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Electron Spin Resonance Study on Copper Salicylate Tetrahydrate (Blue Green) and Anhydrous Copper Salicylate (Brown)

By

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Electron spin resonance studies are performed on copper salicylate tetrahydrate (blue green) and anhydrous copper salicylate (brown) in the temperature interval 77 to 300 K. The spectra correspond to dimeric and normal copper salt, respectively. The spin Hamiltonian parameters for the dimeric compound are: $g_x = 2.059 \pm 0.003$, $g_y = 2.015 \pm 0.005$, $g_z = 2.28 \pm 0.005$, $D = (0.318 \pm 0.005) \text{ cm}^{-1}$, $E = (0.007 \pm 0.002) \text{ cm}^{-1}$. The smaller value of g_z in CuSal (blue green) suggests a greater magnitude of the cubic component of the ligand field compared to other dimeric copper compounds. The mean magnetic susceptibility is determined for CuSal (blue green) in the interval 300 to 101 K. The value of exchange integral J is calculated to be $(225 \pm 10) \text{ cm}^{-1}$. Finally an estimate of the approximate Cu-Cu distance (2.59 Å) within the dimers is made. The normal copper salt (CuSal brown) shows an isotropic g value (2.21) which is practically temperature independent in the interval 300 to 77 K. The peak-to-peak derivative linewidth of Cu-Sal (brown) shows a linear increase with temperature. This dependence suggests the influence of phonon modulation of the isotropic exchange interaction in this compound.

Elektron-Spin-Resonanz-Untersuchungen werden an Kupfer-Salicylat-Tetrahydrat (blau-grün) und anhydrirem Kupfersalicylat (braun) im Temperaturintervall 77 bis 300 K durchgeführt. Die Spektren korrespondieren mit dimerischen und normalen Kupfersalzen. Die Spin-Hamilton-Parameter sind für die dimerische Verbindung: $g_x = 2,059 \pm 0,003$, $g_y = 2,015 \pm 0,005$, $g_z = 2,28 \pm 0,005$, $D = (0,318 \pm 0,005) \text{ cm}^{-1}$, $E = (0,007 \pm 0,002) \text{ cm}^{-1}$. Der kleinere Wert von g_z im Cu-Sal (blau-grün) deutet auf eine größere kubische Komponente des Ligandenfeldes hin, verglichen mit anderen dimerischen Kupferverbindungen. Die mittlere magnetische Suszeptibilität wird für Cu-Sal (blau-grün) im Intervall 300 bis 101 K ermittelt. Der Wert des Austauschintegrals J wird zu $(225 \pm 10) \text{ cm}^{-1}$ bestimmt. Schließlich wird eine Abschätzung der Cu-Cu Distanz (2,59 Å) innerhalb der Dimere durchgeführt. Das normale Kupfersalz (Cu-Sal braun) zeigt einen isotropen g -Wert (2,21), der praktisch temperaturunabhängig im Intervall 300 bis 77 K ist. Die Linienbreite (Maximum-Maximum) von Cu-Sal (braun) zeigt einen linearen Anstieg mit der Temperatur. Diese Abhängigkeit deutet auf die Rolle der Phonon-Modulation der isotropen Austauschwechselwirkung in dieser Verbindung hin.

1. Introduction

The compound copper salicylate ($\text{Cu}(\text{C}_6\text{H}_4\text{OHCOO})_2$) exists both in tetrahydrate and anhydrous forms. There are two modifications of the tetrahydrate form: pale blue and blue green. The anhydrous modifications exist in brown, blue green, and green forms. The pale blue form of copper salicylate tetrahydrate shows a normal magnetic moment of $1.92\mu_B$ (Inoué et al. [1]). The crystal class is monoclinic (space group $P_{21/C}-C_{2h}^2$) [2]. The copper(II) ion in the molecule $\text{Cu}(\text{C}_6\text{H}_4\text{OHCOO})_2 \cdot 2 \text{H}_2\text{O}$ is situated

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in a planar configuration with two oxygens of water in transposition at 1.92 Å and two oxygens from the carboxyl group at 1.84 Å distance. The other two carboxyl oxygens are outside the sphere of coordination of the copper atom and the compound is therefore not a chelate. EPR studies of the pale blue form [3] revealed that $g_{\parallel} = 2.271$ and $g_{\perp} = 2.065$. The brown form of the anhydrous modification was also found by Inoue et al. [1] to possess a normal magnetic moment of $1.87\mu_B$. The blue green form of copper salicylate tetrahydrate (in brief, CuSal (BG)) falls among the dimeric copper compounds showing an abnormal moment, i.e. less than $1.73\mu_B$ [1]. These compounds in the majority of cases contain dimers [4 to 13]⁹ with bridging ligands such as halogens, oxygen ion, hydroxyl ion, or carboxylate group and *Oxy* ligands such as pyridine-N-oxides. We have taken up the X-band EPR studies of the blue green form of copper salicylate tetrahydrate (CuSal BG) and the brown form of anhydrous copper salicylate (CuSal BR) in the temperature range 77 to 300 K. Well known methods of extracting the relevant ligand field parameters from analysis of the EPR spectra have been employed. The ligand field properties are described in relation to known dimeric copper compounds.

2. Experimental

CuSal (BG) and CuSal (BR) were prepared by the methods of Inoue et al. [1] and Hanic and Michalov [2] and had satisfactory analyses. Attempts to grow good single crystals of the compounds were unsuccessful.

EPR spectra of the powdered compounds were performed on a Varian X-band instrument (Model E-4) at IIT Madras and recorded at temperatures 300, 250, 200, 150, and 77 K. Spectra were also obtained for the two forms of copper salicylate dissolved in various solvents (concentration 1 wt%) like chloroform, ethanol, pyridine, dimethyl sulfoxide, chloroform dimethyl sulfoxide (80:20), and petroleum ether:pyridine (80:20) at those temperatures.

3. Analysis of EPR Spectra

The EPR spectra of the two salts CuSal (BG) and CuSal (BR) are found to be quite different in the temperature interval (77 to 300 K). We shall first discuss CuSal (BG) spectra.

3.1 Copper salicylate tetrahydrate (blue green modification)

The major features of the spectra of CuSal (BG) at 300 and 77 K (Fig. 1 and 2) are quite similar to the exchange coupled dimeric copper salts [5 to 9]). However, the EPR spectra at intermediate temperatures (250, 200, and 150 K) for the compounds cited above are not available and so could not be compared with those for CuSal (BG). It is seen that at room temperature (300 K) (Fig. 1) only two pronounced peaks

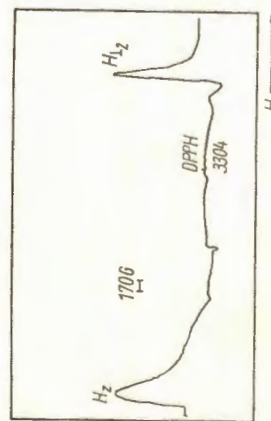


Fig. 1. X-band EPR spectra of CuSal (BG) at room temperature

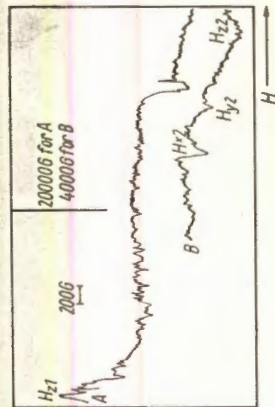


Fig. 2. X-band EPR spectra of CuSal (BG) at 77 K. $\nu = 9.128$ GHz. Resolution of the H_{\perp} line into two lines marked H_{x2} and H_{y2} could be clearly seen

appear. These correspond to the zero-field and to the perpendicular line (Wasson et al. [7]). As the temperature is lowered from 300 to 150 K the perpendicular line gradually broadens and at 77 K this line is seen to be completely split up (Fig. 2) into two components. This splitting corresponds to a rhombic distortion [8] in the crystal-line field at the Cu^{2+} ion in CuSal (BG) at 77 K. At 150 K another peak H_{x2} starts appearing at a very high field (≈ 5800 G) and is clearly seen in the 77 K spectra. This is probably due to a high spin-lattice relaxation rate for the high field parallel transition.

The spin Hamiltonian for the exchange coupled dimeric copper compounds in the presence of a magnetic field is given by [14],

$$\mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + D(S_x^2 - \frac{2}{3}) + E(S_x^2 - S_y^2), \quad (1)$$

where D , E are the zero-field splitting parameters. Here the metal hyperfine lines are omitted, since they only serve to broaden the principal resonance lines. Choosing the z axis to lie along the Cu-Cu bond and the x and y axis to be mutually perpendicular to each other and to the z axis, and assuming that the principal axes of \mathbf{D} and \mathbf{g} tensors coincide, a full matrix calculation of the energy levels [15] provides the following expressions for six resonance fields ($\Delta M_s = \pm 1$):

$$H_{z1}^2 = (g_e/g_x)^2 [(H_0 - D' + E')(H_0 + 2E')], \quad (2)$$

$$H_{z2}^2 = (g_e/g_x)^2 [(H_0 + D' - E')(H_0 - 2E')], \quad (3)$$

$$H_{y1}^2 = (g_e/g_y)^2 [(H_0 - D' - E')(H_0 - 2E')], \quad (4)$$

$$H_{y2}^2 = (g_e/g_y)^2 [(H_0 + D' + E')(H_0 + 2E')], \quad (5)$$

$$H_{x1}^2 = (g_e/g_x)^2 [(H_0 - D')^2 - E'^2], \quad (6)$$

$$H_{x2}^2 = (g_e/g_x)^2 [(H_0 + D')^2 - E'^2], \quad (7)$$

where $H_0 = h\nu/g_e\beta$, $\beta = \mu_B$, $D' = D/g_e\beta$, $E' = E/g_e\beta$.

These equations were already found to be valid for inorganic triplet molecules [7, 16, 17]. For a powder sample the axial resonance fields may be obtained [7] and g_x , g_y , g_z , D , and E can be calculated from these equations. For certain values of H_0/D' (dimensionless), the $\Delta M_s = \pm 2$ line (H_{min}) and the double quantum transition [16, 17 to 19] (H_{dq}) may also be observed. For these lines the following equations hold [17, 18]:

$$H_{\text{min}} = \frac{2.0023}{g_{\text{min}}} \left[\frac{H_0^2}{4} - \frac{D'^2}{3} - E'^2 \right]^{1/2}, \quad (8)$$

$$H_{\text{dq}} = \frac{2.0023}{g_{\text{av}}} \left[\frac{H_0^2}{3} - \frac{D'^2}{3} - E'^2 \right]^{1/2}, \quad (9)$$

$$g_{\text{min}} = [(g_{\perp})^2 + g_{\parallel}^2 \cos^2 \theta], \quad (10)$$

⁹ And references cited in [10].

where

$$g_{\perp}^2 = (g_x g_y)^{1/2} \text{ and } \cos^2 \theta = \frac{9 - 4(D/h\nu)^2}{27 - 36(D/h\nu)^2} \quad (11)$$

and

$$g_{av} = \left[\frac{2(g_{\perp}^2) + g_{\parallel}^2}{3} \right]^{1/2}$$

when $D \gg h\nu$ as is usually the case in compounds containing copper dimers where EPR measurements are performed at X-band, H_{z1} and H_{y1} and the $\Delta M_s = \pm 2$ line can no longer be observed. Four EPR lines at 80, 4500, 5000, and 5800 G have been observed in CuSal (BG) at 77 (Fig. 5 and also Table 1). These are assigned to be H_{z1} , H_{z2} , H_{y2} , and H_{z2} [15, 8, 9]. Since the total number of parameters involved is five (D , E , g_x , g_y , and g_z) four observables H_{z2} , H_{y2} , H_{z1} , H_{z2} given by (3), (5), (6), and (7), respectively, do not permit a unique determination of these parameters. Fortunately seven hyperfine lines characteristic of a Cu dimer could be very clearly observed in the frozen solution of the sample in pyridine (concentration is 1 wt%) at 77 K (see Fig. 4).

Table 1

Field values of the observed peaks in the EPR spectra of SuCal (BG) at 77 K and the spin Hamiltonian parameters derived therefrom

lines assigned	observed field (G)	calculated field (G)	spin Hamiltonian parameters
H_{z1}	80	85	$g_x = 2.059 \pm 0.005$
H_{z2}	4500	4451	$g_y = 2.015 \pm 0.01$
H_{y2}	5000	4850	$g_z = 2.28 \pm 0.01$
			$D = (0.318 \pm 0.003) \text{ cm}^{-1}$
H_{z2}	5800	5860	$E = (0.007 \pm 0.002) \text{ cm}^{-1}$
			$J = (225 \pm 10) \text{ cm}^{-1}$
			($H_0 = 3284 \text{ G}$)

The separation between the successive lines in the seven-line spectrum in the frozen solution is 12 G and should correspond to a hyperfine constant A_{\perp} of the copper dimer. The g value corresponding to the mean position of these seven lines, which is found to be 2.059 should correspond to either g_x or g_y or both (when axial symmetry is valid). We have considered all the possibilities and found that this value corresponds to g_x .

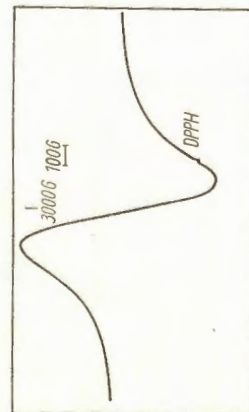


Fig. 3

Fig. 3. X-band EPR spectra of CuSal (BR) at 77 K

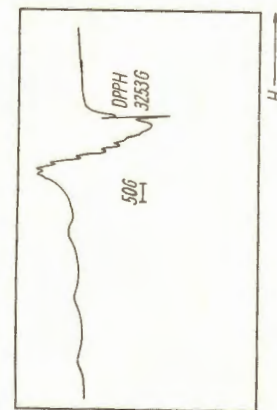


Fig. 4

Fig. 4. X-band EPR spectra of frozen solution of CuSal (BG) in pyridine (concentration is 1 wt%) at 77 K

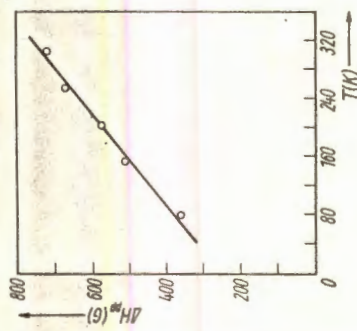


Fig. 5. X-band EPR linewidth as a function of temperature for copper salicylate (brown form)

We then solve these four equations to calculate the parameters uniquely with the help of observed values (H_{z2} , H_{y2} , H_{z1} , H_{z2}). The desired spin Hamiltonian parameters are given in Table 1.

3.1.1 Results and discussion on CuSal (BG)

In most of the cases of dimeric copper(II) carboxylate the g tensor is axial [20] the mean g (\bar{g}) rarely differs from its average (2.171) by more than 0.02. In CuSal (BG) the mean \bar{g} with $[\bar{g} = \frac{1}{3}(g_{\parallel}^2 + 2g_{\perp}^2)^{1/2}]$ is 2.120 and differs from 2.171 by more than 0.02. This is rather unusual. There are some binuclear copper(II) compounds, showing rather smaller values of \bar{g} , e.g. copper (diethylthiocarbamate) $_2$ ($\bar{g} = 2.13$), [Cu(O-hydroxyl) $_2$] ($\bar{g} = 2.13$). This small value of g may be due to stronger ligand fields in these compounds. Of the different binuclear copper complexes, Cu(AC) $_2 \cdot H_2O$ was so far known to have the largest rhombic distortion [5, 8] ($g_x - g_y = 0.04$). Our determination of the parameters for CuSal (BG) shows that the rhombic distortion ($g_x - g_y = 0.044$) is comparable to that of Cu(AC) $_2 \cdot H_2O$. The values of D and g_z in CuSal (BG) are somewhat less than the respective values in Cu(AC) $_2 \cdot H_2O$ and other Cu-carboxylate compounds [20]. Literature shows that D values for the acetate, propionate, butyrate monohydrate, benzoate trihydrate fall in the narrow range 0.327 to 0.350 cm^{-1} except for the cyanoacetate for which $D = (0.39 \pm 0.01) \text{ cm}^{-1}$. The largest value of D (0.72 cm^{-1}) has been observed in di- μ -hydroxo-bis-di (2-methylimidazole) copper(II) diperchlorate dihydrate by Reedijk et al. [17], for which the value of E is also highest, i.e. $E = (0.025 \pm 0.005) \text{ cm}^{-1}$. Lower values of D have been observed in the case of pyridine-N-oxide compounds ($D \approx 0.15$ to 0.21 cm^{-1}) [21], Cu(II) tartaric acid and adenine complexes ($D \approx 0.06$ to 0.12 cm^{-1}) [22], and Cu $_2$ (dimethyl glyoxime) $_4$ ($D = 0.035 \text{ cm}^{-1}$) [23]. Variation in the values of the rhombic component of the ligand field is also evidenced by the differences in the values of E for the copper carboxylates (0.001 cm^{-1} for the Cu-propionate [6] to (0.0147 \pm 0.003 for Cu-benzoate [7]). The value of E for CuSal (BG) is almost the same as that for copper acetate monohydrate. From the above we may conclude that the magnitude of the rhombic component of the ligand field is the same for these two compounds. The smaller value of g_z for CuSal (BG) might be due to the greater magnitude of the cubic component of the ligand field in this salt compared to that in Cu(AC) $_2 \cdot H_2O$. Due to the non-availability of X-ray structural data and ligand field spectra the magnitude of the ligand field and covalency parameters in this salt could not be ascertained.

Usually, the contributions to the experimental D value arise from dipole-dipole interactions between the unpaired electrons, D_{dd} , and a pseudo-dipolar interaction,

(originating in spin-orbit coupling), D_{psd} , so that

$$D_{\text{expt}} = D_{\text{ad}} + D_{\text{psd}} \quad (12)$$

For both of these terms theoretical expressions are known [22]

$$|D_{\text{ad}}| = 0.65g_z^2/R^3 \quad (13)$$

in which R is the averaged distance between the two electrons, usually taken as the Cu-Cu internuclear distance, and [14]

$$D_{\text{psd}} = (J/8) [(g_z - 2)^2/4 - (g_{\perp} - 2)^2], \quad (14)$$

where J , the exchange integral, representing the energy separation between the ground singlet and excited triplet state of the copper dimer.

The mean susceptibility of CuSal (BG) was measured at two temperatures 304 and 101 K. We can use these data (see Table 2) to obtain a value of J with the help of the

Table 2

Mean gram molar susceptibility data at temperatures 304 and 101 K of CuSal (BG) in units of 10^{-6} cgs

χ_{corr}	1939	1325
temp (K)	304	101

Bleaney-Bowers equation [14] for the mean gram molar susceptibility of the dimeric copper compound (after correction for diamagnetism):

$$\chi_{\text{corr}} = \frac{2g_m^2 N \beta^2}{kT} \frac{1}{3 + \exp(-J/kT)} + \text{temperature independent paramagnetic contribution}, \quad (15)$$

where $g_m^2 = \frac{1}{3}(g_z^2 + g_y^2 + g_x^2)$.

The value of J , determined using the above relation and the relevant experimental parameters given in Table 1 and 2 was found to be $(225 \pm 10) \text{ cm}^{-1}$. The temperature independent part came out to be 115×10^{-6} cgs units. Using (14) and the values of $g_z = 2.28$, $g_{\perp} = \frac{1}{2}(g_z + g_y) = 2.037$, the value of D_{psd} was found to be 0.513 cm^{-1} . Finally D_{ad} was derived (see (12) and Table 1), $D_{\text{ad}} = -0.195 \text{ cm}^{-1}$. Then, using (13) the value of R was estimated to be 2.59 \AA . This value is close to that (2.64 \AA) in copper acetate monohydrate for which $J = 310 \text{ cm}^{-1}$. However, the X-ray value of R in CuSal (BG) is not available to verify the derived R value. Of course it is to be kept in mind that there are certain approximations involved in the derivation of (13) and (14). Bleaney and Bowers [14] showed that the splitting of the triplet depends on the exchange interaction between one cupric ion in the ground state and the other cupric ion in an excited orbital; there are in fact two such excited orbitals involved, which have matrix elements to the ground orbital through the spin-orbit coupling. Allowing different values of the exchange interaction when the excited orbital is involved, one should write

$$D_{\text{psd}} = (1/8)\{J_1(g_z - 2)^2 - J_2(g_{\perp} - 2)^2\}. \quad (16)$$

However, there is no evidence as to the value of J_1 , J_2 . The point dipole approximation involved in [13] gives rise to significant error in the estimation of R . Electron delocalisation (covalency) certainly will influence R . Finally there may be non-coincidence between the g and the D principal axes directions that also influences (13) and (14) which have been used to calculate R .

3.2 EPR of CuSal (BR)

3.2.1 g values

EPR spectra of CuSal (BR) obtained at different temperatures were found to be quite distinct from that of CuSal (BG) (Fig. 3, only one spectrum at 77 K is shown). The spectra could be well described by an isotropic g value which is practically constant (2.210 to 2.20) in the temperature range 300 to 77 K and an isotropic peak-to-peak linewidth. Only the room temperature mean magnetic moment ($1.87\mu_B$) (Inoue et al. [1]) is available. This is characteristic of the existence of only copper monomer units in CuSal (BR). The EPR spectra also show absence of any dimeric copper units. An isotropic g value in copper salt is in general characteristic of Cu(II) ions embedded in regular or trigonally distorted octahedral co-ordination due to ligands. X-ray structural data of CuSal (BR) are not available. As mentioned in the Introduction, Cu(II) ions in the molecules of the pale blue CuSal tetrahydrate are in planar conformations with oxygen ligands. Thus, it follows from our EPR observation that it is reasonable to assume that either a regular octahedral co-ordination or a trigonally distorted one around Cu(II) with oxygen ligands is possible in this case. This means that Cu(II) is subjected to a dynamic Jahn-Teller effect at room temperature and it is expected that a dynamic to a static Jahn-Teller transition that is a transition from isotropic to anisotropic g values will occur at some low temperature. However, in the temperature range studied (300 to 77 K) no such transition has been observed in the EPR spectra.

3.2.2 EPR linewidth of CuSal (BR)

The linear temperature dependence of the observed derivative linewidth ΔH_{pp} (Fig. 5) in CuSal (BR) is rather interesting. Recently similar observations have been made by several workers in copper salts [24 to 26] in the temperature interval 77 to 300 K and in concentrated H manganese salt [27] in the high temperature region. In manganese salts, however, the rate of increase of linewidths with temperature (about 10 to 15 G per 1000°C temperature rise) is observed to be very small compared to that in copper salts. The following factors in general contribute to the width of EPR absorption lines from solid samples: a) interactions with magnetic dipoles of neighbouring electronic and nuclear spins, b) hyperfine interactions, c) spin-lattice relaxation, d) exchange interactions with neighbouring unpaired electrons. Of these the first two factors are usually temperature independent. Spin-lattice relaxation rates are temperature dependent and therefore can contribute towards the thermal dependence of linewidths. Considering relaxation mechanisms one obtains $\Delta\omega \sim (1/T_2 + 1/2T_1)$ where $\Delta\omega$ is the linewidth in frequency and T_2 , T_1 are the spin-spin and spin-lattice relaxation times. Only one phonon-Waller process and one phonon direct process (Kronig [28], van Vleck [29]) can give rise to a linear dependence of $1/T_1$ on temperature, i.e., (i) $1/T_1 \sim H^4/T$ for Kramers ions for the latter process in presence of an external magnetic field H . However, the corresponding T_1 are too long compared to T_2 to produce effectively a linear dependence of linewidth ΔH_{pp} on temperature (at ordinary temperatures). Recently considerable attention has been focused on the possibility that the exchange interaction may be temperature dependent and quite a lot of experimental evidences [30, 31] exist to support this thermal dependence. It may be noted that the symmetric anisotropic part of the total exchange interaction [32] is of the order $(\Delta g/g^2)J$ where Δg is the anisotropy in g factors and J is the isotropic exchange interaction. As in our present case of CuSal (BR), g is isotropic, this part of the exchange interaction factor does not contribute to the linear dependence of linewidth on temperature in the said interval. Seehra and Castner [26] explained the linear beha-

viator for $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$ by phonon modulation of the antisymmetric exchange interaction. In such cases $\Delta H \sim J^2(\Delta g/g)^2 T$. It might be recalled that this antisymmetric exchange interaction [33] is of the order of $(\Delta g/g) J$ and vanishes under certain symmetry conditions about the disposition of the ionic axes of the neighboring paramagnetic ion. Though X-ray structural data on $\text{CuSal}(\text{BR})$ are not available the isotropy of g factors suggests that the above mechanism does not play an important role in the linewidth behavior in $\text{CuSal}(\text{BR})$. Earlier Harris and Owen [34] suggested the mechanism of direct phonon modulation of the exchange integral J to explain the temperature dependence of exchange interactions and thereby of EPR linewidths in $(\text{NH}_4)_2(\text{Ir}, \text{Pt})\text{Cl}_6$. Recently Zaspel and Drumheller [35] worked out the problem of phonon modulation of the symmetric exchange interaction J and obtained $\langle J \rangle$ which is the thermal average over the vibrational states of a dimer. They had applied their calculations successfully to $\text{Cu}(\text{II})$ complexes of the type $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$. The linewidths in these complexes range between 20 and 80 G and vary linearly over a temperature interval 300 to 100 K. Though the linear temperature dependence of linewidths observed in $\text{CuSal}(\text{BR})$ suggests the importance of the role of phonon modulation of the exchange interaction in this compound, it is to be noted that the linewidths are much larger in $\text{CuSal}(\text{BR})$ in comparison to those in $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$. This may be due to either or both of the following two factors:

- (i) Lower values of exchange interactions in $\text{CuSal}(\text{BR})$,
- (ii) larger values of dipolar interactions in $\text{CuSal}(\text{BR})$.

However, we feel that further investigations including X-ray studies are necessary to throw more light on the actual cause of such behavior in this copper complex. This is in progress.

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References

- [1] INOUE MOTOMICHI, K. MICHIIKO, and K. MASAJI, *Inorg. Chem.* **3**, 239 (1964).
- [2] F. HANIC and J. MICHALOV, *Acta cryst.* **13**, 299 (1960).
- [3] E. V. SUTTSOV, A. V. ABLOV, G. A. POROVICH, and G. A. KIOSSE, *Dokl. Akad. Nauk SSSR* **179**, 1352 (1968).
- [4] G. F. KOKOSAKA and H. C. ALLEN, JR., *J. chem. Phys.* **47**, 10 (1967).
- [5] J. N. VAN NIEKERK and F. R. L. SCHOENING, *Acta cryst.* **6**, 227 (1953).
H. ABE and J. CHIMADA, *J. Phys. Soc. Japan* **12**, 1255 (1957).
- [6] G. F. KOKOSAKA, M. LINZER, and G. GORDON, *Inorg. Chem.* **7**, 1730 (1968).
- [7] J. R. WASSON, C. I. SHRY, and C. TRAPP, *Inorg. Chem.* **7**, 469 (1968).
- [8] N. DENNIS CHASTEEN, *Inorg. Chem.* **10**, 2339 (1971).
- [9] F. G. HERRING, R. C. THOMPSON, and C. F. SCHMERDTFEGER, *Canad. J. Chem.* **47**, 555 (1969).
- [10] P. W. BALL, *Coord. chem. Rev.* **4**, 361 (1969).
- [11] K. E. HYDE, G. GORDON, and G. F. KOKOSKA, *J. inorg. nuclear Chem.* **30**, 2155 (1968).
- [12] Y. MUTO, M. KATO, H. B. JONASSEN, and L. C. CUSACHS, *Bull. Chem. Soc. Japan* **42**, 417 (1969).
- [13] P. H. VOSSER, L. O. JENNINGS, and R. E. RUNDLE, *J. chem. Phys.* **32**, 1590 (1960).
- [14] B. BLEANEY and K. D. BOWERS, *Proc. Roy. Soc. A214*, 451 (1952).
- [15] E. WASSERMAN, L. C. SNYDER, and W. A. YAGER, *J. chem. Phys.* **41**, 1763 (1964).
- [16] J. REEDJIK, *Rec. Trav. Chim.* **88**, 86 (1969).
- [17] J. REEDJIK, D. KNETSCH, and B. NIEUMENHUYSE, *Inorg. Chim. Acta* **5**, 568 (1971).
- [18] H. J. VAN DER VALLS and M. S. DE GROOT, *Mol. Phys.* **2**, 333 (1959); **3**, 190 (1960).

- [19] M. S. DE GROOT and J. H. VAN DER WAALS, *Physica (Utrecht)* **29**, 1128 (1963).
- [20] R. W. JOTHAM, S. F. A. KETTLER, and J. A. MARKS, *J. Chem. Soc. (Dalton)*, 428 (1972).
- [21] G. KOKOSKA and H. C. ALLEN, *J. chem. Phys.* **46**, 3010, 3030 (1967).
- [22] N. D. CHASTEEN and R. L. BELFORD, *Inorg. Chem.* **9**, 169 (1970).
- [23] J. F. VILLA and W. E. HATFIELD, *Inorg. nuclear Chem. Letters* **6**, 511 (1970).
- [24] I. YAMADA and M. IBEKE, *J. Phys. Soc. Japan* **33**, 1334 (1972).
- [25] J. E. DRUMHELLER, D. H. DICKEY, R. P. REKTTIS, C. E. ZASPEL, and S. J. CLASS, *Phys. Rev. B* **5**, 4631 (1972).
- [26] M. S. SEEHRA and T. G. CASTNER, *Phys. kondens. Materie* **7**, 185 (1968).
- [27] E. DORMANN and V. JACCARINO, *AIP Conf. Proc.* **18**, 529 (1973).
- [28] R. DE L. KRONIG, *Physica (Utrecht)* **6**, 33 (1939).
- [29] J. H. VAN VLECK, *Phys. Rev.* **57**, 426, 1052 (1940).
- [30] T. A. KENNEDY, S. H. CHOH, and G. SEIDEL, *Phys. Rev. B* **2**, 3645 (1970).
- [31] T. OKUDA and M. DATE, *J. Phys. Soc. Japan* **28**, 308 (1970).
- [32] T. MORIYA, *Phys. Rev.* **120**, 91 (1960).
- [33] I. DZIALOSHINSKI, *J. Phys. Chem. Solids* **4**, 241 (1958).
- [34] A. HARRIS and J. OWEN, *Proc. Soc. Roy. A289*, 122 (1966).
- [35] C. E. ZASPEL and J. E. DRUMHELLER, *Phys. Rev. B* **16**, 1771 (1977).

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