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# An electron paramagnetic resonance (EPR) study on exchange coupling in the bimetallic chain compound copper(II) bisethylenediamine manganese(II) tetrachloride (CEMC) and interpretation of EPR linewidth data of two other Cu–Mn bimetallic chain compounds

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**Abstract.** Investigations of the linewidth, lineshape and intensity of the X-band EPR line observed in several crystallographic planes of the bimetallic chain compound copper(II) bis ethylenediamine manganese(II) tetrachloride (CEMC) are carried out at room and liquid nitrogen temperatures. The observed angular anisotropy of the linewidth has been satisfactorily explained on the basis of the anisotropic exchange model and of the effective spin  $S = 2$  formalism. It is inferred that the CEMC crystal is well described as constituted of FM coupled Cu–Mn dimeric chains oriented parallel to the  $c$ -axis of the monoclinic crystal. Within each Cu–Mn dimer exchange coupling is, however, of AFM type. The above model has also been successfully applied to interpret anisotropic linewidth data obtained in two other Cu–Mn bimetallic chain monoclinic compounds, namely,  $\text{MnCu}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$  and  $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$ .

## 1. Introduction

One-dimensional magnetism is an important field in which both physicists and chemists are interested. The studied compounds have generally been regular homometallic chains, in which the magnetic centres are equally spaced along the chain. Next, alternating homometallic chains, in which there are two intrachain exchange parameters, were discovered. More recently, regular bimetallic chains were prepared and investigated both theoretically and experimentally [1]. It has been firmly established that EPR is an important tool for studying low dimensionality in magnetic materials. Ample literature has appeared which shows that EPR can provide first-hand information on spin dynamics and on interactions that eventually lead to three-dimensional order [2, 3] at low temperature. Richards, Legendijk and others [2], are the pioneers in developing ‘spin-diffusion’ theory, and in showing that for Mn(II) magnetic systems room temperature EPR linewidth, anisotropy and lineshape studies are helpful in determining the magnetic dimensionality as well as evaluation of isotropic Heisenberg exchange present in those magnetic substances even though they are in the paramagnetic state. In Cu(II) low dimensional magnetic systems Soos and others [3] have pointed out that, due to the presence

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of non-zero S.O. coupling, anisotropic exchange interactions are required to be incorporated in the EPR linewidth theory and have shown their importance in explaining the observed orientational dependence of linewidth.

EPR studies on magnetic dimensionality of few Cu–Mn bimetallic chain compounds, namely,  $\text{MnCu}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$  (denoted '1'),  $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$  (denoted '2') (pba is 1,3-propanediylbis(oxamato); pbaOH is 2-hydroxy-1,3-propanediylbis(oxamato)) and  $\text{Mn-Cu}(\text{obp})(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}$  (denoted '3') (obp = oxamidbis(N,N'-propionato) are available [4, 5]. The angular dependence of linewidth data in these cases has been explained on the basis of spin diffusion formalism. However, it has been also noticed that in some crystallographic planes the experimental data could not be fitted at all. In view of the fact that the magnetic component of the copper(II) ions of these Mn–Cu bimetallic chains have substantial S.O. coupling ( $\lambda = -829 \text{ cm}^{-1}$ ), Soos and others' anisotropic exchange formalisms based on the non-zero value of S.O. coupling have been applied to see how far the observed angular variation of linewidths in '1' and '2' compounds can be accounted for.

Recently, preparation, x-ray crystallography and magnetic susceptibility of a new Cu–Mn bimetallic chain compound, namely, copper(II)bisethylenediamine manganese(II) tetrachloride,  $\text{Cu}(\text{en})_2\text{MnCl}_4$  (hereafter, for short, CEMC), where en stands for ethylenediamine, have appeared in the literature [6]. The special feature of this monoclinic compound is that its structure is built up of chains in which alternating Mn(II) and Cu(II) ions are bridged by chlorine ligands. The chains lie parallel to the *c*-axis. The separations between adjacent Cu(II) and Mn(II) ions in the chain are alternately 4.612 Å and 4.824 Å. The nearest separations among the Cu(II) and Mn(II) ions in the adjacent chains are 5.566 Å and 5.715 Å respectively. So, from the structural dispositions of magnetic Cu(II) and Mn(II) ions, the magnetic dimensionality is not too obvious. However, one feature of the structure in favour of magnetic one dimensionality is that Cu and Mn ions in the chains parallel to the *c*-axis are bonded by 'superexchange', through bridging Cl ligands. Analysis of magnetic susceptibility data obtained in the temperature range 2–300 K [6] has, however, not provided any definite clue about the nature of magnetism in this bimetallic compound in the high temperature regime above 20 K. Further, from the analysis of magnetic data taken in the temperature range 20–10 K Chiari *et al* [6] concluded that their magnetic data could be reproduced comparably well by two inconsonant models based on either a vanishingly small Mn(II) . . . Cu(II) interaction that leads to dominant AF coupling of second-neighbour Mn(II) ions or, alternatively, cooperative intrachain Mn(II) . . . Cu(II) interactions of opposite signs. In this backdrop of the uncertainty regarding the magnetic dimensionality and the nature of Mn–Cu exchange in CEMC as stated above it has been thought worthwhile to undertake measurements of lineshape, linewidth and intensity of the EPR line at X-band in different crystallographic planes of newly grown crystals of the title compound both at room temperature (RT) and liquid nitrogen temperature (LNT) and their analysis in the light of relevant theories available in order to throw new light on the nature of exchange in this bimetallic compound.

## 2. Experiment

Single crystals of CEMC are prepared by following the method of Chiari *et al* [6]. Crystals are grown from alcoholic solution by the slow evaporation method by which we have obtained good quality crystals of violet colour and of rhombohedral shape. A CHN analyser and atomic absorption spectrometer are employed for estimating the atomic percentages of various elements in the crystal, which confirms the composition of the title compound. A Varian X-band E-109 Century series EPR spectrometer is employed to record the spectra in *ac*- and *bc*-planes of the monoclinic crystal at RT as well as LNT by rotating the crystal mounted on a

quartz rod fixed to a goniometer through different angles within a X-band rectangular cavity working in TE<sub>102</sub> mode. At RT, a structureless symmetric derivative line is observed at all angles in a given plane. The nature of the spectra and the magnitude of linewidth remain unaltered at LNT. The experiment was carried out at low microwave power level of the order of 0.1 mW.

### 3. Results and discussion

#### 3.1. Effect of X-band microwave power level on EPR spectrum

We have studied the effects of microwave power on peak-to-peak derivative EPR linewidths ( $\Delta H_{p-p}$ ) along the chain axis ( $c$ ) and the  $b$ -axis both at RT and LNT. It is observed that at RT,  $\Delta H_{p-p}$  values along the  $c$ -axis and  $b$ -axis remain constant up to the 1 mW power level. At LNT  $\Delta H_{p-p}$  along the  $b$ -axis in the  $bc$ -plane remains unchanged up to 1 mW but along the chain direction ( $c$ -axis) only up to 0.2 mW. In one-dimensional organic metals there are some studies of anisotropic linewidth with very elaborate  $T_1$  and  $T_2$  relaxation time measurements by pulsed EPR which take dipolar interactions between conduction electrons and spin-orbit coupling into account [7]. In the present 1D system the observed anisotropic dependence of linewidth on microwave power particularly at LNT might arise from anisotropic relaxation phenomena of spin-spin or spin-lattice relaxation type. However, to avoid any complexity all linewidth measurements are carried out at the microwave power level of 0.1 mW. This microwave power level is chosen so that  $\Delta H_{p-p}$  values measured at RT and LNT are not affected by minor variation in microwave power around it.

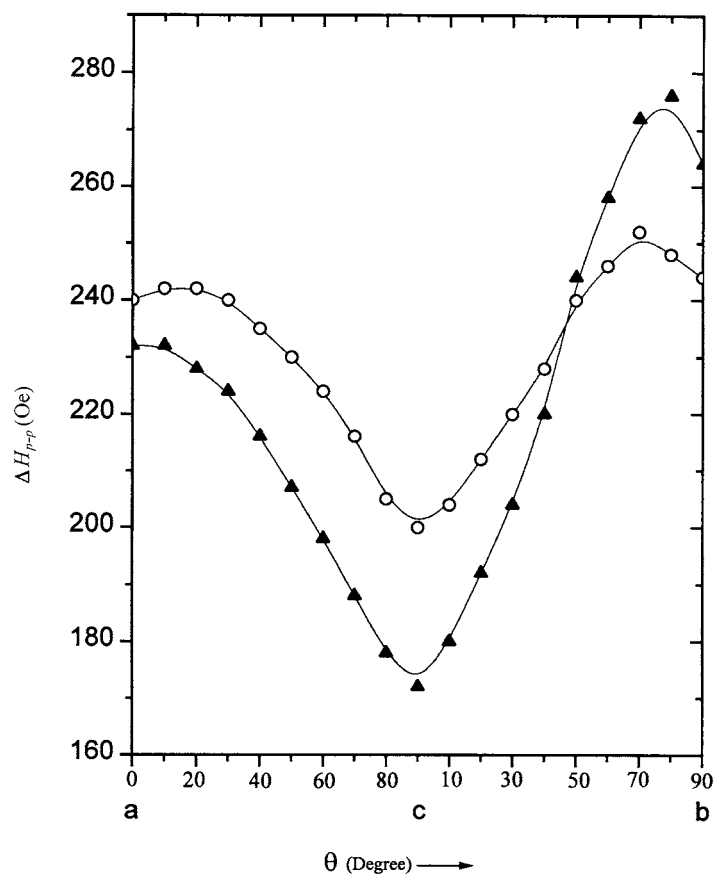
#### 3.2. Linewidth and $g$ -factor

The angular variations of  $\Delta H_{p-p}$  in  $ac$ - and  $bc$ -planes at RT and LNT are shown in figure 1. At room temperature it is seen in the  $ac$ -plane that  $\Delta H_{p-p}$  is a minimum along the  $c$ -axis (172 Oe) and a maximum (232 Oe) in a direction at 90° from the  $c$ -axis (approximately the  $a$ -axis since the monoclinic angle  $\beta = 91.26^\circ$ ). In the  $bc$ -plane  $\Delta H_{p-p}$  is 264 Oe along the  $b$ -axis. It is interesting to observe at LNT that while there is an increase in  $\Delta H_{p-p}$  along the  $c$ -axis (from 172 Oe to 200 Oe), a decrease in  $\Delta H_{p-p}$  occurs along the  $b$ -axis (264 Oe to 244 Oe). In both  $ac$ - and  $bc$ -planes the  $g$ -value is isotropic ( $g = 2.03$ ) at RT as well as LNT. The value of  $g$  neither conforms to those usually observed in an Mn<sup>2+</sup> complex or in a Cu<sup>2+</sup> complex. It may be described as the mean  $g$ -value corresponding to the Cu<sup>2+</sup>-Mn<sup>2+</sup> pair, the exchange between the pair resulting in a single line.

In section 3.5 from fitting of linewidth data it is shown that the exchange coupling between Cu<sup>2+</sup> and Mn<sup>2+</sup> ions of a Cu-Mn pair is AFM, i.e.  $S = 2$ . In that case it has been shown [8] that the effective  $g$  is given by

$$g_{eff} = (7g_{Mn} - g_{Cu})/6. \quad (1)$$

Assuming the value of  $g$  for Mn<sup>2+</sup> (high spin 5/2) as 2.00 (isotropic) and the  $g$ -values obtained in Cu(en)<sub>2</sub>Cl<sub>2</sub>.H<sub>2</sub>O (where Cu<sup>2+</sup> has octahedral coordination of four N atoms in the equatorial positions and one Cl and one H<sub>2</sub>O molecule in the axial positions, similar to that in CEMC) [9] applicable for Cu<sup>2+</sup> ions in the present system effective  $g$ -values in the parallel and perpendicular directions of tetragonally distorted Cu<sup>2+</sup> octahedra derived using equation (1) are  $g_{\parallel}^{eff} = 1.96$ , and  $g_{\perp} = 1.99$ . Thus the effective  $g$ -anisotropy is very close to the observed  $g$ -value of 2.03 ( $g_{av} = (g_{\parallel}^{eff} + 2g_{\perp})/3 = 1.98$ ).



**Figure 1.** Observed angular dependence of derivative linewidth ( $\Delta H_{p-p}$ ) of CEMC at RT and LNT. -▲-▲-▲-:  $\Delta H_{p-p}$  at LNT. -○-○-○-:  $\Delta H_{p-p}$  at RT.

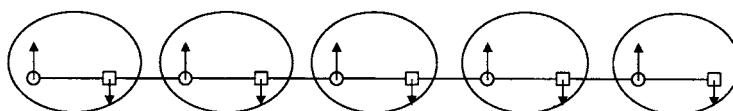
### 3.3. Lineshape

Lineshapes of single symmetrical structureless lines obtained along the  $c$ -axis (chain direction), the magic angle direction ( $54.7^\circ$  to the  $c$ -axis) in the direction at right angles to the  $c$ -axis in the  $ac$ -plane, the  $b$ -axis and also along several directions in the  $ac$ -plane are analysed following the method of a normalized plot [10]. It follows in each case that the lineshape is nearly Lorentzian. The lineshape remains unaltered at LNT. So, the absorption linewidth at half height  $\Delta H_{1/2}$  and the derivative linewidth  $\Delta H_{p-p}$  are related as follows:

$$\Delta H_{1/2} = (\sqrt{3}/2)\Delta H_{p-p}.$$

### 3.4. Temperature dependence of EPR line intensity

The nature of exchange coupling among Cu–Mn bimetallic dimers within the magnetic chain of CEMC is evident from the thermal dependence of EPR intensity. The intensity ( $I$ ) of an EPR line may be taken as nearly proportional to  $I'(\Delta H_{p-p})^2$ , provided that lineshape does not change with temperature.  $I'$  is the peak-to-peak height of the derivative line. The relative intensities of lines along different crystallographic axes at LNT (with respect to those at RT) are shown in table 1. A significant increase in intensity of the EPR spectra (under identical



**Figure 2.** Schematic representation of effective spin of Cu–Mn dimeric unit in the chain direction. The arrows indicate manganese spins as well as copper ions arranged along opposite directions within each dimeric unit.

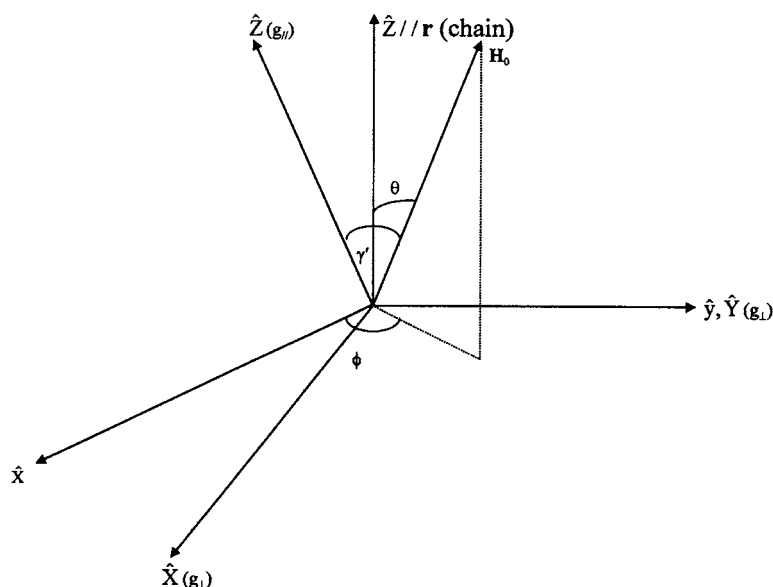
**Table 1.** Relative intensity of EPR line along three crystallographic axes of CEMC.

Axis	Relative intensity = $I_{LNT}/I_{RT}$
<i>a</i>	3.5
<i>b</i>	11.8
<i>c</i>	5.5

gain and identical magnetic field modulation amplitude) with decrease in temperature has been observed. It is relevant here to consider the arrangement of Mn and Cu ions in a chain to understand the observed thermal behaviour of EPR line intensity. The Mn(II) ion is under a distorted tetrahedral crystal field (weak crystal field) and so most likely is in the spin state  $5/2$  ( $S_{Mn}$ ). The Cu(II) ion can only be in the spin state  $1/2$  ( $S_{Cu}$ ). Along the chain direction (*c*-axis) Mn and Cu ions are bridged by Cl ligands and thus the neighbouring Mn and Cu ions in the chain are superexchange coupled via intermediary Cl ligands. In the chain direction alternate Cu . . . Mn distances are slightly but significantly different: 4.612 and 4.824 Å. So there is an alternation in separation among neighbouring Mn and Cu ions along a chain (*c*-axis). We assume neighbouring Mn(II) and Cu(II) ions having smaller separation (4.612 Å) together form a bimetallic dimeric unit. Cu(II) and Mn(II) ions within each bimetallic unit may be coupled ferromagnetically (FM) and then the ground state spin will be  $S = 3$ . Alternatively, they may be coupled antiferromagnetically (AFM) and in that case the ground state spin will be  $S = 2$  (figure 2). Thus from the observed increase in the intensity of the EPR line with decrease in temperature it may be inferred that exchange among Cu–Mn dimeric units in the magnetic chain is probably of ferromagnetic (FM) type.

### 3.5. Theoretical considerations and fitting of angular dependence of linewidths in principal crystallographic planes of CEMC crystal

From the spin diffusion theory of Richards and others [2] it follows that lineshape should be non-Lorentzian along the chain direction and Lorentzian at the magic angle. But the EPR lineshape analysis has shown that contrary to the spin-diffusion prediction the EPR lineshape is nearly Lorentzian in all directions of CEMC crystal. Further, it is seen from the linewidth–angular orientation graphs in crystallographic *ac*- and *bc*-planes (figure 1) that the linewidth is a minimum along the chain direction (*c*-axis) and the maximum at  $90^\circ$  orientation. These observations are directly in conflict with the spin diffusion theory, which predicts that the linewidth should have a maximum along the chain direction, a minimum at the magic angle ( $54.7^\circ$  to the chain axis) and a second maximum in a direction at right angles to the chain axis. It is thus evident that the spin diffusion mechanism may not be operative in the present system although one of the magnetic partners of the bimetallic system is Mn(II) for which spin diffusion theory is valid. As discussed earlier CEMC may be conceived as chains of Cu–Mn dimeric units and the Cu(II) ion, a constituent ion of the dimer, possesses spin–orbit coupling



**Figure 3.** Co-ordinate system used in theoretical treatment of various interactions. The Z-axis is defined along the direction of strong exchange (the chain axis) and  $H_0$  represents the direction of the applied magnetic field.

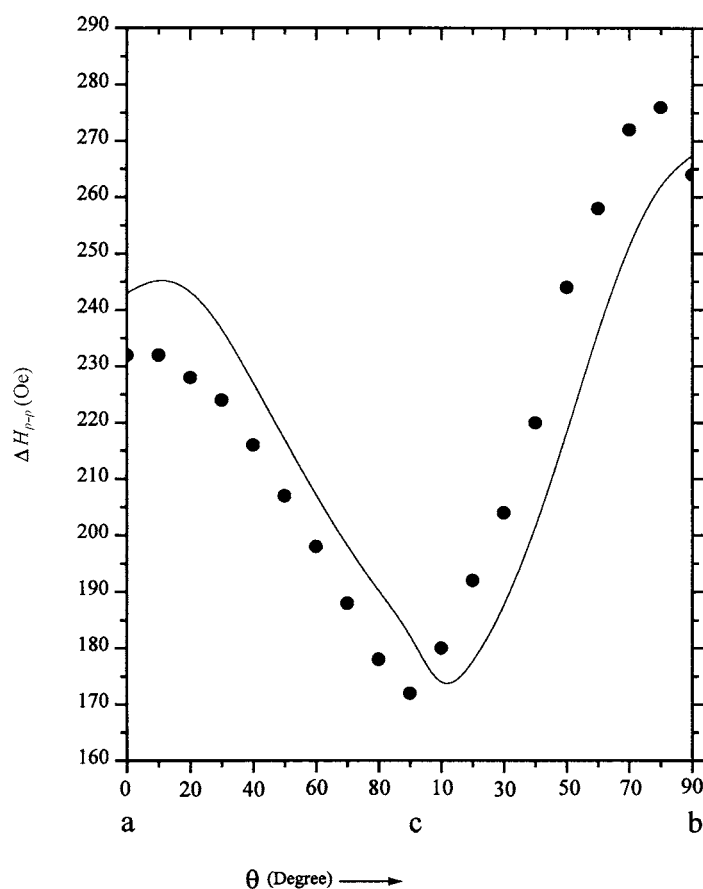
of considerable magnitude ( $-829 \text{ cm}^{-1}$ ). So, the presence of anisotropic exchange cannot be ruled out. Again, from the structural point of view there is a lack of inversion symmetry among these bimetallic units along the chain and so over and above the anisotropic symmetric exchange (a.s.e.), anisotropic antisymmetric exchange (a.a.e.) needs due consideration in any linewidth analysis of 1D spin chains having non-zero spin-orbit coupling for the magnetic units. McGregor and Soos [3] calculated the absorption width of the EPR line by using general linewidth theory for a Cu(II) 1D system, i.e. the  $S = 1/2$  1D system, by including the Blume-Hubbard result for the spin dynamics [11] and preferentially weighting a.s.e. as well as a.a.e. with dipolar terms. Ritter *et al* [12] extended this theory to situations where the symmetry of anisotropic symmetric exchange is orthorhombic and, in addition, a.a.e. interaction is present. We have applied the linewidth theories of McGregor and Soos [3] and Ritter *et al* [12] to explain the observed linewidth anisotropy in the CEMC system. As discussed earlier, in CEMC two situations may arise, i.e. 1D chains consisting of  $S = 2$  (AF coupled) or  $S = 3$  (FM coupled) bimetallic Mn(II), Cu(II) dimers.

Following Soos and others [3, 12], and neglecting next-nearest neighbour dipolar and hyperfine interactions, the theoretical expression for the absorption linewidth  $\Delta H_{1/2}$  is given by

$$\Delta H_{1/2} = (2\sqrt{2}/3J) (M'_2 + \rho M'_2(0) + M_2^A) \quad (2)$$

where  $J$  is the Heisenberg symmetric exchange.  $M'_2$ , the second moment containing the non-secular contribution of the dipolar and anisotropic exchange terms in the co-ordinates of figure 3, is given by

$$M'_2 = 3S(S+1)/h^2 \times \left[ \begin{array}{l} (1/3)(D_e)^2\{(3-2\Delta)\cos^2\gamma' + (3+2\Delta)\} + D_d^2(\cos^2\theta + 1) - (D_e D_d/3) \\ \left\{ \begin{array}{l} [(3+\Delta)\cos^2\gamma' - (1+\Delta)](3\cos^2\theta - 1) \\ + (1/3)[-2\Delta + (3+\Delta)\sin^2\gamma']\sin^2\theta\cos[2(\alpha+\phi)] \end{array} \right\} \end{array} \right] \quad (3)$$



**Figure 4.** Angular dependence of  $\Delta H_{p-p}$  of CEMC at RT. ●: experimental points. —: best fitted curve under the most general condition.

where

$$D_d = (\bar{g}\beta)^2/r^3 \quad \bar{g} = (g_a^2 + g_b^2 + g_c^2)/3. \quad (4)$$

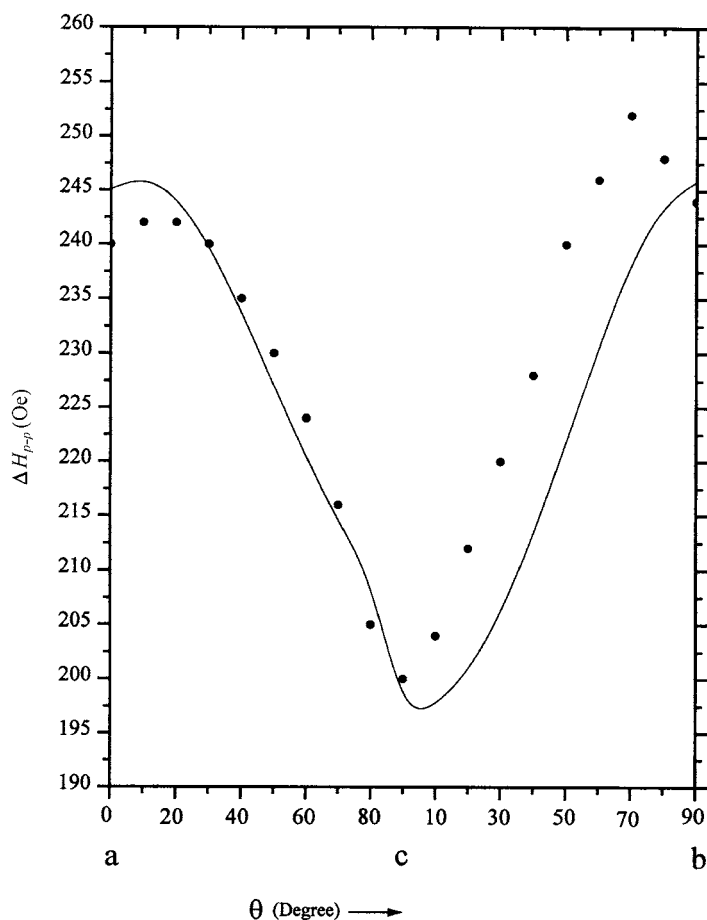
$D_e$  and  $\Delta$  are axial and orthorhombic components of the a.s.e. tensor respectively and  $r$  is the nearest neighbour intrachain separation along the chain axis ( $z$ ), i.e. in the present case, the separation between two bimetallic units. The angle  $\alpha$  represents the rotation of  $D_e^{mol}$  (a.s.e. tensor) which results from the transformation to laboratory co-ordinates, and  $D_e^{mol}$  is given by

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

where  $q$  and  $p$  are given by  $q = -1 - \Delta$  and  $p = -1 + \Delta$  in order to maintain a zero trace operator. The angles  $\theta$  and  $\phi$  define the orientation of the magnetic field  $H_0$  and  $\gamma'$  is the angle between  $H_0$  and the Cu-Mn dimeric unit's  $Z$  axis. It has been customary to assume that the principal axes of the a.s.e. and  $g$ -tensors are coincident. The purely secular part  $M'_2(0)$  is given by

$$M'_2(0) = 3S(S+1)/2h^2[(D_e/3)[(3+\Delta)\cos^2\gamma' - (1+\Delta)] - D_d(3\cos^2\theta - 1)]^2. \quad (5)$$





**Figure 5.** Angular dependence of  $\Delta H_{p-p}$  of CEMC at LNT. ●: experimental points. —: best fitted curve under the most general condition.

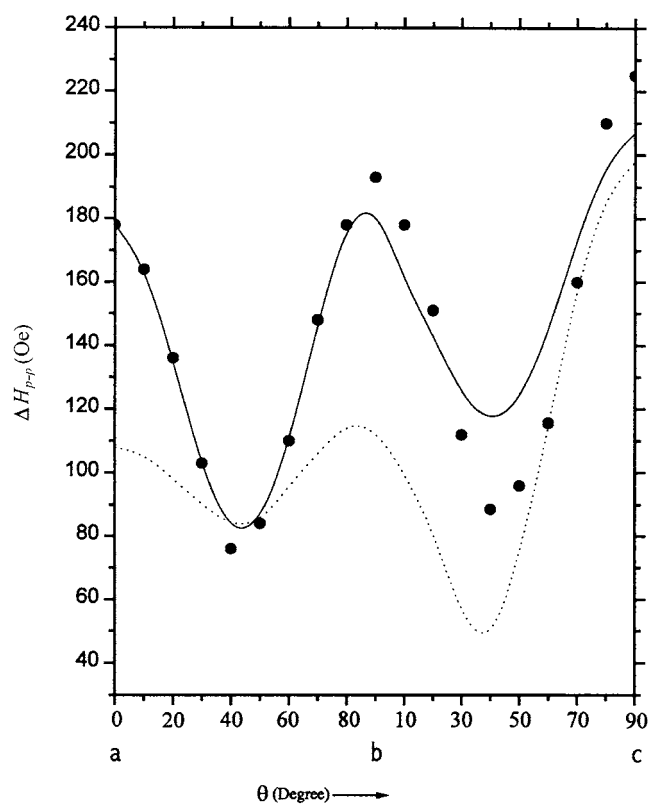
The value of the parameter  $\rho$  ranges from 0 to  $\infty$ .  $\rho$  enhances the secular contribution.  $\rho \rightarrow 0$  in the magnetic 3D case.

The a.a.e. interaction, i.e.  $S \times S$  interaction is also described in the co-ordinates of figure 3. According to the symmetry rules of Moriya [13], if  $\mathbf{d}$  (a.a.e. vector) lies completely in the  $ac$ -plane, the contribution to the second moment is given by

$$M_2^A = (d^2/8)\{2 + \sin^2(\theta - \theta_A)\} \quad (6)$$

where  $d$  is the a.a.e. parameter and  $\theta_A$  is the angle made by  $\mathbf{d}$  with the  $a$ -axis of the crystal. For simplicity we have assumed  $\gamma' = \theta$  for the CEMC system.

We have applied the theory of Soos and others modified as outlined above in order to fit the observed angular anisotropy in linewidth in  $ac$  and  $bc$  crystallographic planes of the CEMC crystal for both  $S = 2$  and  $S = 3$  situations. For the  $S = 3$  case, it is seen that the observed linewidth anisotropy data cannot be fitted at all for all ranges of values of five parameters, namely,  $J$ ,  $D$ ,  $d$ ,  $\Delta$  and  $\rho$ . Next, for the  $S = 2$  case the fitting of experimental linewidth (figures 4 and 5) is attempted under different conditions, i.e. (i)  $\Delta = 0$ ,  $\rho = 0$ ; (ii)  $\Delta = 0$ ,  $\rho \neq 0$ ; (iii)  $\Delta \neq 0$ ,  $\rho = 0$ ; (iv)  $\Delta \neq 0$ ,  $\rho \neq 0$ . The best fitting at LNT as well as RT has been obtained under the most general condition (iv). These are shown in figures 4 and 5. Best fitted



**Figure 6.** Fitting of angular dependence of  $\Delta H_{p-p}$  of pba at RT. ●: experimental points. ....: dotted line based on 'diffusion model' employed by Gatteschi *et al.*. —: solid line following 'anisotropic exchange model' employed by the present authors.

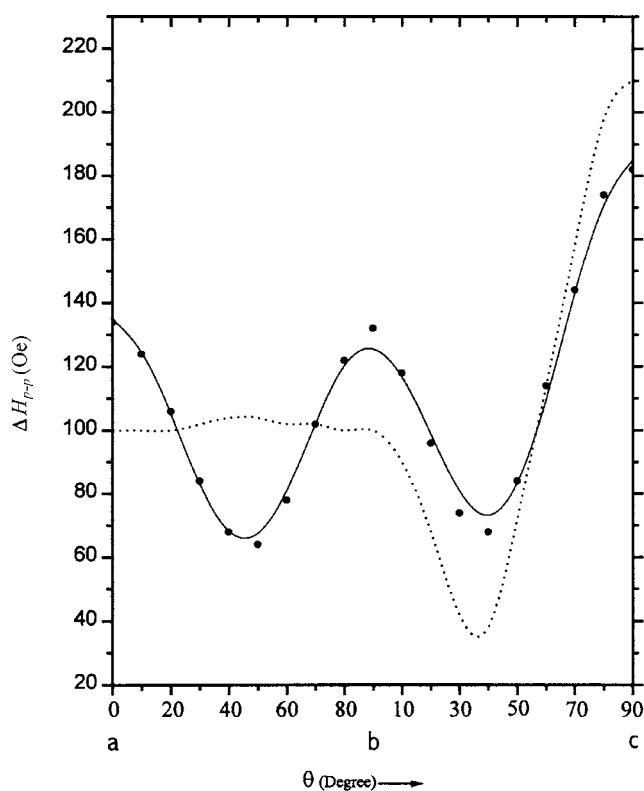
**Table 2.** Best fitted exchange related parameters at RT and LNT for CEMC 'anisotropic exchange theory'.

Parameters	RT	LNT
$J$ ( $\text{cm}^{-1}$ )	6	4.9
$D$ ( $\text{cm}^{-1}$ )	0.15	0.15
$\Delta$	2.6	1.2
$d$ ( $\text{cm}^{-1}$ )	0.2	0.2
$\rho$	0.1	0.1

values of isotropic exchange, anisotropic exchange and other relevant parameters are shown in table 2. It is seen that only  $J$  and  $\Delta$  show some variation with temperature. Other parameters, namely,  $D$ ,  $d$  and  $\rho$  show no temperature dependence. Non-zero  $\rho$  is in conformity with the magnetic one-dimensionality of CEMC.

### 3.6. Analysis of anisotropic EPR linewidth obtained by Gatteschi *et al* [4] in two other Cu–Mn bimetallic chain compounds on the basis of the anisotropic exchange model

EPR studies including the angular dependence of linewidth of two bimetallic pseudo-one-dimensional orthorhombic Mn–Cu systems, namely,  $\text{MnCu}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$  (1) and



**Figure 7.** Fitting of angular dependence of  $\Delta H_{p-p}$  of pbaOH at RT. ●: experimental points. ·····: dotted line based on 'diffusion model' employed by Gatteschi *et al.* —: solid line following 'anisotropic exchange model' employed by the present authors.

MnCu(pbaOH)(H<sub>2</sub>O)<sub>3</sub> (2), were performed by Gatteschi *et al* [4] Space groups of '1' and '2' are, however, different (in 1 it is  $P_{nma}$ , in '2' it is  $P2_12_12_1$ ). In each case the structure consists of bimetallic chains running along the  $b$ -axis with Mn(II) and Cu(II) ions bridged by oxamato groups. The nearest neighbour distances between Cu and Mn ions within a chain are 5.412 Å for '1' and 5.433 Å for '2'. The authors of [4] attempted an explanation of the angular dependence of  $\Delta H_{p-p}$  in different crystallographic planes of these crystals on the basis of spin diffusion formalism. However, their fittings are not at all satisfactory. Their fittings have been shown by a dotted line (·····) in figures 6 and 7. It would be interesting to inspect whether the fittings can be improved upon by adopting the anisotropic exchange model in these crystals as has been successfully applied in case of CEMC. For both the crystals experimentally three maxima and three minima in the linewidth curve in three crystallographic planes are observed. Theoretically speaking there are five unknown parameters, namely,  $J$ ,  $D$ ,  $d$ ,  $\Delta$  and  $\rho$ , which are to be evaluated. So, in contrast to the case of CEMC, no approximation regarding neglect of some parameters at the first instance is needed for the relevant fitting. The results of our fitting are shown by continuous lines in the two cases in figures 6 and 7 respectively. It is clearly seen that the fitting based on the anisotropic exchange model provides much better fitting. The relevant fitted parameters are shown in table 3. However, it is to be noted that the estimated values of the isotropic exchange  $J$  are much larger compared to those derived from magnetic susceptibility data, i.e. 83 and 113 cm<sup>-1</sup> respectively for '1' and '2' bimetallic

**Table 3.** Best fitted exchange related parameters obtained in pba and pbaOH using anisotropic exchange theory of EPR linewidth.

Parameters	MnCu(pba)(H <sub>2</sub> O) <sub>3</sub> .2H <sub>2</sub> O	MnCu(pbaOH)(H <sub>2</sub> O) <sub>3</sub>
$J$ (cm <sup>-1</sup> )	83	113
$D$ (cm <sup>-1</sup> )	0.3	0.38
$\Delta$	1.25	1.75
$d$ (cm <sup>-1</sup> )	0.1	0.1
$\rho$	4.0	2.1

systems while from magnetic susceptibility data  $J$  is 23.4 cm<sup>-1</sup> for both systems. The reason may be that different models have been applied in the two cases. The much larger values of  $J$  obtained in crystal systems '1' and '2' compared to that in CEMC are conceivable because of the fact that in the former systems exchange between Cu<sup>2+</sup> and Mn<sup>2+</sup> ions of each dimer occurs through double oxygen bridging from oxamato groups while in the latter compound exchange takes place via single chloride ligand bridge.

#### 4. Concluding remarks

The above analysis of linewidth, lineshape and line intensity at room and liquid nitrogen temperatures on the basis of the anisotropic exchange model reveals that the CEMC crystal may be conveniently described as constituted of FM coupled Cu–Mn dimeric chains oriented parallel to the  $c$ -axis of the crystal. Within each Cu–Mn dimer exchange coupling, however, is AFM type. It has been shown further that the linewidth anisotropy data of Gatteschi *et al* [4] obtained in two other Cu–Mn bimetallic chain compounds, namely, MnCu(pba)(H<sub>2</sub>O)<sub>3</sub>.2H<sub>2</sub>O and MnCu(pbaOH)(H<sub>2</sub>O)<sub>3</sub>, are also much better explained on the basis of the 'anisotropic exchange model' employed in the case of CEMC.

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