Non-equivalence of Cu crystal sites in $CuGeO_3$ as evidenced by NQR

LETTER TO THE EDITOR

Non-equivalence of Cu crystal sites in CuGeO₃ as evidenced by NQR

A A Gippius†‖, E N Morozova†, D F Khozeev†, A N Vasil'ev†, M Baenitz‡, G Dhalenne§ and A Revcolevschi§

† Faculty of Physics, Moscow State University, 119899 Moscow, Russia
‡ MPI for Chemical Physics of Solids, Bayreuther Strasse 40, H16, D-01187 Dresden, Germany
§ University of Paris, 91405 Orsay Cédex, France

E-mail: `gippius@mail.ru`

Abstract. Nuclear quadrupole resonance results on the inorganic spin–Peierls compound CuGeO₃ were re-examined using a single crystal and enhanced resolution. A clear splitting of ^{63,65}Cu NQR lines of about 250 kHz at 4.2 K was observed. Such a splitting has not been previously seen in Cu NQR spectra measured on polycrystalline samples of CuGeO₃ (Itoh M *et al* 1995 *Phys. Rev.* B **52** 3410, Kikuchi *et al* 1994 *J. Phys. Soc. Japan* **63** 872). The mean frequency of the Cu doublet is in agreement with the Cu NQR frequency observed on powder samples. The splitting does not disappear with increasing temperature above T_{sP} exhibiting only a slight kink at around 16 K. This points to a non-magnetic origin of the splitting which can be attributed to existence of at least two non-equivalent Cu crystal sites in CuGeO₃ structure, as predicted by precise x-ray study and EPR measurements (Hidaka M *et al* 1997 *J. Phys.: Condens. Matter* **9** 809, Yamada I *et al* 1996 *J. Phys.: Condens. Matter* **8** 2625).

CuGeO₃ is known as the first inorganic spin–Peierls compound exhibiting a transition into the spin ordered state at $T_{sP} \cong 14.5$ K. It is generally believed that it crystallizes in the space group *Pbmm* (D_{2h}^5) reported by Völlenkle *et al* [5] in 1967. This structure has an inversion centre at the midpoint between nearest-neighbour Cu sites on the *c*-axis and therefore two Cu sites in the neighbouring CuO₆ octahedra are identical. However, two papers recently appeared, which demonstrated that the symmetry of the CuGeO₃ structure must be lower than that given by the *Pbmm* space group. In the first paper [4] Yamada *et al* reported the results of an EPR study of CuGeO₃ which revealed the existence of the Dzyaloshinsky–Moriya (DM) antisymmetric exchange interactions of the form $\sum_i \boldsymbol{d}_{ii+1} \cdot (\boldsymbol{S}_i \times \boldsymbol{S}_{i+1})$ between nearest-neighbour Cu spins along the *c*-axis. To allow this interaction, the crystal structure must have no inversion centre in between nearest Cu sites. In the second paper [3] Hidaka *et al* re-examined the room temperature crystal structure of CuGeO₃ by x-ray diffraction experiments and observed the new superlattice reflections, which were attributed by the authors to the $P2_12_12$ (D_2^3) space group with the $2a_p \times b_p \times 4c_p$ unit cell where $a_p \times b_p \times c_p$ is the pseudo-unit cell proposed by Völlenkle *et al* [5]. This structure has no inversion centre and therefore allows the antisymmetric interaction observed by Yamada *et al* [4].

‖ Corresponding author and present address: Low Temperature Department, Faculty of Physics, Moscow State University, Vorob'evy Gory, 119899 Moscow, Russia.
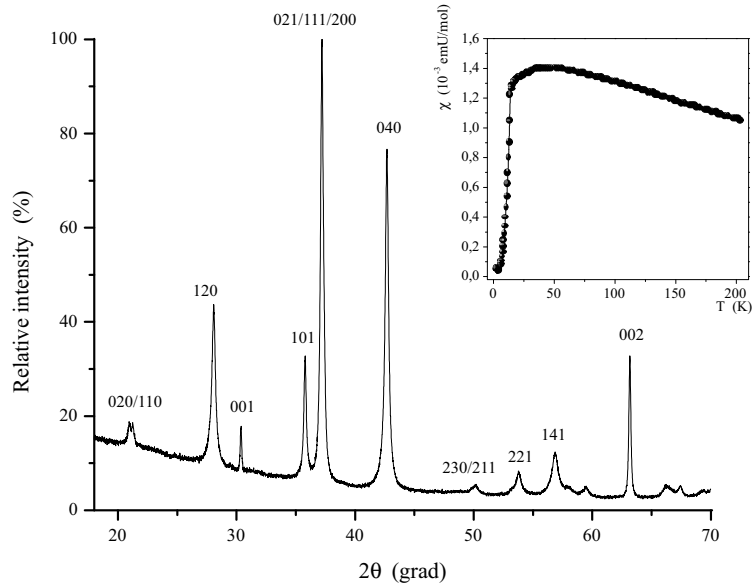
Figure 1. X-ray diffraction spectrum with Miller indexes of CuGeO$_3$ single crystal. Relative intensities are partially affected by residual texture effect. Inset: the temperature dependence of the dc magnetic susceptibility measured at $H = 5$ T.

It is well known that nuclear quadrupole resonance (NQR) is a powerful microscopic tool which is very sensitive to structural peculiarities and especially to non-equivalence of the crystal sites occupied by NQR nuclei. However, in the literature we found only two papers where the NQR spectra of CuGeO$_3$ have been reported: by Kikuchi *et al* [2] and by Itoh *et al* [1]. In both papers NQR spectra have been measured on polycrystalline samples of CuGeO$_3$ and contain a single NQR line at frequency of 34.22(1) MHz and 31.66(2) MHz for ^{63}Cu and ^{65}Cu isotope, respectively. This seems to coincide with only one non-equivalent position of Cu in CuGeO$_3$ and therefore supports the crystal structure of the *Pbmm* space group [5]. Nevertheless, to clarify the situation we decided to re-examine the NQR spectra of CuGeO$_3$ by performing careful NQR measurements on a high quality single crystal of CuGeO$_3$.

The single crystal of CuGeO$_3$ used in our experiments was grown at the University of Paris by a floating zone technique [6]. No special annealing procedure like that described in [3] was used after the sample growth. The sample was characterized by the x-ray diffraction spectrometer STADI-P using Cu Kα_1 radiation. The resulting spectrum presented in figure 1 shows the absence of impurity phases and confirms that the sample is a monophase high quality single crystal with CuGeO$_3$ structure corresponding to the *Pbmm* space group, as proposed in [5]. The sample has been also characterized by the dc-magnetization technique. The temperature dependence of the dc magnetic susceptibility measured at magnetic field $H = 5$ T is presented in the inset in figure 1. It shows the typical behaviour of a spin–Peierls system with the broad maximum around 45 K followed by an abrupt fall near the temperature of spin–Peierls transition $T_{sP} \cong 14.5$ K.

Cu NQR spectra were obtained using a point-by-point spin-echo technique in a temperature range of 4.2–34 K. In order to increase the sensitivity and decrease the influence of the resonance circuit ringing after the RF pulse we used a low-noise fast-recovery broad-band preamplifier MITEQ AU-1313 and a full 32-pulse phase cycling sequence. The spin-echo signal was
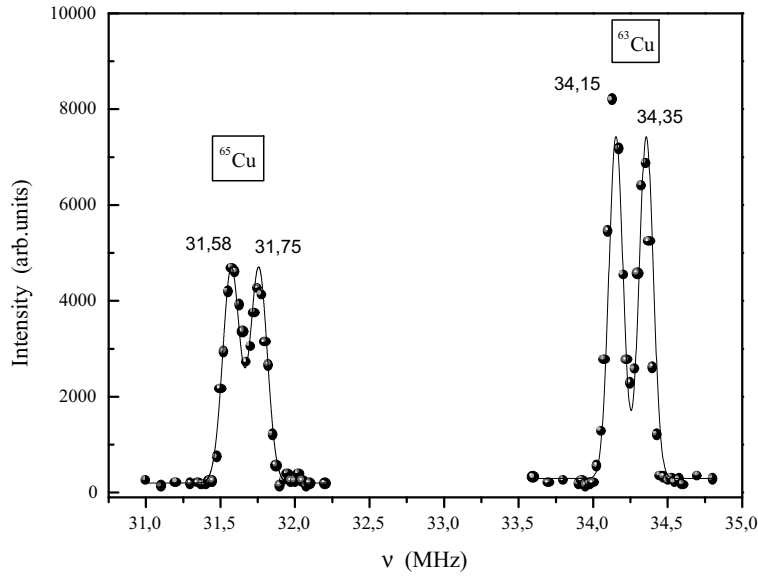
Figure 2. ^{63,65}Cu NQR spectrum of CuGeO$_3$ single crystal measured at 4.2 K.

accumulated during 2 (at 4.2 K)–32 (at 34 K) repetitions of the phase cycling sequence taken at each frequency point. In order to increase the resolution of spectra registration we used a relatively long (90°) RF pulse of 10 μs duration with an effective excitation bandwidth less than 100 kHz and decreased the filter width of the spectrometer down to 100 kHz.

The ^{63,65}Cu NQR spectrum of the CuGeO$_3$ single crystal measured at 4.2 K is presented in figure 2. To our great surprise it shows a clear line splitting for both Cu isotopes. In the following we will concentrate only on the ^{63}Cu NQR line. Since each doublet component exhibits almost the same amplitude and width, the spectrum was fitted to the sum of two Gaussian functions with equal amplitude and width. The maxima of the resulting best fit (solid line in figure 1) correspond to frequencies $\nu_{c1} = 34.125(5)$ MHz and $\nu_{c2} = 34.375(5)$ MHz. It is worth noting that the mean frequency $\nu_c = 0.5 \times (\nu_{c1} + \nu_{c2}) = 34.25(1)$ MHz is in agreement with the ^{63}Cu NQR frequency obtained in [2] and [1]. The full line width at half maximum (FWHM) $\cong$ 300 kHz is very close to that found by Kikuchi *et al*, while the individual width of each Gaussian component is about 90 kHz.

The origin of this symmetric NQR line splitting can be either magnetic caused by some internal local magnetic field appearing at the Cu site below the spin–Peierls ordering temperature $T_{sP} \cong 14.5$ K or structural. In order to distinguish between these two possibilities we measured NQR spectra of CuGeO$_3$ at various temperatures below and above T_{sP}. Several typical spectra are presented in figure 3. The resulting temperature dependence of the line splitting $\Delta\nu = \nu_{c2} - \nu_{c1}$ is plotted in figure 4(b). We also calculated the mean frequency ν_c at each temperature point and plot it in figure 4(a) together with the temperature dependence of the NQR frequency obtained by Itoh *et al* [1]. This reveals that the mean frequency ν_c coincides within the experimental error with the NQR frequency in a polycrystalline sample [1]. From these data it is clear that the line splitting does not disappear at T_{sP} but exhibits a kink slightly above T_{sP} whereas $\nu_c(T)$ does not feel T_{sP} and is almost temperature independent in good agreement with results of Itoh *et al* [1] and Kikuchi *et al* [2]. This fact rules out the magnetic origin of the splitting and confirms the existence of two non-equivalent Cu sites in

23 K

16.5 K

10.7 K

8 K

4.2 K

33,6   33,8   34,0   34,2   34,4   34,6   34,8

ν (MHz)
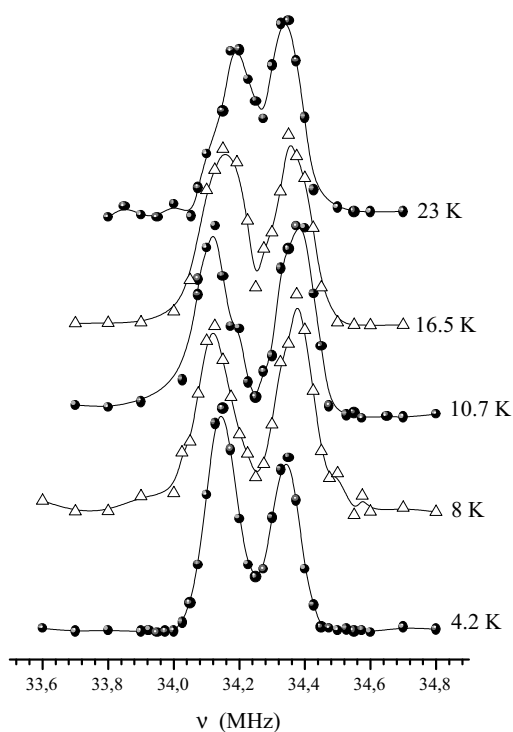
Figure 3. ^{63}Cu spectra obtained at different temperatures.

the CuGeO$_3$ crystal structure. Shifting of the kink to 16 K possibly reflects the instability of Cu[O(2)]$_2$ ribbons against twist or rotation deformations slightly above T_{sP} found by Braden *et al* [7].

Since the splitting of the NQR line is nearly symmetric the occupation factor of both non-equivalent Cu sites should be equal to 1/2. According to the results of Hidaka *et al* [3] four neighbouring CuO$_6$ octahedra stacked along the *c*-axis are slightly distorted thus forming the superlattice along the *c*-axis. The existence of long-range order of the octahedral distortion is confirmed by observing the x-ray reflections corresponding to the superlattice which could not be observed if the distortions have a random spatial distribution. It should be noted that the superlattice observed in [3] appears due to the special procedure of annealing and very slow cooling down of the CuGeO$_3$ single crystal grown by the floating zone method. If one uses only the as-grown crystal (as we and Yamada *et al* did) the superlattice is not formed due to the fast cooling of the sample, which causes a random ordering of the distorted CuO$_6$ octahedra along the *c*-axis. This is confirmed by the absence of the superlattice reflections in the x-ray spectrum of our CuGeO$_3$ crystal (see figure 1). However, even in that case it is possible to observe the NQR line splitting since the NQR frequency depends mainly on the local symmetry of the Cu site.

The question arises, why do we observe only two NQR line and not four as could be predicted from [4]? According to the structure refinement performed in this paper one can divide four non-equivalent superlattice Cu sites into two pairs (Cu1, Cu3) and (Cu2, Cu4) with close values of copper–oxygen distances. We can suppose that the resolution of the NQR method is not enough to distinguish between two Cu sites within the pairs. Since the EPR results by Yamada *et al* show the existence of the antisymmetric DM exchange interactions between nearest-neighbouring Cu spins along the *c*-axis we can conclude that Cu-site non-
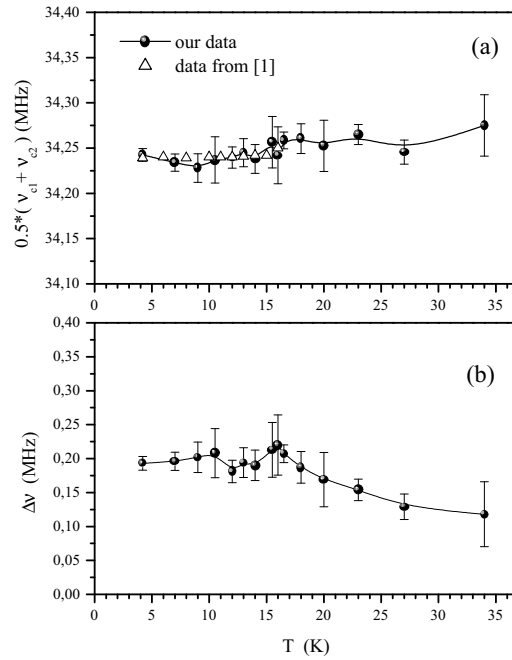
Figure 4. (a) Mean frequency of ^{63}Cu NQR line in dependence on temperature. For comparison the NQR frequency values obtained for a polycrystalline sample by Itoh *et al* [1] are shown. (b) The temperature dependence of the line splitting $\Delta\nu$.

equivalency occurs on a short-range scale, probably between nearest-neighbour Cu sites along the *c*-axis.

In conclusion, we have observed the splitting of ^{63,65}Cu NQR lines in a CuGeO$_3$ single crystal. The splitting does not disappear with increasing temperature above T_{sP}. This demonstrates the non-magnetic origin of the splitting which can be attributed to the existence of at least two non-equivalent Cu crystal sites in the CuGeO$_3$ structure, as predicted by precise x-ray and EPR study [3, 4].

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