EPR studies on melaminium hexachlorodicuprate - a one-dimensional dimeric copper (II) chain system

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Abstract
X-band EPR studies of the monoclinic crystal melaminium hexachlorodicuprate (MHCC) constituted of ladder-like chains of copper (II) dimers ($S = 1$) running parallel to the a-axis are carried out in the temperature interval 77–295 K. Spectra recorded in the two crystallographic planes (010) and (001) have revealed some features quite distinct from those of true dimeric compounds such as copper acetate monohydrate. Only a single line spectrum has been observed in all orientations of the single crystal. A large disparity was observed between the mean g-value (2.11) directly obtained from EPR measurements and that (2.21) derived from mean magnetic susceptibility data based on the 'mean field corrected dimer model' of Colombo et al (Colombo A, Menabue L, Motori A, Pellacani G C, Porzio W, Sandrolini F and Willet R D 1985 $Inorg.$ $Chem.$ **24** 2900). EPR lineshape is Lorentzian in all directions of the crystal. The linewidth has appreciable anisotropy (1000–600 Oe). The observed angular variation of linewidth in the said crystallographic planes has been analysed on the basis of the anisotropic exchange theory of Ritter et al (Ritter M B, Drumheller J E, Kite T M, Snively L O and Emerson K 1983 $Phys.$ $Rev.$ **28** 4949) suitably modified to be applicable in the present case of the $S = 1$ 1D system. The thermal dependence of EPR line intensity has also been investigated. It has been shown that the MHCC system is best described as an antiferromagnetic exchange coupled $S = 1$ 1D system. The presence of orthorhombic anisotropic symmetric exchange has also been confirmed.

1. Introduction

X-ray structure studies by Colombo et al [1] have revealed that melaminium hexachlorodicuprate (abbreviated as MHCC) is an interesting magnetic system which exhibits
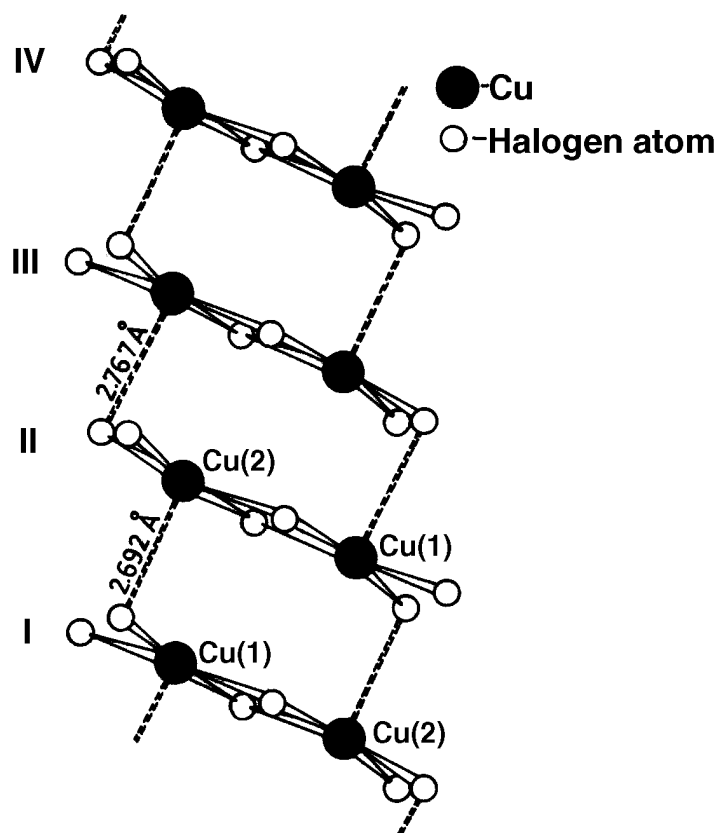
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Figure 1. Crystal structure of MHCC showing stacking of $Cu_2Cl_6^{2-}$ dimeric units along the b-axis.

a new kind of stacking of copper (II) dimers, resulting in the formation of a ladder-like infinite chain along the a-axis of the monoclinic crystal with the cross-bars of the ladder being formed by the Cu–Cu dimer while the side of the ladder is formed by the Cu–Cl bonds (figure 1). The separation between alternate dimers in a chain varies slightly between 2.69 and 2.76 Å. Colombo *et al* [1] also performed a powder magnetic susceptibility investigation in the temperature range 1.6–300 K. The magnetic data were first fitted to a 'simple dimer model'. The Curie constant obtained from fitting gave a mean g-value of 2.27. However, the derived g-value being unrealistically large, the magnetic susceptibility data were next fitted to a 'mean field corrected dimer model', which yielded a mean g-value of somewhat reduced magnitude, i.e. $g = 2.21$. It was stated that the magnetic structure of MHCC may be considered as built up of ferromagnetically coupled antiferromagnetic dimers.

It is well known that EPR is best suited in understanding the spin-dynamics of a low dimensional (D) magnetic system. So it is expected that EPR studies on single crystals of MHCC will be helpful to verify which of the two magnetic models, namely 'dimeric interaction' and 'low magnetic dimensionality', is applicable to illustrate the magnetism of MHCC. Further EPR, unlike magnetic susceptibility measurements, provides direct measurements of spin-Hamiltonian parameters, such as g and zero field splitting parameters (D, E), which throws light on the ligand field characteristics of magnetic ions. With the above objects, lineshape, linewidth and structure (if any) of the EPR spectra have been investigated. It is relevant to

mention here that non-zero D and E parameters, if present, will certainly go in support of the dimeric nature of the compound. However, doublet structure, characteristic of a Cu (II) dimeric compound, has not been detected in a general direction of any crystallographic plane of the MHCC crystal in the liquid nitrogen temperature range (discussed in section 3) and so the spin Hamiltonian parameters D and E need not be considered. So the other alternative, i.e. the low dimensional (D) magnetism of MHCC, will be critically examined in detail. The magnitudes as well as the orientations (with respect to crystallographic axes) of the principal ionic g-values are also determined. These data will provide useful information about the symmetry and the strength of the ligand field associated with Cu (II) ions (of MHCC) having square pyramidal ligand conformation.

2. Experiment

Single crystals of MHCC are grown from the filtrate obtained by reacting equimolecular weights of $CuCl_2.2H_2O$ and melamine $[C_3N_3(NH_2)_3]$ in concentrated HCl. A green filtrate is obtained, which, on slow evaporation in presence of sodium hydroxide, results in the formation of brick red crystals. Good single crystals of MHCC are prepared by using seeds. The crystals thus obtained are elongated along the a-axis.

With the help of a Varian E-line century series X-band EPR spectrometer in conjunction with a goniometer and a cryostatic arrangement first derivative spectra in two crystallographic planes (010) and (001) of the crystals are recorded in the temperature range of 77–295 K. Precise measurements of the microwave frequency are made with the help of a Hewlett–Packard microwave frequency counter (model No 5350B).

3. Experimental results and discussion

3.1. Determination of spin Hamiltonian parameters (g-factors)

From x-ray structural analysis of the crystal [1] it is evident that Cu (II) ions of a given dimer as well as of a given chain are magnetically equivalent, i.e. their symmetry axes are parallel. Although all the Cu (II) dimeric chains are aligned parallel to each other, i.e. parallel to the crystallographic a-axis, the symmetry axes of Cu (II) ions of any two neighbouring chains are non-parallel. For symmetry reasons, however, their symmetry axes are equally inclined to the monoclinic symmetry axis (b-axis). If the magnetic dimeric property ($S = 1$) of the Cu (II) pairs is prevalent doublet spectra should be observed in the (010) plane. However, only a single broad spectrum with its linewidth varying in the 600–1000 Oe range has been recorded. It is thus evident that the dimeric character is suppressed in favour of low dimensional magnetism, i.e. the relevant spin-Hamiltonian parameters (zero-field splitting parameters: D, E), characteristics of Cu (II) dimers, have been averaged out to zero. So, the spin-Hamiltonian involving only g-parameters is relevant. It is worthwhile to mention here that from EPR studies of Zn doped dimeric compound, copper acetate monohydrate, it has been shown that Cu (II) monomers and Cu (II) dimers of this compound have identical principal ionic g-values [2]. So it is justified to calculate principal ionic g-values from principal crystalline g-values which are equally applicable for dimers. Since Cu (II) ions become magnetically equivalent with respect to the (010) plane, only crystalline g-values are obtained in this plane. With respect to the (100) plane the two types of Cu (II) ion have unequal projections and two lines should have been observed. However, only a single line has been observed. This indicates the presence of interchain exchange, which causes a merger of the two lines. X-ray data reveal that the angle between the symmetry axes of the Cu (II) ions belonging to any two neighbouring Cu (II)
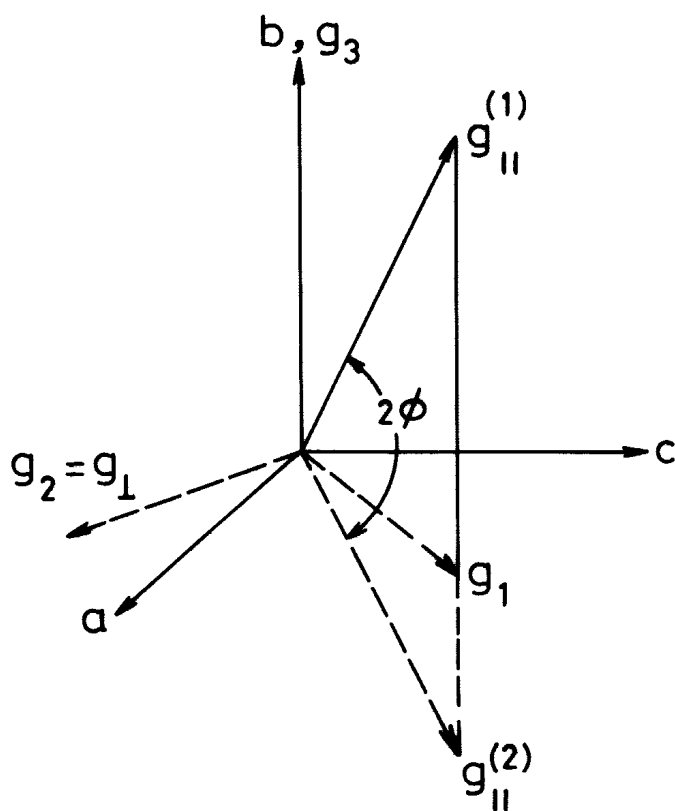
Figure 2. Orientation of $g_\parallel$ and $g_\perp$ and of principal crystalline axes (g_1, g_2 and g_3) with respect to crystallographic axes (a, b, c) in the crystal.

Table 1. Values of principal crystalline (g_1, g_2, g_3) and ionic g-values ($g_\parallel$, $g_\perp$) and angular separation (2ϕ) between tetragonal axes of Cu (II) ions in neighbouring sites in MHCC.

g_1	$g_2 = g_\perp$	g_3	$g_\parallel$	2Φ (°)
2.200	2.050	2.090	2.230	24 (20)[a]

[a] The value of 2ϕ within parentheses is obtained from x-ray data [1].

chains is only 20° and so even a small amount of interchain exchange is sufficient for the merger of the said lines.

From measurements of EPR spectra in (010) and (100) planes, the principal crystalline g-values, g_1, g_2, g_3 are obtained, where g_1 and g_2 are respectively the maximum and minimum g-values in the (010) plane while g_3 corresponds to the g-value along the b-axis (figure 2). The values of g_1, g_2, g_3 and the angle between g_1 and the c-axis obtained are shown in table 1. It is found that $g_1 > g_2 > g_3$. No appreciable change in g_1, g_2, g_3 is observed in the temperature range 77–300 K.

Due to the fact that the signals due to magnetically inequivalent Cu (II) ions cannot be resolved the principal orthorhombic ionic g-values cannot be evaluated from crystalline g-values. To obtain ionic g-values from the crystalline g-values, the ligand field symmetry is assumed to be axial (tetragonal in the present case). It has been shown [3] that the principal ionic g-factors (in this case $g_\parallel$ and $g_\perp$) and the angle 2φ between the ionic symmetry axes

$(g_\parallel^{(1)}$ and $g_\parallel^{(2)})$ of two magnetically inequivalent Cu (II) ions can be derived from principal crystalline g-values with the help of the following relations [3]:

$$g_\perp = g_2 \qquad g_\parallel^2 = g_1^2 + g_3^2 - g_2^2 \qquad \cos 2\Phi = \frac{(g_1^2 - g_3^2)}{(g_\parallel^2 - g_\perp^2)}. \qquad (1)$$

The derived values of $g_\parallel$ and $g_\perp$ and angle 2Φ are included in table 1. Ionic g-values so obtained may be compared with those obtained in Cu (II) doped single crystals of K_2PdCl_4 in which the Cu (II) ion has square planar coordination with four Cl^- ions [4]. Ionic g-values obtained in this case are $g_\parallel = 2.230$ and $g_\perp = 2.049$, which are in excellent agreement with those found in MHCC (table 1). This is understandable because in MHCC, although Cu^{2+} ion has a square pyramidal conformation of Cl^- ions, the Cl^- ion at the apex of the pyramid is situated at a larger distance of 2.7 Å from the Cu^{2+} ion compared to four Cl^- ions situated at the four corners of the square base of the pyramid (the average separation is 2.3 Å), this configuration of the Cu^{2+} site may be approximated as square planar. The angle between the symmetry axes of two magnetically inequivalent Cu^{2+} ions (2ϕ) obtained from EPR studies is in fair agreement with that obtained from x-ray measurements [1], justifying the assumption of axial (tetragonal) symmetry of the ligand field of Cu^{2+} ions to be valid.

It is significant to note that the mean g-value obtained from direct EPR measurements (2.110) widely differs from that derived from fitting of the magnetic susceptibility data (2.210). This observation suggests that the 'mean field corrected dimer model' proposed by Colombo *et al* is not tenable in case of MHCC.

3.2. Lineshape and linewidth

From the above it is apparent that MHCC may be treated as a one-dimensional (1D), $S = 1$ system.

The EPR lineshape is found to have Lorentzian lineshape in all directions. This is not in conformity with the one dimensional spin diffusive theories of Richards and others [5], which predict that the lineshape should be non-Lorentzian along the chain axis and Lorentzian at the magic angle, i.e. $54.7°$ to the chain axis. The observed lineshape also remains unaltered in the temperature range 77–300 K.

First derivative linewidths are plotted versus orientation in (010) and (001) planes (figures 3(a) and (b)). From figures 3(a) and (b) it is evident that the linewidth is a maximum (1000 Oe) along the chain axis (a-axis) and is a minimum (600 Oe) perpendicular to the chain axis, i.e. b-axis and c^*-direction. The c^*-direction is chosen as perpendicular to the a-axis and is lying in the (010) plane. Thus the observed linewidth anisotropy is also not in agreement with the prediction of 1D spin-diffusion theory, which prescribes that the linewidth should be a maximum along the chain axis and a minimum at the magic angle. Under the above circumstances, to account for the above findings it seems worthwhile to take recourse to the anisotropic exchange theories of Soos and others [6], which have been largely successful in explaining linewidth properties of several double halide bridged 1D Cu (II) systems [7] as well as single oxygen bridged 1D Cu (II) system [8]. McGregor and Soos [6] were the first to acknowledge the importance of anisotropic exchange interaction originating from non-zero s.o. coupling in non-S-state ions (like Cu^{2+} ions) in calculating EPR linewidth. They calculated the width of the EPR line by using general linewidth theory [9, 10] for a Cu (II) 1D system and by including the Blume–Hubbard [11] results for spin dynamics and preferentially weighting anisotropic symmetric exchange (a.s.e.) and dipolar terms in one dimension. Ritter *et al* [6] extended the theory to situations where the symmetry of a.s.e. is orthorhombic and, in addition, anisotropic antisymmetric exchange (a.a.e.) interaction is present. In a chain system,
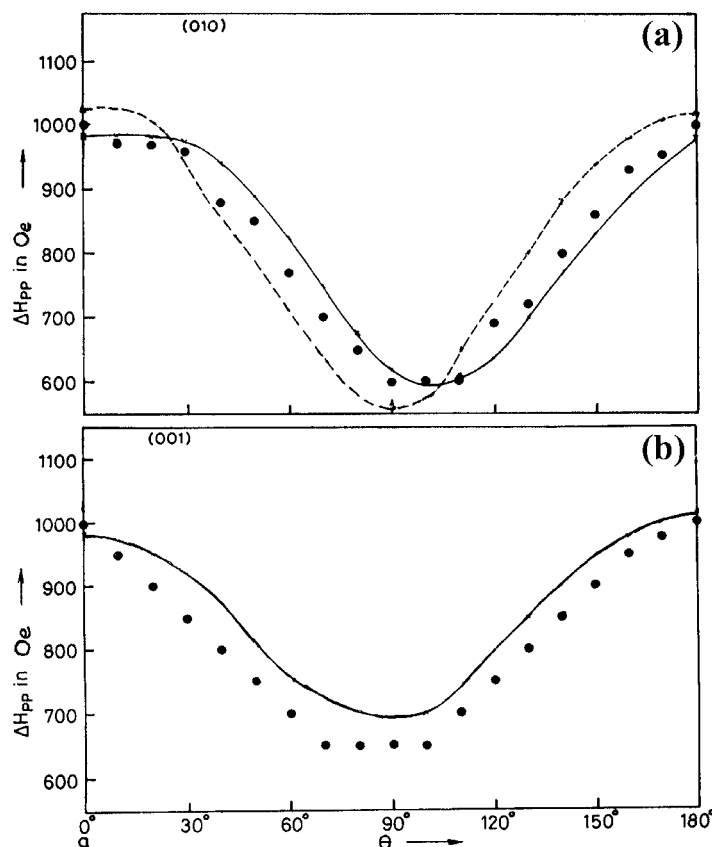
Figure 3. ΔH_{pp} against orientation θ in (a) (010) and (b) (001) crystallographic planes of MHCC. (● ● ●) Experimental points. Theoretical curves considering: (– – –) a.e. along $g_{\parallel}$, (——) a.e. along chain axis.

except for the two neighbouring sites in a chain all other sites are situated at large distances and the magnetic dipolar contributions due to them have been ignored in the second moment calculation. Since the nearest neighbours in a chain are quite close, the hyperfine interaction term in comparison to dipolar terms can be neglected. The contributions of the dipolar and a.s.e. terms to the second moment in the co-ordinates of figure 4 is given by [6]
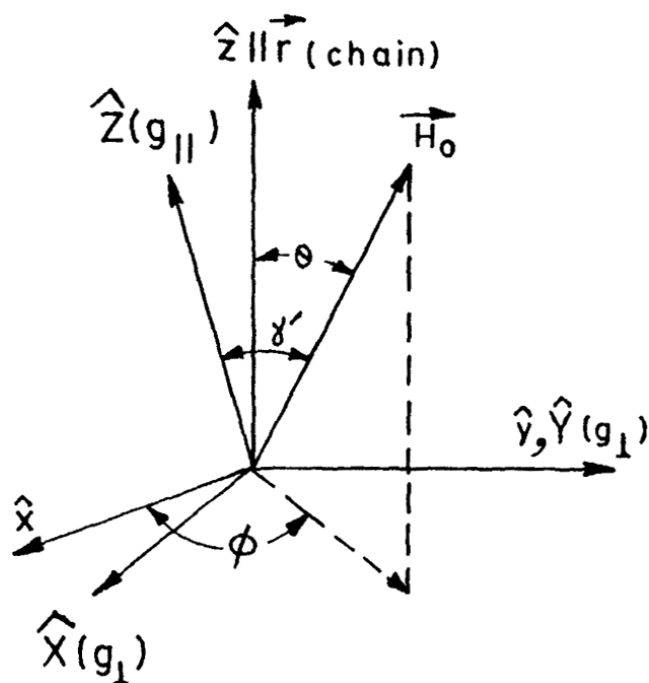
$$M_2' = \frac{3S(S+1)}{h^2}\left[\frac{1}{3}\left(\frac{D_e}{3}\right)^2\{(3-2\Delta)\cos^2\gamma' + (3+2\Delta)\} + D_d^2(\cos^2\theta + 1)\right.$$

$$-\left(\frac{D_e D_d}{3}\right)\{[3+\Delta)\cos^2\gamma' - (1+\Delta)](3\cos^2\theta - 1)$$

$$\left.+(1/3)[-2\Delta + (3+\Delta)\sin^2\gamma']\sin^2\theta\cos[2(\alpha+\phi)]\}\right] \qquad (2)$$

where

$$D_d = (\bar{g}\beta)^2/r^3 \qquad (3)$$

and

$$\bar{g}^2 = (g_1^2 + g_2^2 + g_3^2)/3 \qquad (4)$$

Figure 4. Co-ordinate system for the theoretical treatment with z along the direction of strong exchange r defining the orientation of the applied field H_0 and a.e. interaction chosen in the xz plane.

(g_1, g_2 and g_3 are the principal crystalline g-values). r is the nearest-neighbour intrachain separation along the chain axis (z). D_e and Δ are respectively the axial and orthorhombic components of the a.s.e. tensor. The direction of D_e has been chosen along the chain direction, i.e. the a-axis. The angle α represents the rotation of D_e^{mol} (a.s.e. tensor in the molecular frame) about Z (the z-direction of the principal g-tensor), which results from the transformation to laboratory co-ordinates,

$$D_e^{mol} = (D_e^e/3) \begin{vmatrix} q & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & 2 \end{vmatrix} \tag{5}$$

where q and p are given by $q = -1 - \Delta$ and $p = -1 + \Delta$ in order to maintain a zero trace operator. The angles θ and ϕ define the orientation of the magnetic field H_0 with respect to crystallographic axes and γ' is the angle between H_0 and Z (figure 4). It has been customary to assume that the principal axes of the a.s.e. and g-tensors are coincident. The purely secular part is given by

$$M_2'^{(0)} = \frac{3S(S+1)}{2h^2}[(D_e/3)[(3+\Delta)\cos^2\gamma' - (1+\Delta)] - D_d(3\cos^2\theta - 1)]^2. \tag{6}$$

Neglecting next-nearest neighbours and hyperfine interactions, the relationship between calculated and observed linewidths is expressed as

$$(3/2)\Delta H_{pp} = (2/3J)[M_2' + \rho M_2'(0)]. \tag{7}$$

J is the isotropic exchange parameter. ρ is a semipositive parameter which enhances secular contribution to the second moment.

Table 2. Best fitted isotropic exchange (J), and anisotropic exchange (D_e, Δ) parameters.

D_e (cm^{-1})	Δ	J (cm^{-1})
0.85	0.80	5.00

From x-ray structural data it is seen that in MHCC copper dimers exist. However, they are not isolated but coupled forming chains along the crystallographic a-axis. Analysis of magnetic susceptibilities [1] also confirms the presence of the copper dimers and predicts that these dimers are weakly exchange coupled. As discussed in the preceding section, EPR spectra do not show any dimeric character of copper dimers, i.e. doublet structure in the (010) plane, and it is suggested that the presence of the magnetic exchange among the copper dimers in a chain have the effect of averaging out the doublet structure. For a copper dimer $S = 0$ and $S = 1$ states exist but the $S = 0$ state, being non-magnetic, does not participate in magnetic exchange. So the coupled copper (II) dimeric chain may be considered as an $S = 1$ 1D system. Under the circumstances the theory of Soos and others as outlined above has been applied in the present case by using the values of $S = 1$ and $\alpha = 0$ in the theoretical expressions (equations (2), (6) and (7)). The results of computer fitting of linewidth anisotropy are shown in figures 3(a) and (b). The black dots (● ● ●) in the figure denote experimental points, whereas the continuous line (——) denotes the computer fitted curve. It is evident from the figures that the theoretical linewidth curves follow accurately the experimental points in (001) and (010) planes. Best fitted parameters are shown in table 2. It may be just a coincidence that the isotropic exchange parameter J (5.0 cm^{-1}) obtained from fitting of the linewidth data compares favourably with the value of interdimer exchange parameter (7 cm^{-1}) deduced by Colombo *et al* [1] from analysis of their mean magnetic susceptibilities on the basis of the 'mean field corrected dimer model' [1]. The value of anisotropic exchange parameter D_e evaluated from linewidth fitting (0.85 cm^{-1}) is much larger than that (0.02 cm^{-1}) derived using the Moriya relation $D_e \approx (\Delta g/\bar{g})^2$ where Δg is the difference of the mean g-value ($\bar{g}$) from the free electron g-value (g_e) [12]. Such a discrepancy has been observed in many other cases, questioning the validity of the Moriya relation. It is possible that the Moriya relation is not strictly applicable in an $S = 1$ system as in the present case. Non-zero values of $\Delta(\Delta = 0.8)$ indicates that there is some orthorhombicity in the anisotropic symmetric exchange.

It is worth mentioning here that the linewidth data obtained in two crystallographic planes cannot be fitted at all by treating MHCC as a 1D $S = 1/2$ system and employing 'anisotropic exchange' equations (2), (6) and (7) of Soos *et al*.

3.3. Temperature dependence of EPR intensity

The intensity I_T of the EPR line may be taken as nearly proportional to $I'(\Delta H_{pp})^2$ where I is the peak-to-peak height of the line and ΔH_{pp} is the peak-to-peak first derivative linewidth. It is observed that lineshape has not changed in the temperature range 77–295 K, so keeping the spectrometer parameters like amplification and magnetic field modulation constant for a given crystal in a given direction the ratio of the EPR line intensity at 77 K ($I_{77\ K}$) to that at 295 K ($I_{295\ K}$) is found to be 0.92, signifying that the exchange is antiferromagnetic in nature.

Using the Heisenberg model to describe an antiferromagnetic 1D system Wagner and Friedberg [13] use the Hamiltonian $H = -2J \Sigma S_i S_j$ where J is the isotropic exchange parameter describing interchain coupling. With J positive (antiferromagnetic), the population of an energy level belonging to the total spin S has a temperature variation [14]

$$I_S = \{\exp[-JS(S+1)/2kT]\}/Z \tag{8}$$

where $Z = \Sigma(2S+1)\exp[-JS(S+1)/2kT]$ and is the partition function for all states of total

spin, $S = 0, 1, \ldots, S^i + S^j$. S^i and S^j are adjoining spins of copper dimers in the chain. In the present case of $S = 1$, 1D system $S^i = S^j = 1$. The intensity of the EPR line (I_T), at a given temperature arising from transition within a state S, is then proportional to I_S and is given by

$$I_T = k\{\exp[-JS(S+1)/2kT]\}/Z$$

where k is a proportionality constant.

In the present case ($S = 1$, 1D system), I_T is given by

$$I_T = k\frac{\exp(-3J/kT)}{1 + 2\exp(-J/kT) + 5\exp(-3J/kT)}. \tag{9}$$

With the help of the equation (9) and using the observed epr line intensity ratio (0.92), J is found to be about 6.1 cm^{-1}.

Considering the approximations involved, this value of J agrees fairly well with that obtained from fitting of linewidth data (5.0 cm^{-1}).

4. Concluding remarks

(1) Observation of a single symmetric EPR line and the large discrepancy between the mean g-value derived directly from EPR and the mean g-value estimated from mean magnetic susceptibility data based on the 'mean field corrected dimeric model' of Colombo *et al* [1] indicates that the 'dimeric model' does not provide a true picture of the magnetism of MHCC system.

(2) From analysis of EPR linewidth measurements adopting the 'anisotropic exchange 1D model' of Soos and others [6] and the temperature dependence of the EPR line intensity it has been shown that MHCC is best described as an antiferromagnetic exchange coupled 1D $S = 1$ system and anisotropic symmetric exchange is present.

Acknowledgments

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