NMR and NQR study of the tetrahedral frustrated quantum spin system Cu$_2$Te$_2$O$_5$Br$_2$ in its paramagnetic phase

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The quantum antiferromagnet Cu$_2$Te$_2$O$_5$Br$_2$ was investigated by NMR and NQR. The $^{125}$Te NMR investigation showed that there is a magnetic transition around 10.5 K at 9 T, in agreement with previous studies. From the divergence of the spin-lattice relaxation rate, we ruled out the possibility that the transition could be governed by a one-dimensional divergence of the spin-spin correlation function. The observed anisotropy of the $^{125}$Te shift was shown to be due to a spin polarization of the 5$x^2$ “E” doublet of the [TeO$_5$] tetrahedra, highlighting the importance of tellurium in the exchange paths. In the paramagnetic state, Br NQR and NMR measurements led to the determination of the Br hyperfine coupling and the electric field gradient tensor, and to the the spin polarization of Br $p$ orbitals. The results demonstrate the crucial role of bromine in the interaction paths between Cu spins.

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I. INTRODUCTION

In quantum antiferromagnets, triangular or tetrahedral coordination generates strong frustration. Unusual singlet ground states deriving from this frustration have been theoretically predicted and actively searched for in the recent years, mainly on Kagome or pyrochlore systems, in which the frustrated units (triangle or tetrahedra) are sharing corners. A different type of geometry, in which the tetrahedra units are isolated, and only weakly coupled has been discovered with the geometry, in which the tetrahedra units are isolated, and

Nevertheless, the results of Jensen et al. and Jagličič et al. appear to favor a 3D over 1D nature of the magnetic transition. It is likely that both the intratetrahedral (and thus the frustration), leading to a creation of spin-gaps, and the intertetrahedral interactions, inducing a magnetic long range order, are present and compete together.

One of the important unsettled questions is the relative strength of the various exchange couplings within and between tetrahedra, which determine the dimensionality of the system. In this paper, we present NMR and NQR measurements performed on single crystals of Cu$_2$Te$_2$O$_5$Br$_2$. The purpose of this study was to address the question of the magnetic phase dimensionality via an investigation in the vicinity of the phase transition and to determine the spin polarization of the Cu ligands. One challenge that came along was the rather intricate assignment of the various NMR transitions possible in this system.

II. TELLURIUM NMR

A. Spectrum structure

Tellurium has two NMR-active isotopes and both have a spin+$\uparrow$ nucleus, but the natural abundance of $^{125}$Te is about 8 times higher than the one of $^{123}$Te. For this reason, all Te NMR measurements were performed on $^{125}$Te. Cu$_2$Te$_2$O$_5$Br$_2$ crystalizes in the $\overline{P}^\perp$ $(a = b = 7.8$ Å,
The elementary pattern Cu₂Te₂O₅Br₂ is present four times in each unit cell. As a consequence, although $^{125}\text{Te}$ has a spin-½ nucleus and therefore yields to a single resonance line, the crystal has four inequivalent Te sites for an arbitrary orientation with respect to the direction of the external magnetic field $B_0$. Thus, the $^{125}\text{Te}$ NMR spectrum in Cu₂Te₂O₅Br₂ is generally composed of four lines. However, by applying the field in the $ab$-plane, two sites become equivalent, while applying it along the $c$-axis, all four sites become equivalent (see Fig. 1 for a full description of the crystal symmetry, see e.g. the article of Johnsson et al.).

**B. Hyperfine shift**

The temperature dependence of the electron spin susceptibility of Cu₂Te₂O₅Br₂ has been extensively studied by means of DC and AC susceptibility measurements. NMR measurements provide a way to probe the local electron spin susceptibility through hyperfine interactions with the advantage of being essentially insensitive to paramagnetic impurities. This is of particular interest for probing magnetic systems at low temperature when the contribution from paramagnetic impurities becomes larger than the system intrinsic susceptibility. The temperature dependence of the resonance frequencies, proportional to the macroscopic spin susceptibility, of the four inequivalent $^{125}\text{Te}$ nuclei in the crystal and their temperature dependence measured in a field of 9 T parallel to a direction nearly parallel to [110] is shown in Fig. 2. The data is superimposed to the SQUID susceptibility measurements performed with a field of 0.1 T oriented along [110] on the same single crystal.

The data plotted in Fig. 2 allows for the determination of the $^{125}\text{Te}$ hyperfine coupling by comparing the temperature dependence of the NMR frequencies to the temperature dependence of the magnetic susceptibility as shown in Fig. 3. In doing so, we took advantage of the multiple sites, and thus the multiple resonances, to determine the zero-shift frequency as the extrapolated frequency at which all sites have the same resonance frequency, in the present case $f_0 \approx 121.5$ MHz. This value corresponds to the $^{125}\text{Te}$ frequency for which the contribution of the Cu electron spins polarization is zero. Note however that it is not the resonance frequency of the “bare” $^{125}\text{Te}$ nuclear spin (121.07 MHz) since the Te electron shells also shift (essentially isotropically) the resonance. We observe here that this shift is about 0.35%, which is in the range of the observed shifts in transition-metal tellurides. Conjunctively, the dependence of the NMR frequencies on the crystal orientation (see Fig. 4) yields to the full determination of the hyperfine tensor. The data shown in Fig. 4 we deduced that the tellurium hyperfine shift (re-
reflecting the spin susceptibility) is mainly isotropic with a small anisotropic part in the \(ab\)-plane along a principal axis nearly parallel to the \([110]\) direction. Assuming an environment of axial symmetry (i.e. neglecting a small anisotropy in the plane perpendicular to \([110]\)), we can define the hyperfine shift along the external magnetic field \(B_0\) as 
\[ K(\theta) = K_{iso} + K_{ax}(3\cos^2\theta - 1)/2, \]
where \(\theta\) is the angle between \(B_0\) and the principal anisotropy axis of the Knight shift tensor \(K\). \(K_{iso}\) is the isotropic part of \(K\) and \(K_{ax}\) its anisotropic part along the principal anisotropy axis. The data lead to \(K_{iso}=3.2\,T/\mu_B\) and \(K_{ax}=0.8\,T/\mu_B\). A simple computation of the dipolar contribution of a single Cu electron spin cannot account for either the amplitude, which is 8 times weaker than the observed value, nor the angular dependence shown in Fig. 3. Considering transferred polarization on Br atoms cannot account for our observations as well. However, the measured angular dependence can be well described by considering the contribution of a Te orbital pointing towards the center of the Br-Br axis (see simulation shown in the inset of Fig. 4). Johnsson et al. pointed out that the Te atom is placed at the center of the \(O_3E\) tetrahedron, where \(E\) represents the \(5s^2\) lone pair of the Te atom. As shown in Fig. 4(b), the “E” apex of the tetrahedron stands in between two bromine atoms along the \(c\)-axis and the “E” orbital should therefore point in the \([110]\) direction. Our results thus suggest that part of the spin polarization is located in this orbital. This observation is fully compatible with the description of Johnsson et al. who suggest that the “E” orbital participates in the electronic structure binding the two neighboring Br atoms along the \(c\)-axis.

A quantitative estimation of this contribution is more delicate. First, it should be noted that a nearly axial symmetry around the \([110]\) direction is not compatible with a transfer of polarization from the three oxygens forming the tetrahedral environment of the tellurium atom, the “E” orbital being the fourth corner. In order to respect the symmetry, all 3 oxygen atoms should equally contribute, which is highly unlikely as their local environment differs dramatically from one another (see Fig. 5). Assuming that the “E” orbital can be described by a superposition of \(5s\) and \(5p\) orbitals (the tetrahedral symmetry of tellurium site suggests a \(sp^3\) hybridization) with one \(sp^3\) orbital pointing in the \([110]\) direction, we can write that 
\[ K_{ax} = 6/5f_p\mu_B, \]
where \(f_p\) is the fraction of unpaired electron in the corresponding orbital and \(<r^{-3}>\) is the mean value of \(1/r^3\) over the 5p orbital. By taking \(<r^{-3}> = 104 \cdot 10^{24}\,cm^{-3}\), one finds that \(f_p=0.7\%\). Similarly, from \(K_{iso} = 8\pi/3f_s\mu_B <\Psi(0)^2>\), with \(<\Psi(0)^2>\) being the square of the \(s\)-wave function at the nucleus averaged over those electrons at the Fermi surface, one can estimate the spin density in the \(5s\) contribution to \(sp^3\) orbital to give a contact term consistent with the isotropic spin part. Knowing that in an ideal \(sp^3\) orbital the \(s\) contribution is 4 times smaller than in pure \(s\) orbital, by taking the value given by Morton, i.e. \(<\Psi(0)^2> = 0.170 \cdot 10^{24}\,cm^{-3}\), one finds \(f_s=0.96\%\). This value is nearly identical to the value of \(f_p\) determined from dipolar contribution, which confirms this description in terms of \(sp^3\) orbital.

In conclusion, this contribution from the “E” orbital well describes the measurements. In addition, only a small spin polarization is needed in the Te “E” doublet to quantitatively account for the data. One should note...
that this interpretation is not compatible with the model proposed by Whangbo et al., in which the interactions between tetrahedral clusters are presumably from two types of super-supercrystalline paths: one is Cu-O-O-Cu path in the c direction and the other Cu-Br-Br-Cu path in the ab-plane with a path Cu-Br-Br-Cu. Our results suggest that the relevant path is Cu-Br-“E”-Br-Cu in the c direction.

C. Magnetic phase transition

It has been reported in an earlier study that the system undergoes a magnetic transition at a temperature $T_C$ of about 12 K in an external magnetic field of 9 T. In the present study, we observe that the $^{125}$Te resonance line suddenly disappears, as the temperature is lowered towards $T_C$. Although it was possible to observe the resonance at temperatures very close to $T_C = 12$ K, we were not able to observe the signal at temperatures below the magnetic transition temperature. This might be due to a significant broadening of the line, a strong shortening of the spin-spin relaxation time, a very large frequency shift or possibly a combination of these effects.

The temperature dependence of the $^{125}$Te spin-lattice relaxation rate measured on the lowest-frequency resonance (filled diamonds in Fig. 2 and Fig. 3).

The value determined by Lemmens et al.2.

III. BROMINE NMR AND NQR IN THE PARAMAGNETIC STATE

Halogen nuclei have a large quadrupole moment and they have been extensively studied by nuclear quadrupole resonance (NQR). NQR frequencies strongly depend on the ionic character of the M-X bond where M is a metal ion and X is the halogen ion. Both bromine isotopes have a spin-3/2 nucleus and $^{79}$Br and $^{81}$Br have almost equivalent natural abundance (Br nuclear properties are summarized in Table I). Cu$_2$Te$_2$O$_5$Br$_2$ contains tetrahedral arrangements of Cu atoms each one of them placed at the center of a distorted square CuO$_4$Br. As shown in Fig. 1 (see also Fig. 2), copper-bromine bonds are almost perpendicular to the c-axis of the crystal (90 ± 4.42 degrees). While Cu-Br and Cu$_{iii}$-Br$_{iii}$ are nearly parallel to the [110] direction, Cu$_{ii}$-Br$_{i}$ and Cu$_{i}$-Br$_{iii}$ are nearly parallel to the [101] one. As for tellurium, there are four inequivalent Br sites, which reduce to two inequivalent sites when the direction of $B_0$ is in the ab-plane, and to one single site if $B_0$ is parallel to the c-axis.

The total Hamiltonian of a Br nuclear spin in the Cu$_2$Te$_2$O$_5$Br$_2$ paramagnetic phase can be written as

\[ H = \sum \beta \cdot \mathbf{M} \cdot \mathbf{H} + Q \cdot \mathbf{I} \cdot \mathbf{I}^\text{\dagger} \]
\( \hat{H} = -\gamma_n \hbar B_0 \cdot \mathbf{I} - \gamma_n \hbar B_0 \cdot \mathbf{K} \cdot \mathbf{I} + \frac{eQ}{2I(2I-1)} \mathbf{I} \cdot \mathbf{V} \cdot \mathbf{I}, \) \( (1) \)

where the first term is the nuclear Zeeman Hamiltonian, the second term is the hyperfine Hamiltonian with \( \mathbf{K} \) the Knight shift tensor, and the third term is the quadrupole Hamiltonian, in which \( e \) is the elementary charge, \( Q \) is the quadrupole moment and \( \mathbf{V} \) is the electric field gradient (EFG) tensor. In its principal axis coordinate system \((X,Y,Z)\), the electric field gradient is diagonal and traceless. In this particular frame, Eq.\( \text{[1]} \) can be rewritten as

\[ \hat{H} = -\gamma_n \hbar B_0 \cdot \mathbf{I} - \gamma_n \hbar B_0 \cdot \mathbf{K} \cdot \mathbf{I} + \frac{1}{6} \nu_Q [3I_Z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2)], \] \( (2) \)

where \( \eta = (V_{XX} - V_{YY})/V_{ZZ} \) is the asymmetry parameter of the electric field gradients, and \( I_+ = I_X + iI_Y \) and \( I_- = I_X - iI_Y \) are the spin raising and lowering operators. For \( I = 3/2 \), \( \nu_Q = \nu_{NQR}(1 + \eta^2/3)^{-1/2} \), where \( \nu_{NQR} \) is the pure quadrupole resonance frequency.

At 15 K and in the absence of applied static magnetic field \( B_0 \), we observed two lines of identical intensity, one at \( 79\nu_{NQR} = 87.41 \text{ MHz} \) corresponding to the \( ^{79}\text{Br} \) quadrupole resonance, and the other at \( 81\nu_{NQR} = 73.02 \text{ MHz} \) corresponding to that of \( ^{81}\text{Br} \) (see Fig.\( \text{[7]} \)). These values are in agreement with the ratio of the nuclear quadrupole moments published in the literature\(^{22} \). Given the gyromagnetic ratio of the two bromine isotopes (c.f. Table\( \text{[I]} \), it is clear that the high-field approximation, which consists in considering the quadrupole interaction as a perturbation to the Zeeman one, will not yield to the correct transition energies for standard NMR field values. Unlike in the case of a Zeeman only or a quadrupole only Hamiltonian, the eigenvectors of the total Hamiltonian are not pure and therefore the so-called forbidden transitions can have a non-zero probability of occurring. For \( I = 3/2 \), the six possible transitions between the different available spin states are shown in Fig.\( \text{[8]} \)(a). As a consequence, analytical solutions cannot be calculated and a numerical computation is required.

For the present study, we developed a MATLAB routine to calculate the field dependence of the resonance frequencies and their associated intensities for Br sites in an arbitrary orientation of the field. The code was written such as to numerically diagonalize the Hamiltonian described in Eq.\( \text{[2]} \) compute the resonance frequencies from its eigenvalues and determine the expected relative intensity of each transition by calculating \( | < \varphi_i | \gamma_n \hbar \mathbf{B}_1 \cdot \mathbf{I} | \varphi_j > |^2 \), \( i \neq j \), where \( \mathbf{B}_1 \) is the radio-frequency excitation field created in the NMR coil and \( \varphi_i, \varphi_j \) are eigenstates of the Hamiltonian. In the \( x,y,z \) laboratory frame, \( \mathbf{B}_1 \cdot \mathbf{I} \) can be expressed in terms of the \( X,Y,Z \) projections of \( \mathbf{I} \) using two Euler angles, \( \Omega \) and \( \Psi \) defined in Fig.\( \text{[8]} \)(b)), giving \( \mathbf{B}_1 \cdot \mathbf{I} = B_1(I_X \sin \Omega \cos \Psi + I_Y \sin \Psi + I_Z \cos \Omega). \) The magnitude of the transition probabilities will thus strongly depend on the intensity of \( \mathbf{B}_0 \) as well as on its direction in the \( X,Y,Z \) frame, i.e. on the crystal orientation. This is particularly important in the present study where the Zeeman and quadrupolar terms are of comparable magnitude.

Having determined the bromine NQR frequencies by experiment, the remaining unknown parameters in the Hamiltonian given in Eq.\( \text{[2]} \) are the Knight shift tensor, the orientation of the EFG tensor principal axes with respect to the crystal axes and the associated asymmetry parameter \( \eta \). Several frequency and field scans were performed in the range 10 to 220 MHz and 5 to 15 T, respectively, with field applied along 4 different directions,
namely [100], [110], [210], and [001]. As an example, a frequency scan performed with \( B_0 = 14 \) T applied along [110] is shown in Fig. 9. The computed NMR frequencies and associated intensities calculated for various \( \eta \) values with \( \mathbf{K} = 0 \) were compared to the measurements. We concluded that the Z-axes of the local EFG tensors are along the Cu-Br bonds, one of which being oriented along a direction close to [110] (its exact direction is \( [1 \ 0.9834 \ -0.0124] \)). In addition, a largely anisotropic Knight shift tensor with its Z-axis also parallel to the Cu-Br bonds needed to be introduced in the Hamiltonian in order to match the computed frequencies with the measured ones. Furthermore, up to the precision of our measurements, we deduced that \( \mathbf{K} \) is isotropic in the \( X - Y \) plane perpendicular to the Cu-Br bond. To simplify the Hamiltonian, we defined the \( X \)- and \( Y \)-axes to be parallel to the \( X \)- and \( Y \)-axes of the EFG tensor. It was then possible to perform experiments to fully determine the Knight shift tensor. Indeed, for \( B_0 \) applied along a Cu-Br bond, that is \( [1 \ 0.9834 \ -0.0124] \), the temperature dependence of the Br resonance frequencies leads to the determination of \( K_{zz} \). Similarly, \( K_{xx} = K_{yy} \) can be determined by applying \( B_0 \) perpendicular to a Cu-Br bond and measuring the temperature dependence of the Br resonances.

By comparing these measurements to the temperature dependence of the macroscopic susceptibility, we obtained \( K_{zz} = 12 T/\mu_B \) and \( K_{xx} = K_{yy} = 0.97 T/\mu_B \) (see Fig. 10). From \( K_{zz} = 8/5 f_p \mu_B < r^{-3} > \), with \( < r^{-3} > = 103 \cdot 10^{-24} \text{cm}^3 \), the experimental \( K_{zz} \) value leads to \( f_p = 4.8% \) along the \( Z \)-axis. Such a rather large value of \( f_p \) indicates that the bromine ligands are involved in the exchange path between Cu spins.

To determine the only remaining unknown parameter \( \eta \), we used a modified version of the MATLAB routine designed to minimize the difference between the measured resonance frequencies and fields, and the fitted frequencies and fields with \( \eta \) as free parameter. This led to \( \eta = 0.25 \pm 0.01 \). It should be noted that we had to take into account a slight misalignment of the crystal in the coil since a tilt of just one degree away from a specific direction results in dramatic frequency shifts. In Fig. 11, we plot the results of simulations for \( B_0 \) aligned along a direction close to [110] (the precise direction is \( [1 \ 1 \ -0.08] \)) and corresponds to an experimental crystal orientation, which was estimated from the comparison between the measurements shown in Fig. 9 and the calculations). The field dependence of the 48 transitions of the 2 bromine isotopes located on the 4 inequivalent sites are plotted. The calculated intensities are shown on a color scale shown on the right of the figure. On top of the calculated transitions, horizontal and vertical bars are sketched at the frequencies, respectively fields, of the observed resonances measured at fixed field (9 T and 14 T), respectively fixed frequency (110 MHz). The bars reported at 14 T correspond to the measurements shown in Fig. 9.

Although it was not the purpose of the present work to detect all the transitions, many of them had to be measured in order to correctly interpret the data and to accurately determine the unknown parameters in the Hamiltonian. The observed line intensity ratios do not exactly match the calculated intensity ratios. The reason for this discrepancy is related to the large variations and short spin-spin relaxation times (typically on the order of 5-15 \( \mu s \) at 15 K). It should also be noted that the field dependence of the NMR frequencies of a spin 3/2 with large quadrupolar couplings placed in a strong external field has already been numerically calculated using the Liouvillian formalism and the results were compared to measurements performed in a \( ^{35} \text{Cl} \)-sodium chlorate NMR study. However, the intensity ratios of the transitions were not computed in this previous study.

IV. CONCLUSIONS

The temperature dependence of the Te NMR relaxation rate clearly demonstrates the three-dimensional nature of the magnetic phase transition. This implies that intertetrahedral interactions along the \( c \)-axis as well as those in the \( ab \)-plane are important. The transition temperature was found to be 10.5 K at 9 T. A Br NMR and NQR study in the paramagnetic phase of \( \text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2 \).
FIG. 10: Br hyperfine shift vs. magnetic susceptibility with $T$ as an implicit parameter. NMR shifts were measured on $^{79}$Br at 9 T between 12 and 50 K. Black dots correspond to $K_{zz}$, parallel to the Cu-Br bond, and open circles to $K_{xx} = K_{yy}$.

allowed us to demonstrate the important role of bromine in the interaction paths between Cu spins. In addition, via tellurium NMR, we showed that the $[\text{TeO}_3\text{E}]$ tetrahedra participates in binding the Br atoms.

The theoretical modelization of this frustrated spin system, topic of several recent publications, will be clearly facilitated by this new information. A complete NMR study of this material in its magnetic phase is currently in progress and is expected to shed light on its complex magnetic phase.

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1 M. Johnsson, K. W. Toernroos, F. Mila, and P. Millet, Chem. Mater. 12, 2853 (2000).

2 P. Lemmens, K.-Y. Choi, E. E. Kaul, C. Geibel, K. Becker, W. Brenig, R. Valenti, C. Gros, M. Johnsson, P. Millet, et al., Phys. Rev. Lett. 87, 227201 (2001).

3 O. Zaharko, A. Daoud-Adiadine, S. Streule, J. Mesot, P.-J. Brown, and H. Berger, Phys. Rev. Lett. 93, 217206 (2004).

4 O. Zaharko, H. Rosnow, J. Mesot, S. J. Crowe, D. M. Paul, P. J. Brown, A. Daoud-Aladine, A. Meents, A. Wagner, M. Prester, et al., Phys. Rev. B 73, 064422 (2006).
5 W. Brenig and K. W. Becker, Phys. Rev. B 64, 214413 (2001).
6 K. Totsuka and H.-J. Mikeska, Phys. Rev. B 66, 054435 (2002).
7 C. Gros, P. Lemmens, M. Vojta, R. Valenti, K.-Y. Choi, H. Kageyama, Z. Hiroi, N. V. Mushnikov, T. Goto, M. Johnsson, et al., Phys. Rev. B 67, 174405 (2003).
8 V. N. Kotov, M. E. Zhitomirsky, and O. P. Sushkov, Phys. Rev. B 63, 064412 (2001).
9 M.-H. Whangbo, H.-J. Koo, and D. Dai, Inorg. Chem. 42, 3898 (2003).
10 V. N. Kotov, M. E. Zhitomirsky, M. Elhajal, and F. Mila, Phys. Rev. B 70, 214401 (2004).
11 W. Brenig, Phys. Rev. B 67, 064402 (2003).
12 R. Valenti, T. Saha-Dasgupta, C. Gros, and H. Rosner, Phys. Rev. B 67, 245110 (2003).
13 J. Jensen, P. Lemmens, and C. Gros, Europhys. Lett. 64, 689 (2003).
14 Z. Jaglićić, S. E. Shawish, A. Jeromen, A. Bilušić, A. Smontara, Z. Trontelj, J. Bonča, J. Dolinšek, and H. Berger, Phys. Rev. B 73, 214408 (2006).
15 J. Jensen, Phys. Rev. B 79, 014406 (2009).
16 M. Prester, A. Smontara, I. Živković, A. Bilušić, D. Drobac, H. Berger, and F. Bussy, Phys. Rev. B 69, 180401 (2004).
17 I. Orion, J. Rocha, S. Jobic, V. Abadie, R. Brec, C. Fernandez, and J.-P. Amoureux, J. Chem. Soc., Dalton Trans. 20, 3741 (1997).
18 J. R. Morton and K. F. Preston, J. Magn. Res. 30, 577 (1978).
19 E. A. C. Lucken, Nuclear Quadrupole Coupling Constants (Academic Press, London and New York, 1969).
20 P. Morgen and W. W. Filho, J. Chem. Phys. 62, 2183 (1975).
21 CRC Handbook of Chemistry and Physics (CRC Press, 2003), 84th ed.
22 R. E. Alonso, A. Svane, C. O. Rodriguez, and N. E. Christensen, Phys. Rev. B 69, 125101 (2004).
23 M. Khasawneh, J. S. Hartman, and A. D. Bain, Molec. Phys. 102, 975 (2004).