Magnetic Raman scattering of the ordered tetrahedral spin-$\frac{1}{2}$ clusters in $Cu_2Te_2O_5(Br_{1-x}Cl_x)_2$ compounds

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Abstract. – Raman light-scattering experiments in the antiferromagnetic phase of the $Cu_2Te_2O_5(Br_{1-x}Cl_x)_2$ compounds are analyzed in terms of a dimerized spin model for the tetrahedral Cu-clusters. It is shown that the longitudinal magnetic excitation in the pure Br system hybridizes with a localized singlet excitation due to the presence of a Dzyaloshinskii-Moriya anisotropy term. The drastic change of the magnetic scattering intensities observed when a proportion of Br is replaced by Cl ions, is proposed to be caused by a change of the magnetic order parameter. Instead of being parallel/antiparallel with each other, the spins in the two pairs of spin-$\frac{1}{2}$ order perpendicular to each other, when the composition x is larger than about 0.25.

The compounds $Cu_2Te_2O_5Br_2$ and $Cu_2Te_2O_5Cl_2$ are spin-$\frac{1}{2}$ Cu-systems with coupled spin tetrahedra. The tetragonal $P\overline{4}$ crystal structure of the two compounds and the susceptibility measurements are presented in ref. [1]. While the high-temperature susceptibility approaches that of uncoupled spins, at low temperatures the susceptibility is reduced and goes through a maximum at, respectively, 30 and 23 K. The maximum indicates that the 2^4 spin-$\frac{1}{2}$ states of the Cu-ions in the (distorted) tetrahedral clusters are dimerized so as to create a singlet ground state separated from the excited states by a gap of about 40 K. Both the susceptibility and the heat capacity measurements clearly indicate a transition to an ordered phase at a temperature, 11.4 K in the Br and 18.2 K in the Cl system [2,3], well below that of the maximum. Some of the bulk properties and the Raman-scattering results of the Br compound have been analyzed successfully by Gros *et al.* [4] in terms of a dimerized model for the four Cu spins of one tetrahedron, as determined by the following Hamiltonian:

$$\mathcal{H}_t = J_1(\boldsymbol{S}_1 + \boldsymbol{S}_2) \cdot (\boldsymbol{S}_3 + \boldsymbol{S}_4) + J_2(\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + \boldsymbol{S}_3 \cdot \boldsymbol{S}_4), \tag{1}$$

J_1 and J_2 are both positive. Defining the ratio $r = J_2/J_1$, then the energy differences between the singlet ground state $|s_1\rangle$ and the excited states are: $2(1-r)J_1$ to a singlet $|s_2\rangle$, J_1 to a

one-triplet state $|t_1\rangle$, $(2-r)J_1$ to two degenerate triplets $|t_2\rangle$ and $|t_3\rangle$, and $3J_1$ to a quintuplet $|q\rangle$. This tetrahedral unit is coupled to the neighboring ones, and the Heisenberg interaction assumed in ref. [4] is

$$\mathcal{H}_{\mathrm{MF}}^{(\mathrm{Br})} = -J_c M_z \big(S_1^z + S_2^z - S_3^z - S_4^z\big) + 2J_c M_z^2, \quad M_z = \frac{1}{4}\big\langle S_1^z + S_2^z - S_3^z - S_4^z\big\rangle \qquad (2)$$

within the mean-field (MF) approximation, *i.e.*, the order parameter is one where the spins on each of the pairs 1-2 and 3-4 are parallel, but antiparallel with respect to the other pair of spins. This ordering takes full advantage of the J_1-interaction on the expense of the J_2-interaction. In the model of Gros *et al.* [4] for the Br compound $r = 0.66$ is smaller than 1, and the system is close to quantum criticality with a coupling parameter $J_c = 0.85J_1$, only 13% larger than the critical value $J_c^{(\mathrm{qc})} = 0.75J_1$. The model was investigated analytically neglecting the modifications due to higher-lying levels. The high-temperature susceptibility is accounted for using $J_1 = 47.7\,\mathrm{K}$, the Néel temperature increases with an applied field, and the frequency of the longitudinal magnetic excitation in the ordered phase is estimated to be close to that observed by Raman spectroscopy. Here we shall present a complete MF analysis, which includes the calculation of the susceptibility and the bulk magnetization in the ordered phase and the field dependence of T_{N}. It is performed numerically accounting for all effects of the total level scheme. The Raman-scattering cross-section is derived within the RPA, and the field-induced $|s_2\rangle$ singlet excitation in the Raman spectrum is determined to be due to an intrinsic Dzyaloshinskii-Moriya (DM) anisotropy term in the Hamiltonian of the Cu spins and not to a DM contribution to the Raman-scattering operator as proposed in [4].

The bulk properties of $\mathrm{Cu}_2\mathrm{Te}_2\mathrm{O}_5(\mathrm{Br}_{1-x}\mathrm{Cl}_x)_2$ change gradually with x. This suggests that the only modification occurring is an increase of the effective J_c in proportion to x, corresponding to the increase of T_{N} from 11.4 to $18.2\,\mathrm{K}$. However, the Raman scattering experiments, and to some extent also the magnetization measurements in the ordered phase indicate that the nature of the ordered phase is substantially modified when x becomes larger than about 0.25. After a thorough analysis of alternatives to the M_z order parameter in (2), we conclude that the only one which is in accord with the experiments is the following:

$$\mathcal{H}_{\mathrm{MF}}^{(\mathrm{Cl})} = -J_c^{xy} M_{xy}\big(S_1^x - S_2^x - S_3^y + S_4^y\big) + 2J_c^{xy} M_{xy}^2, \quad M_{xy} = \frac{1}{4}\big\langle S_1^x - S_2^x - S_3^y + S_4^y\big\rangle. \quad (3)$$

The M_{xy} parameter describes an ordered state in which each pair of spins, 1-2 or 3-4, is in an antiparallel configuration, and the spins on the two different pairs are perpendicular to each other. When each pair of spins is antiferromagnetically ordered, the free-energy contribution of the J_1 interaction cancels out to leading order. Thus the angle between the spins on the two different pairs is left undetermined by the intra-tetrahedral interactions in eq. (1), whereas the DM-anisotropy favors the perpendicular configuration.

The MF/RPA theory and the Raman-scattering cross-section. – The ground-state properties and the excitations of the tetrahedral Cu-systems have been analyzed in terms of a general MF/RPA theory, see, for instance, [5]. The MF order parameter is determined in a self-consistent fashion, from a numerical diagonalization of the total MF Hamiltonian followed by a calculation of the thermal expectation value of the order parameter. The linear response at zero or non-zero frequency is derived from the non-interacting susceptibility tensor $\overline{\overline{\chi}}^0(\omega)$, with the components $\chi_{AB}^0(\omega)$ determined in terms of the operators $\hat{A}$ and $\hat{B}$, see sect. 3.3 in [5]. By introducing the MF-coupling constant J_c in (2), then the 3×3 susceptibility tensor $\overline{\overline{\chi}}(\omega)$, corresponding to $\hat{A}$ and $\hat{B}$ equal to the three components of $\boldsymbol{S}_1 + \boldsymbol{S}_2 - \boldsymbol{S}_3 - \boldsymbol{S}_4$, is determined from the non-interacting one according to $\overline{\overline{\chi}}(\omega) = \overline{\overline{\chi}}^0(\omega)[\overline{\overline{1}} - (J_c/4)\overline{\overline{\chi}}^0(\omega)]^{-1}$. Introducing a

new, independent operator $\hat{D}$, then the response $\chi_{DD}(\omega)$ is derived from the 4×4 susceptibility tensor defined in the vector space consisting of the three Cartesian components plus $\hat{D}$ as the fourth component. Hence $\chi_{DD}(\omega)$ is the 44 component of the interacting susceptibility tensor determined from the non-interacting one as above, except that $(J_c/4)$ is replaced by a diagonal matrix with a zero in the 44 position and $(J_c/4)$ in the remaining part of the diagonal.

According to Brenig and Becker [6], the Raman-scattering cross-section R may be written as $\sum_{lm} a_{lm}(\boldsymbol{e}_i \cdot n_{lm})(\boldsymbol{e}_o \cdot n_{lm})\boldsymbol{S}_l \cdot \boldsymbol{S}_m$, where $\boldsymbol{e}_i$ and $\boldsymbol{e}_o$ are the unit vectors of the incoming and outgoing electric field and $\boldsymbol{n}_{lm}$ are the unit vectors connecting exchange-coupled sites. When the incoming and the outgoing lights are polarized along the c-axis, then R is proportional to

$$\sum_i \left[(\boldsymbol{S}_1^i+\boldsymbol{S}_2^i)\cdot(\boldsymbol{S}_3^i+\boldsymbol{S}_4^i)+\alpha_0(\boldsymbol{S}_1^i+\boldsymbol{S}_2^i)\cdot(\boldsymbol{S}_3^{i-1}+\boldsymbol{S}_4^{i-1})+\alpha_0(\boldsymbol{S}_3^i+\boldsymbol{S}_4^i)\cdot(\boldsymbol{S}_1^{i+1}+\boldsymbol{S}_2^{i+1})+\cdots\right]\xrightarrow{\text{RPA}}$$

$$\xrightarrow{\text{RPA}} \sum_i \left[(\boldsymbol{S}_1^i + \boldsymbol{S}_2^i) \cdot (\boldsymbol{S}_3^i + \boldsymbol{S}_4^i) - 2\alpha\boldsymbol{M} \cdot (\boldsymbol{S}_1^i + \boldsymbol{S}_2^i - \boldsymbol{S}_3^i - \boldsymbol{S}_4^i)\right]. \tag{4}$$

This RPA expression includes all neighboring exchange-coupled pairs via the introduction of an effective α. Defining the operators $\hat{D} \equiv (\boldsymbol{S}_1+\boldsymbol{S}_2)\cdot(\boldsymbol{S}_3+\boldsymbol{S}_4)$ and $\hat{A} \equiv S_{1z}+S_{2z}-S_{3z}-S_{4z}$, then the scattering intensities in the Raman experiments are determined by

$$I(\omega) \propto \frac{1}{1 - e^{-\hbar\omega/k_B T}} \operatorname{Im}\left\{\chi_{DD}(\omega) + 4\alpha^2 M_z^2\chi_{AA}(\omega) - 2\alpha M_z[\chi_{AD}(\omega) + \chi_{DA}(\omega)]\right\}. \tag{5}$$

If $\alpha = J_c/2J_1$, then R_{RPA} commutes with the MF Hamiltonian. This corresponds to the case of $\beta = b$ considered by Brenig and Becker [6]. The Raman-scattering intensity vanishes identically in this case, independent of the value of M_z. The value of α is unknown, and in the following we simply assume that $\chi_{DD}(\omega)$ is the dominating term, *i.e.*, that $\alpha \approx 0$.

Analysis of the experiments. – The final model for $Cu_2Te_2O_5Br_2$ includes J_1, J_2, J_c, and J_c^{xy} defined by eqs. (1)-(3) plus two additional parameters. J_f is the coupling parameter for the uniform magnetization component,

$$\mathcal{H}_Z = -\left(J_f\boldsymbol{M}_f + 2\mu_B\boldsymbol{H}\right) \cdot (\boldsymbol{S}_1+\boldsymbol{S}_2+\boldsymbol{S}_3+\boldsymbol{S}_4)+2J_f M_f^2, \quad \boldsymbol{M}_f = \frac{1}{4}\langle\boldsymbol{S}_1+\boldsymbol{S}_2+\boldsymbol{S}_3+\boldsymbol{S}_4\rangle \tag{6}$$

of importance in the presence of an external field $\boldsymbol{H}$. The S_4 symmetry of the tetrahedra allows different kinds of anisotropic interactions. Based on the analysis of the Raman-scattering experiments, we shall concentrate on the following DM anisotropy term:

$$\mathcal{H}_A = D_c[(\boldsymbol{S}_1 - \boldsymbol{S}_2) \times (\boldsymbol{S}_3 - \boldsymbol{S}_4)]_c \tag{7}$$

proportional to the c component of the cross product. The values of the five (six) parameters in the case of $Cu_2Te_2O_5Br_2$ are determined to be ($J_c^{xy} < 2.17J_1 \Rightarrow M_{xy} = 0$)

$$J_1 = 47.5\,\text{K}, \qquad J_2 = 0.7J_1, \qquad D_c = 0.06J_1, \qquad J_c = 0.856J_1, \qquad J_f = 0.6J_1. \tag{8}$$

The strongest coupling in the system J_1 is derived from the high-temperature susceptibility measurements assuming fixed values for the remaining ones. The value of J_f is mainly determined by the high-field magnetization measurements in the ordered phase, see fig. 1, but still has a large uncertainty of about 20%. Due to the D_c anisotropy, the bulk susceptibility becomes anisotropic. The anisotropy is minute in the paramagnetic, but substantial in the ordered phase. Independently of its sign, D_c implies that the ordered staggered moment M_z in eq. (2) is directed along the c-axis. The bulk susceptibility along this direction is predicted
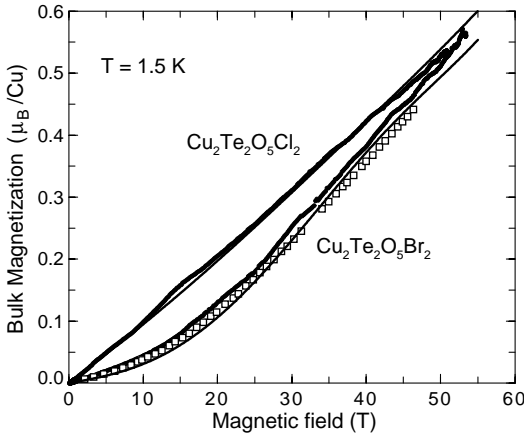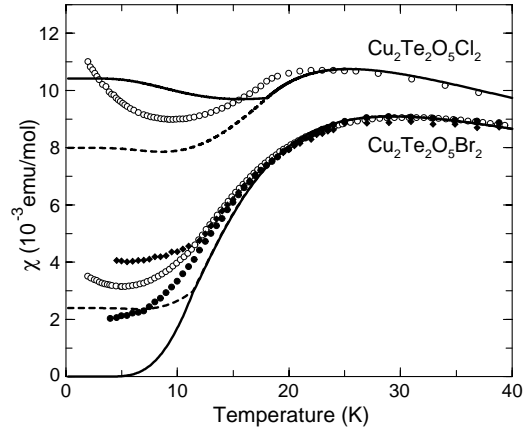
Fig. 1

Fig. 2

Fig. 1 – High-field magnetization measurements after ref. [4]. The smooth lines are the results of the model calculations.

Fig. 2 – The bulk susceptibility at low temperatures. The open circles are the experimental results for polycrystalline samples [2,4]. Single-crystal results with field parallel and perpendicular to the c-axis are shown (solid symbols) for the case of the Br compound [4]. All experimental results have been scaled so that they approach the theoretical high-temperature value of $0.7503/T$[K] emu/mol. The solid/dashed lines are the calculated results when the field is parallel/perpendicular to the c-axis.

to vanish exponentially at low temperatures, whereas the perpendicular component stays approximately constant below T_N. This is in qualitative agreement with experiments, as shown in fig. 2. The experimental data are unfortunately somewhat disturbed by other contributions, as reflected, for instance, in a sample dependence of the results. The Zeeman energy gained in the perpendicular case induces a spin-flop transition, when the field is parallel to the c-axis, to a phase where the staggered moments become perpendicular to the field. The model predicts the spin-flop field to be 3.7 T, nearly independent of the temperature below T_N. This spin-flop transition has not yet been observed, but the anisotropy measurements in fig. 2 were made at a field of 5 T indicating that the spin-flop field is larger than 5 T. J_c has no influence on the bulk susceptibility, above T_N, and is adjusted so that the model predicts $T_N = 11.4$ K at zero
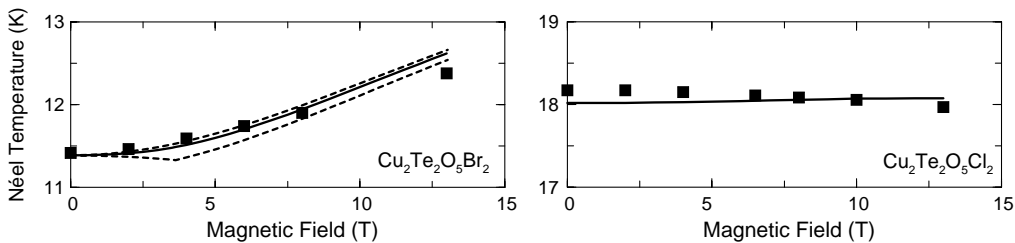

Fig. 3 – The Néel temperature as a function of applied field. The dashed lines (in the Br case) show the calculated T_N when the field is perpendicular (upper one) or parallel (lower one) to the c-axis. The solid lines are for the averaged value to be compared with experimental results [2,4] obtained from polycrystalline samples (the solid squares).
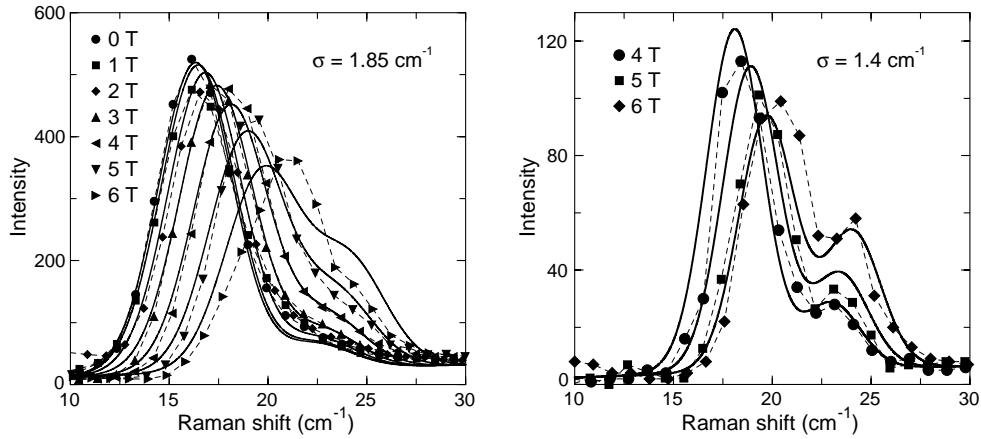
Fig. 4 – Raman spectra of $Cu_2Te_2O_5Br_2$ at $2.1\,K$ in a magnetic field applied perpendicular to the
c-axis. The experimental results (symbols connected by dashed lines) [2–4] have been obtained with
two different resolutions and the theoretical intensities (solid lines) have been folded with Gaussians
with the specified values of σ. The calculated Raman shifts have all been subtracted by $1.6\,cm^{-1}$.

field. Figure 3 shows the transition temperature for a polycrystalline sample as a function of
field. It is remarkable that T_N increases with the field.

The Raman spectra of the $Cu_2Te_2O_5(Br_{1-x}Cl_x)_2$ compounds have been studied in de-
tail [2–4]. The longitudinal magnetic excitation at zero wave vector is observed in the Br
system at $2.1\,K$, when the incoming and scattered light are polarized along the c-axis. This
part of the results is shown in fig. 4. The high-resolution data revealed an additional peak at
slightly higher energy than the longitudinal excitation, appearing when a field is applied per-
pendicular to the c-axis. Gros *et al.* [4] interpreted the extra peak to be the $|s_2\rangle$ singlet level,
which is becoming visible due to a DM component in the cross-section combined with the
level mixing induced by the field. The problem with this explanation is that the field-induced
mixing is weak, and a DM cross-section as large as the normal part would only produce a
peak of the size of a hundredth of the main one. The alternative explanation is that it is the
Hamiltonian itself, which is responsible for the mixing of the levels. The only possible term
producing such an effect is the D_c coupling defined by eq. (7). D_c gives rise to a coupling
between the longitudinal mode and the $|s_2\rangle$ level even at zero field. The application of a field
perpendicular to the c-axis diminishes the energy difference between the two levels and the
hybridization is strongly increased. The two peaks would attain equal intensities at a field
slightly larger than the experimental maximum field. Figure 4 compares the intensities pre-
dicted by the model, eq. (5) with $\alpha = 0$, with the experimental ones. In these calculations D_c
and J_2, plus one intensity scale parameter in each of the two cases, have been utilized as ad-
justable parameters. The experimental Raman shifts are subjected to an absolute uncertainty
of the order of $4\,cm^{-1}$ and a relative one of the order of $1\,cm^{-1}$. The relative uncertainty has
been reduced by performing a translation of each spectrum so that the phonon frequencies
in each case coincide with those observed in the sample at zero field. Because of the large
absolute uncertainty, we have tried to mimic the relative behavior rather than to get the
right values for the absolute frequencies. The model thus leads to a good account of both the
frequencies and the intensities if shifting all the calculated peaks rigidly by $-1.6\,cm^{-1}$.

The model we shall present now for the $Cu_2Te_2O_5Cl_2$ system is more speculative. In
comparison with the Br compound, the a and c lattice parameters in the Cl system are
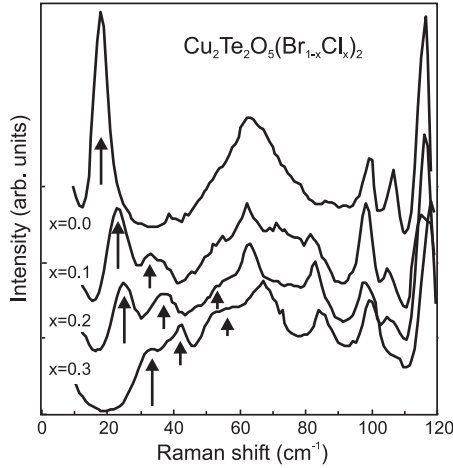
Fig. 5 – Raman spectra obtained for small concentration x of Cl ions at zero field and 4 K, after ref. [7]. The arrows indicate the positions of magnetic scattering peaks. The intensity of the longitudinal magnetic excitation rapidly decreases with x and new peaks develop at higher frequencies.

reduced by 3 and 1%, respectively, whereas the intra-tetrahedral distances between the Cu atoms are increased by about 1%, see ref. [1]. In correspondence to these changes, J_1 is reduced in the Cl compound, whereas the Néel temperature is increased. A first guess of a model for the Cl compound would be the same one as discussed above with some appropriate adjustments of the coupling parameters. The model based on this assumption predicts a strong Raman-scattering peak at about $40\,\mathrm{cm}^{-1}$, two to three times as intense as in the Br system if assuming the scattering coefficients a_{lm} to be the same. However, the Raman spectra clearly show a quick and systematic reduction of the magnetic scattering with the concentration x of the Cl ions, see fig. 5. One possible explanation would be that it is the Raman-scattering circumstances, not the model itself, which is drastically changed. This could be achieved by introducing a non-zero α in eq. (4), and this α should then approach $J_c/2J_1$ in the pure Cl system. We have analyzed this possibility, but found it to be both implausible and not capable of reproducing the observed non-monotonic changes of the Raman spectra with x.

The analysis of the magnetization measurements shown in fig. 1 indicates that $r = J_2/J_1$ is close to 1 in the Cl compound, so, although J_1 is reduced, J_2 increases with the Cl concentration. When $r \approx 1$, then J_c has to be about $2J_1$ in order to produce a transition to the M_z ordered phase at $T_N = 18.2\,\mathrm{K}$. Another possibility is that in both systems $J_c \approx J_1$, whereas $J_c^{xy} \approx 1.8J_1$, then the increase of r from about 0.7 in the Br to about 1 in the Cl compound is a sufficient cause for a change of the order parameter from M_z to M_{xy}. Based on this possibility, the model of $Cu_2Te_2O_5Cl_2$ is proposed to be ($J_c < 1.95J_1 \Rightarrow M_z = 0$)

$$J_1 = 40.7\,\mathrm{K}, \qquad J_2 = J_1, \qquad D_c = 0.06J_1, \qquad J_c^{xy} = 1.8J_1, \qquad J_f = 0.6J_1. \qquad (9)$$

This model produces the magnetization and susceptibility results displayed in figs. 1 and 2, and T_N is found to be nearly independent of an external field, as shown in fig. 3. Most importantly, the assumption of an M_{xy} instead of an M_z ordering implies a reduction of the calculated magnetic Raman-scattering intensities by nearly a factor of 10. Furthermore, instead of one longitudinal mode the present model predicts two main peaks (at 43 and $75\,\mathrm{cm}^{-1}$), plus a third one (at $57\,\mathrm{cm}^{-1}$) observable if the polarization vectors of the light have a component

perpendicular to the c-axis. This is, at least qualitatively, in much better agreement with the Raman experiments [3,7] than that predicted by an M_z ordered phase.

Conclusion. – The analysis by Gros *et al.* [4] of the tetrahedral spin-$\frac{1}{2}$ cluster system $Cu_2Te_2O_5Br_2$ has been extended, and the Raman-scattering results have been explained quantitatively by introducing a Dzyaloshinskii-Moriya anisotropy term in the Hamiltonian, and this term also accounts (partly) for the anisotropy of the system below T_N. The ordered phase in this compound is the one where $\langle \boldsymbol{S}_1 + \boldsymbol{S}_2 \rangle$ is parallel and $\langle \boldsymbol{S}_3 + \boldsymbol{S}_4 \rangle$ antiparallel with the c-axis. A spin-flop transition is predicted to occur when applying a field along the c-axis. It is worth pointing out that the magnetic Raman spectrum (leaving out the two-magnon scattering part) depends on the resulting mean field, but not on the relative orientation of the magnetic moments on neighboring tetrahedra. A determination of this would require a neutron-diffraction investigation. The present analysis of the Raman spectra indicates that the ordering in $Cu_2Te_2O_5Cl_2$ compound is of the J_2-type, where $\langle \boldsymbol{S}_1 - \boldsymbol{S}_2 \rangle$ and $\langle \boldsymbol{S}_3 - \boldsymbol{S}_4 \rangle$ are perpendicular to each other and to the c-axis. The evidences are indirect and the J_2-structure needs to be verified by diffraction experiments.

The mean-field/random-phase approximation is a relevant starting point, whenever the interactions are strong enough to induce magnetic ordering. This is also true close to quantum criticality (Pr-metal may serve as a good example for that [5]). The non-mean-field behavior of the present frustrated system appears to be accounted for by the treatment of each tetrahedral Cu-spin cluster as a local dimerized unity. The analysis shows that the specification of the properties of the local spin clusters requires at least three parameters J_1, J_2, and D_c. The values of the three MF parameters J_f, J_c, and J_c^{xy}, which correspond to three different combinations of the exchange interactions between neighboring tetrahedra, indicate that both the interactions perpendicular and parallel to the c-axis chains of tetrahedra are important and therefore that the system is three- rather than one-dimensional. The good coincidence between the predictions of the MF/RPA theory and the experimental results is a further argument for a three-dimensionality of the magnetic interactions in the two compounds.

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