - \text{Cu} - \text{O} \) bond (\( Z_\| \parallel \mathbf{c} \)) (figure 1).

![Figure 1. Fragment of the CuCrO2 crystal structure.](image)

In the delafossite structure of CuCrO2 the EFG at Cu\(^+\) ions is determined mainly by the nearest \( \text{O}^{2-} \) ions. The variation of their relative positions during transition to magnetic ordered phase should lead to a change of the charge distribution nearby the copper nuclei. Figure 2 shows the \( ^{63,65}\text{Cu} \) NQR spectra \((H = 0)\) in the paramagnetic phase (PM), in the antiferromagnetic phase (AF) and the curves used for spectrum processing. The inhomogeneous magnetic broadening of the \( ^{63,65}\text{Cu} \) NQR spectrum is determined by distribution in the crystal of the local dipole and isotropic hyperfine fields [9]. The two-peaked shape of the broadened NQR lines is indicative of an incommensurate magnetic order developing in CuCrO2 far below \( T_N \) [3, 4, 9-11]. The position of the center of gravity of the NQR line in the magnetically ordered phase coincides with the peak position, \( ^{63,65}\nu_{\text{NQR}} \), of the NQR lines in the paramagnetic phase, thus indicating that a product \( ^{63,65}\nu_{\text{NQR}} = ^{63,65}\nu_Q (1 + \eta^2/3)^{1/2} \) does not vary at the Cu sites upon magnetic phase transition.
Moreover, to determine the direction of the EFG principal axes in the magnetically ordered phase, the $^{63,65}$Cu NMR spectra were recorded in external magnetic fields directed along two mutually perpendicular crystallographic axes ($H \parallel a$ and $H \parallel c$) (figure 3). The simulating Cu NMR curves are calculated by using the same model of magnetic order as it was done for the corresponding Cu NQR curves in figure 2.

The difference in the number of lines used to describe the spectra recorded for two different orientations can be explained by the symmetry of the CuCrO$_2$ lattice. Based on the symmetry of that crystal, the authors of [1 – 4] argued in favor of the coexistence of six magnetic structures in the crystal with magnetic moments, the planes of rotation of which were perpendicular to the crystallographic directions [100], [110], and [010]. For each of those magnetic structures, the plane of rotation of magnetic moments of chromium included the axis $c$. Therefore, if the direction of the external magnetic field coincides with the direction of the axis $c$, the distribution of the local fields on the copper nuclei induced by each of the magnetic structures will be indistinguishable. However, in the case of the orientation $H \parallel a$, the normal to the plane of rotation of magnetic moments of chromium is either parallel to the direction of the external magnetic field or forms an angle of 60° with this direction. In these cases, the distributions of the projections local field on the major quantization axis also differ from each other. The narrow line 1 will correspond to the structure with the normals to the plane of rotation that are parallel to the direction of the external magnetic field. The broadened double-peaked line 2 will correspond to the structure with the normals to the plane of rotation that form an angle of 60° with the direction of the external magnetic field [9, 10].

The quadrupole frequencies used for spectrum processing were $^{63}v_Q = 27.1(4)$ MHz and $^{65}v_Q = 25.1(4)$ MHz. The obtained values of $^{63,65}v_Q$ are very close to the data obtained in the paramagnetic phase. Thus, there are no significant changes in both the components of the EFG tensor and the directions of its main axes at the copper positions in the process of magnetic phase transition. These results allow us to conclude that configuration and orientation of the O – Cu – O chains do not change upon the magnetic phase transition.
Figure 3. $^{63,65}\text{Cu}$ NMR spectra of the central transition ($-1/2 \rightarrow 1/2$) and the satellites ($3/2 \rightarrow 1/2$, $-3/2 \rightarrow -1/2$) obtained at $T = 4.2$ K in external magnetic fields directed along two mutually perpendicular crystallographic axes ((a) $\mathbf{H} \parallel \mathbf{c}$ and (b) $\mathbf{H} \parallel \mathbf{a}$). Detailed information about lines 1, 2 is given in [9–11].

It is worth to note, that the spatially fluctuating charge density is considered as a possible mechanism of electric polarization in the delafossite transition-metal oxides with incommensurate helicoidal magnetic structure [12]. Among other things, such fluctuations of charge can be responsible for an additional broadening $\sim (\Delta \nu_Q)$ of the $^{63,65}\text{Cu}$ NMR (NQR) satellite lines in the first order of the perturbation theory and $\sim (\Delta \nu_Q)^2/\nu_0$ of the central transition line in the second order of the perturbation theory. It follows from an analysis of the obtained $^{63,65}\text{Cu}$ NMR spectra showed that the broadening of lines in the copper spectra due to possible fluctuations $(\Delta \nu_Q)$ does not exceed 3% of the quadrupole frequency $(\Delta \nu_Q)<0.03\nu_Q$. This inequality may serve as an upper limit in estimates of the spatial charge fluctuations existing in the magnetic ordered $\text{CuCrO}_2$ crystal.
Acknowledgments

The research was carried out within the state assignment of Ministry of Science and Higher Education of the Russian Federation (“Function” No AAAA-A19-11901290095-0).

References

[1] Seki S, Onose Y and Tokura Y 2008 Phys. Rev. Lett. 101 067204
[2] Kimura K, Nakamura H, Ohgushi K and Kimura T 2008 Phys. Rev. B 78 140401
[3] Frontzek M, Ehlers G, Podlesnyak A, Cao H, Matsuda M, Zaharko O, Aliouane N, Barilo S and Shiryaev S V 2012 J Phys: Condens. Matter 24 016004
[4] Poienar M, Damay F, Martin C, Hardy V, Maignan A and Andre G 2009 Phys. Rev. B 79 014412.
[5] Aktas O, Truong K D, Otani T, Balakrishnan G, Clouter M J, Kimura T and Quirion G 2012 J Phys: Condens. Matter 24 036003
[6] Terada N, Khalyavin D, Manuel P, Tsujimoto Y and Belik A A 2015 Phys. Rev. B 91 094404
[7] Sobolev A, Rusakov V, Moskvin A, Gapochka A, Belik A, Glazkova I, Akulenko A, Demazeau G and Presniakov I 2017 J Phys.: Condens. Matter 29 275803
[8] Frontzek M, Haraldsen J T, Podlesnyak A Christianson A D, Fishman R S, Sefat A S, Qiu Y, Copley J R D, Barilo S, Shiryaev S V and Ehlers G 2011 Phys. Rev. B 84 094448
[9] Smol’nikov A G, Ogloblichev V V, Sadykov A F, Verkhovskii S V and Mikhailov K N 2017 Phys. of Met. and Metallogr. 118 134
[10] Ogloblichev V V, Smolnikov A G, Sadykov A F, Piskunov Yu P, Gerashenko A P, Furukawa Y, Kumagai K, Yakubovsky A Yu, Mikhailov K N, Barilo S N and Shiryaev S V 2018 JMMM 458 1
[11] Sakhratov Yu A, Svistov L E, Kuhns P L, Zhou H D and Reyes A P 2014 JETP 119 880
[12] Arima T, 2007 J. Phys. Soc. Jap. 76 073702