EPR and optical studies in pseudotetrahedral tetramethyl ammonium copper (II) bromide

D. K. De[a)]

Department of Magnetism, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India
(Received 16 August 1982; accepted 8 November 1982)

EPR studies of single crystal copper tetramethyl ammonium bromide, $T_2CuBr_4[T=(CH_3)_4N]$ in the temperature range 77–300 K indicate the largest covalency in this compound compared to similar halogenated pseudotetrahedral copper compounds. The angle $\cos^{-1}\gamma$ between the c axis and the ionic $g_{\parallel}$ axis is 12° and 65° at 250 and 220 K, respectively. The change is continuous down to 200 K. The g shift between 300 and 200 K indicates an increase in the strength of the ligand field with lowering of temperature. The magnetic susceptibility ellipsoid and the g-tensor ellipsoid do not coincide in this material. Optical spectra in $T_2(Cu:Zn)Br_4$ have been assigned. The nonobservation of an EPR signal in $T_2(Cu:Zn)Br_4$ and Cs_2CuBr_4 indicates that ligand field properties in these pseudotetrahedral compounds are quite different from that of T_2CuBr_4.

I. INTRODUCTION

In the past two decades investigations on copper (II) salts having pseudotetrahedral configuration have been carried out by magnetic and optical methods in this laboratory and elsewhere (Gill and Nyholm,[1] 1959; Bates *et al.*[2] 1962; Sharnoff 1964,[4] 1965; Bates 1964, 1967[5]; Karipides and Piper 1962[6]; Furlani and Morpurgo[7] 1963; Ferguson[8] 1964; Lahiry *et al.*[9] 1966, 1971). It is true that many formal aspects of any theory for the electronic states of ions in octahedral coordination are directly applicable with suitable modifications to the case of tetrahedral coordination since the point groups O_h and T_d are isomorphous. However, from the view point of crystal field theory, there are two important differences in the two cases: (i) an inversion of Stark pattern occurs when we switch over from an octahedrally to a tetrahedrally coordinated salt of the same transition metal ion, and (ii) the cubic field separation, 10 Dq of a tetrahedral complex is 4/9th that of the octahedral complex.[11] These facts should have important bearings on the magnetic properties of these salts. There is another nontrivial difference to be incorporated in any theory applied to these cases, namely, that the potential of a tetrahedral array of charges has an odd power term proportional to xyz which does not arise in the octahedral case. This term causes no further splitting of the degenerate d^n levels, but may be effective in removing the parity classification of the basic state eigenfunctions, by causing the ground state $3d^n$ even parity configuration to be mixed with the higher energy $3d^{n-1}4p$ odd parity configuration. In fact, Lohr and Lipscomb[12] (1963), following LCAO(MO) procedure have convincingly shown that the observed geometry having D_{2d} symmetry and sequence of ligand field levels of $[CuCl_4]^{2-}$ ions in $CuCs_2Cl_4$[13,7] can only be accounted for by introducing an appreciable admixture of $4s$ and $4p$ copper orbitals into the primarily $3d$ copper orbitals. Bates *et al.*[2] (1962) and Sharnoff[4] (1965) have also considered the important effects of "d-p" admixture on spin-Hamiltonian parameters like g factors and hyperfine coupling coefficients (A_i).

Nearly a decade ago, a series of isomorphous halogen coordinated tetrahedral Cu(II) compounds, namely, cesium tetrachlorocuprate (Cs_2CuCl_4), cesium tetrabromocuprate (Cs_2CuBr_4), tetramethyl ammonium tetrachlorocuprate (T_2CuCl_4) $[T=(CH_3)_4]$, and tetramethyl ammonium tetrabromocuprate (T_2CuBr_4) was studied by magnetic susceptibility EPR, and spectroscopic methods. All these crystals belong to an orthorhombic system having space-group $Pnma$ and Cu(II) ions in these salts are situated in tetragonally distorted tetrahedral environment (D_{2d} symmetry) formed by four halogen ligands. The distortion from regular tetrahedral disposition of the ligands around Cu(II) ion can be described by the angles X_1CuX_2, X_2CuX_3, X_1CuX_3, X_3CuX_3' (Fig. 1). For a regular tetrahedron these angles are 109° and the deviation of the angles would give a measure of the said distortion which in all these compounds is along one of the S_4 axes. A comparative study of these angles for the compounds given in Table I shows that the distortion increases when the ligand chlorine anions are replaced by heavier bromine anions and the same is true when the alkali metal cesium is replaced by the larger cationic radical tetramethyl ammonium. Hence, in absence of the detailed x-ray structural data of T_2CuBr_4 it is not unreasonable to believe that the magnitude of the distortion in the compound T_2CuBr_4 will be a maximum.

Sharnoff's (1964, 1965)[4] X-band EPR studies of Cs_2CuCl_4 and Cu(II) in Cs_2ZnCl_4 single crystals at 77 K reveal that the g tensors are quite different in these two isomorphous salts and g and A tensors do not coincide in the latter salt. Sharnoff and Reiman's[14] EPR investigations on T_2CuCl_4 reveal that the variation of g values from one salt to another is a lattice effect due to pronounced departure of the $[CuCl_4]^{2-}$ ion from symmetry characterized by the point group T_d as a result of Jahn–Teller effect. Mean magnetic susceptibility and anisotropy studies[9] on T_2CuCl_4, Cs_2CuBr_4, and T_2CuBr_4 reveal that the orbital contribution (3%) to the room temperature mean moment value (p_f^2 value) in T_2CuBr_4 is much lower compared to that (11%) in T_2CuCl_4 and Cs_2CuBr_4. The ionic anisotropy ($K_{\parallel}-K_{\perp}$) also is much lower for T_2CuBr_4 compared to that in Cs_2CuBr_4, T_2CuCl_4, and Cs_2CuCl_4. Moreover, there is an interesting phase transition observed only in T_2CuBr_4 at about

[a)]Present address: Department of Physics, University of Texas at Arlington, Arlington, Texas 76019–0059.

 0021-9606/83/140535-06$02.10

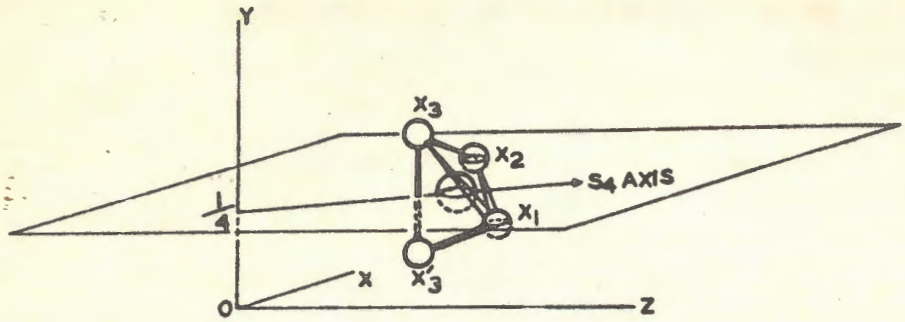

FIG. 1. Distorted tetrahedral disposition of ligands X_1, X_2, X_3 and X_3' around the central copper (II) ion in the isomorphous halogen coordinated Cu(II) compounds such as $CsCuCl_4$ on isomorphic structures.

238 K. At this phase transition point the role of c and a axes become interchanged, i.e., $\chi_c > \chi_a > \chi_b$ above 238 K and $\chi_a > \chi_c > \chi_b$ below 238 K.

Single crystals of T_2CuBr_6, T_2ZnBr_4, and Cs_2CuBr_4 were grown by very slow evaporation of aqueous solutions containing TBr (tetramethyl ammonium bromide) and the corresponding metallic bromides in stoichiometric ratios. The b axis in this crystal can be easily identified as the long axis. The ac plane is found to grow at a right angle to this axis.

X-band EPR studies on CuT_2Br_4 have been undertaken in the temperature range 300–77 K in order to understand the ligand field behavior before and after the phase transition in T_2CuBr_4. The crystal T_2CuBr_4 being opaque to both visible and infrared light, optical spectrum of T_2CuBr_4 diluted with T_2ZnBr_4 was recorded in the region 300–10 000 cm^{-1}. EPR studies have also been carried out in T_2CuBr_4 diluted with T_2ZnBr_4 and in Cs_2CuBr_4.

II. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. EPR

X-band EPR spectra were performed on a Varian X-band EPR spectrometer (E-4 model) for T_2CuBr_4 at 300, 250, 220, 200, and 77 K. K and Q band EPR spectra were also obtained at 300 K for T_2CuBr_4. X-band EPR spectra were also performed in Cs_2CuBr_4 and $T_2(Cu:Zn)Br_4$ containing various Cu:Zn ratios. However, no EPR signal could be detected in these latter crystals in the temperature interval 300–77 K. At 300 K the resonance signal obtained was too broad to be analyzed (derivative peak to peak linewidth 1600G) in single crystal of T_2CuBr_4 (undiluted) at X, K, and Q band microwave region. Though the crystal contains two magnetically inequivalent copper(II) complexes in the unit cell, only one resonance line was obtained at 250 K. The same was true for all other temperatures, i.e., 200, 200, and 77 K. This is obviously due to an exchange interaction between the Cu(II) ions. Similar observation was reported by Sharnoff (1964)[4] in similarly constituted copper salt Cs_2CuCl_4. Principal crystalline g values obtained at different temperatures are shown in Table II. It will be seen that the orthorhombocity in the principal g values are significantly small at 250 K, i.e., above the phase transition temperature 238 K. From Tables II and III it is further noticed that remarkable changes in the principal crystalline g values (g_a, g_b, g_c) as well as in the linewidths occur near the phase transition point. The derivative linewidth along the b axis is found to increase from 37 to 65 G as the temperature is lowered from 220 to 77 K and decreases slightly along the other two axes (Table III).

In absence of detailed x-ray structure of T_2CuBr_4, we have to adopt a "tetragonal approximation" to derive principal ionic g values ($g_\parallel$ and $g_\perp$) from principal crystalline g values with the help of the following equations[9,10]:

$$g_\parallel^2 - g_\perp^2 = \frac{g_c^2 - g_b^2}{\gamma^2 - \beta^2} = \frac{g_a^2 - g_b^2}{\alpha^2 - \beta^2} = \frac{g_c^2 - g_a^2}{\gamma^2 - \alpha^2}, \quad (1)$$

$$g_\parallel^2 + 2g_\perp^2 = g_a^2 + g_c^2 + g_b^2, \quad (2)$$

α, β, and γ are the direction cosines of $g_\parallel$ axis with respect to crystallographic a, b, and c axes.

X-ray structural study on T_2CuBr_4 (Morosin and Lawson 1964)[15] has established that this salt is isomorphous with Cs_2CuBr_4 and T_2CuCl_4 (Morosin and Lingafelter 1961,[16,17] 1960). In these salts the two ionic S_4 axes ($g_\parallel$ axes) in a unit cell (Fig. 1) lie in the ac plane so that $\beta = 0$. Equation (1) then leads to the following equation:

$$g_\parallel^2 - g_\perp^2 = (g_c^2 - g_b^2) + (g_a^2 - g_b^2), \quad (3)$$

and further,

$$\gamma = \frac{1}{\sqrt{2}}\left[1 + \frac{g_c^2 - g_a^2}{g_\parallel^2 - g_\perp^2}\right]^{1/2}. \quad (4)$$

We can then determine $g_\parallel$, $g_\perp$, and γ from Eqs. (2), (3),

TABLE I. Distortions in several pseudotetrahedral copper compounds.

Compounds	Angle X_1CuX_3	Angle X_2CuX_4	Angle X_1CuX_2	Angle X_3CuX_3'	References
Cs_2CuCl_4	123°	117°	107°	101°	18
T_2CuCl_4	131.5°	127.4°	101.5°	99.4°	17
Cs_2CuBr_4	130.4°	126.4°	101.9°	99.9°	15

TABLE II. Principal crystalline g values in T_2CuBr_4 at different temperatures.

Temp. (K)	g_a	g_b	g_c
250	2.10 ± 0.01	2.09 ± 0.01	2.30 ± 0.01
220	2.245 ± 0.005	2.060 ± 0.003	2.100 ± 0.003
200	2.220 ± 0.003	2.060 ± 0.003	2.080 ± 0.003
77	2.220 ± 0.003	2.060 ± 0.003	2.080 ± 0.003

(4). There are two possibilities: (i) $g_{\parallel} > g_{\perp}$, (ii) $g_{\perp} > g_{\parallel}$. We have seen that only the first one is tenable in the present case. The values of $g_{\parallel}$, $g_{\perp}$ and $\cos^{-1}\gamma$ so determined at different temperatures are listed in Table IV. In Table IV are also listed values of $\cos^{-1}\gamma$ derived from susceptibility anisotropy study by Lahiri *et al.* (1966, 1971).[10]

B. IR spectra

As mentioned earlier, no EPR signal could be detected at X, K, and Q bands in T_2CuBr_4, $T_2(Cu:Zn)Br_4$, and in Cs_2CuBr_4 at room temperature. In case of $T_2(Cu:Zn)Br_4$ (Cu : Zn = 1 : 3, 1 : 5, 1 : 10) and Cs_2CuBr_4, no EPR signal could be observed even at 77 K. This is possibly due to the large difference in spin-lattice relaxation rates of the Cu^{2+} ions in the respective lattices. It is well established (Van Vleck 1940, 1941)[18] that the dominant mechanism for spin-lattice relaxation of $3d$ group of compounds is Kronig–Van Vleck mechanism, i.e., the modulation of the crystalline electric field by lattice vibration is felt by the spins through spin-orbit coupling. The exchange of energy between the spins and the lattice involves phonons taking part in two possible processes: one phonon (or direct) and two phonon (or indirect) processes. The latter processes utilize a very broad spectrum in comparison to the first process and is predominant at high temperatures. Corresponding spin-lattice relaxation time for a Kramers ion at a given temperature besides being dependent on factors such as temperature "T," crystal field matrix elements is proportional (Manenkov and Orbach 1966)[19] to (i) Δ_q^4 for $K\theta_D < \Delta q$ and (ii) $C[\exp(\Delta q/kT) - 1]\Delta_q^3 + c'\Delta_q^4$ for $K\theta_D > \Delta q$. Δq is the energy separation between the ground Kramer's doublet and the first excited Kramer level which is coupled to the ground state through spin-orbit coupling.

θ_D is the Debye temperature of the paramagnetic lattice c, c' are two proportionality constants. So it is

TABLE III. Derivative linewidths W_a, W_b, W_c along three principal crystallographic axes in T_2CuBr_4 at different temperatures.

Temp. (K)	W_a (G)	W_b (G)	W_c (G)
250	480 ± 15	500 ± 15	530 ± 15
220	84.0 ± 5.0	37.0 ± 5	81.0 ± 5.0
200	73 ± 5.0	53 ± 5.0	70.0 ± 5.0
77	75 ± 5.0	65 ± 5.0	72 ± 5.0

TABLE IV. Principal ionic g values and angle between ionic $g_{\parallel}$ and c axis ($\cos^{-1}\gamma$) in T_2CuBr_4.

Temp. (K)	$g_{\parallel}$	$g_{\perp}$	$\cos^{-1}\gamma$ (EPR)	$\cos^{-1}\gamma$[a]
250	2.31	2.09	12°	34.47°
220	2.28	2.06	65.5°	62.96°
200	2.24	2.06	70.8°	62.43°
77	2.24	2.06	70.8°	63.32°

[a] $\cos^{-1}\gamma$ as obtained from magnetic anisotropy studies by Lahiry *et al.* (Refs. 9 and 10).

evident from above that Kramer compounds having low lying excited levels (spin-orbit coupled to ground level) are expected to have short spin-lattice relaxation time.

The IR spectra of T_2CuBr_4 and T_2CuBr_4 diluted with T_2ZnBr_4 in KRr pellets were obtained with a Beckmann IR-20A recording spectrometer. Optical spectra were performed on T_2CuBr_4 diluted with T_2ZnBr_4 in the ratio (1 : 10) on Carl–Zeiss VS2-P spectrophotometer.

To see whether any low lying crystal field level exists in T_2CuBr_4, $T_2(Cu:Zn)Br_4$, and Cs_2CuBr_4, infrared spectra of these compounds along with tetramethyl ammonium bromide (TBr) in KBr pellets were recorded in the range 300–4000 cm^{-1}. The spectra in T_2CuBr_4, $T_2(Cu:Zn)Br_4$ (with Cu : Zn = 1 : 3, 1 : 5, 1 : 10), and TBr are found to be identical showing that no ligand field band characteristic of $[CuBr_4]^{-2}$ exists in the 300–4000 cm^{-1} range. In the case of Cs_2CuBr_4, no band is observed in the above spectral range. Thus, no satisfactory explanation can be put forward for the non observation of EPR spectra particularly in Cs_2CuBr_4 and $T_2(Cu:Zn)Br_4$ even at 77 K.

C. Optical spectra

Single crystal copper(II) tetramethylammonium bromide is opaque. So, polarized optical spectra in T_2CuBr_4 (diluted with T_2ZnBr_4 in the ratio 1 : 10) which is rather transparent were performed at room temperature in the spectral region 4000–1000 cm^{-1} with the incident light parallel to the crystallographic a, b axes. The relative absorption intensity with respect to air was measured and plotted against wave number (in cm^{-1}) of incident light (Fig. 2). Three peaks are observed at 9090, 7400, and 5970 cm^{-1} for both $b \parallel E$ and $a \parallel E$ polarizations, E being the electric vector of incident light. This is in contrast to the observation of a broad optical band in Cs_2CuCl_4 by Ferguson (1964)[8] at room temperature. For the c polarization the absorption at 9090 cm^{-1} is very small and the absorption peak at 5970 cm^{-1} is very prominant compared to that for a and b polarization.

D. Assignment of observed ligand field bands

The 2_D state of the free copper(II) ion is split into four states of symmetry $^2A_1$, $^2B_1$, $^2B_2$, and ^2E by a D_{2d} field. The tetrahedron is compressed along one of the S_4 axes so that the ground state will be $^2B_2$ corresponding to a

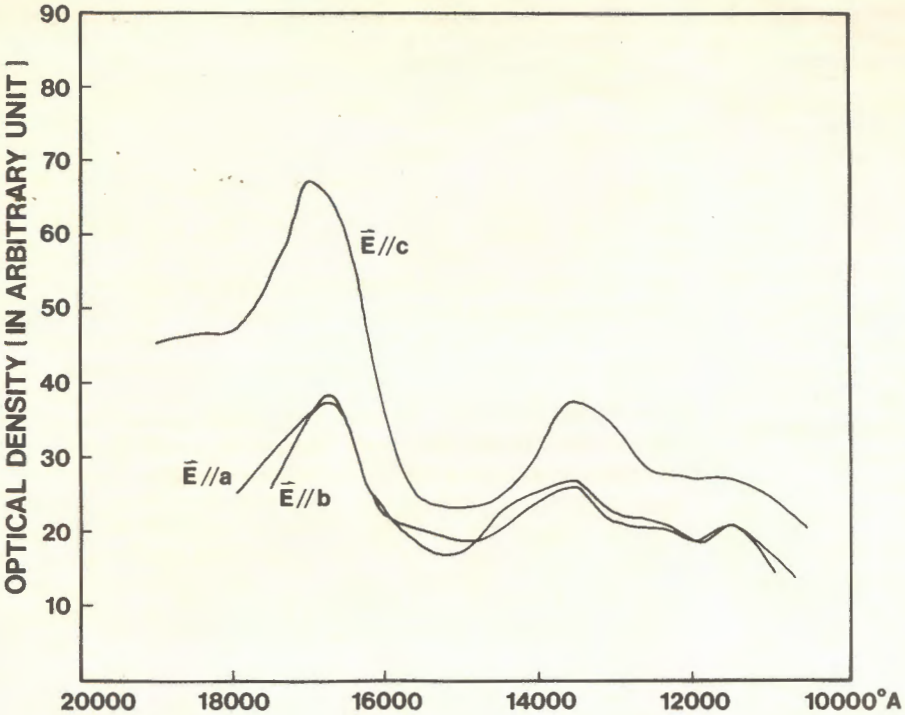

FIG. 2. Polarized optical spectra of single crystal $T_2(Cu:Zn)Br_4$ for Cu : Zn = 1 : 10.

hole in the d_{xy} orbital. This follows from the crystal field consideration of Felsenfeld (1956)[20] and LCAO(MO) calculation of Lohr and Lipscomb (1963).[12] For the transitions $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$, and $^2B_2 \rightarrow {}^2A_1$ the following results for the irreducible representations spanned by purely electric dipole integrals are obtained:

D_{2d}	$^2B_2 \rightarrow {}^2E$	$^2B_2 \rightarrow {}^2B_1$	$^2B_2 \rightarrow {}^2A_1$
$\langle \psi_e \| Z \| \psi_e' \rangle$	E	B_1	A_1
$\langle \psi_e \| (x,y) \| \psi_e' \rangle$	$A_1 + A_2 + B_1 + B_2$	E	E

D_{2d}'	$\Gamma_7 \rightarrow \Gamma_7$	$\Gamma_7 \rightarrow \Gamma_6$
$\langle \psi_e \| Z \| \psi_e' \rangle$	$\Gamma_3 + \Gamma_4 + \Gamma_5$	$\Gamma_1 + \Gamma_2 + \Gamma_5$
$\langle \psi_e \| (x,y) \| \psi_e' \rangle$	$\Gamma_1 + \Gamma_2 + \Gamma_4 + \Gamma_3 + 2\Gamma_5$	$\Gamma_1 + \Gamma_2 + \Gamma_3 + 2\Gamma_5$

and the selection rules stand as

Transitions	Polarization z (∥)	Incident radiation (x,y) (⊥)
$^2B_2(\Gamma_7) \rightarrow {}^2E(\Gamma_7)$	Forbidden	Allowed
$\rightarrow {}^2E(\Gamma_6)$	Allowed	Allowed
$\rightarrow {}^2B_1(\Gamma_7)$	Forbidden	Allowed
$\rightarrow {}^2A_1(\Gamma_6)$	Allowed	Allowed

As evident from Fig. 2, the characteristics of the polarized spectra with electric vector along a and b axes, respectively, are almost identical. This means that g_{11} axis, i.e., the ionic symmetry axis (S_4) should make an equal angle with the a and b axes. Since it is known from x-ray data that S_4 axes in this salt lie in the ac plane, it follows that g_{11} axis should coincide with c axis in $Cu^{2+}:T_2ZnBr_4$. It was also known from our EPR studies on T_2CuBr_4 at 250 K that the angle between g_{11} axis and c axis is quite small that is about 12°. The absorption line at 9090 cm^{-1} which appears to be strong in

It is seen that only $^2B_2 \rightarrow {}^2E$ (xy polarized) and $^2B_2 \rightarrow {}^2A_1$ (z polarized) transitions are electric dipole allowed since each of them totally contains the symmetric representation A_1. If the spin-orbit interaction is also considered the transformation properties of the states will be governed by the character table for the double group D_{2d}' (Table V). In the double group representation we have $\Gamma_1 \times \Gamma_6 = \Gamma_6$, $\Gamma_3 \times \Gamma_6 = \Gamma_7$, $\Gamma_4 \times \Gamma_6 = \Gamma_7$, and $\Gamma_5 \times \Gamma_6 = \Gamma_6 + \Gamma_7$. The $^2E(\Gamma_4)$ level then under s.o. coupling splits into two components Γ_6 and Γ_7. The following representations of the purely electric dipole integrals for the transitions $\Gamma_7 \rightarrow \Gamma_7$ and $\Gamma_7 \rightarrow \Gamma_6$ are obtained:

TABLE V. Character table of the double group D_{2d}'.

		E E	$\bar{E}$	$\bar{C}_2$ C_2	$2S_4$	$2\bar{S}_4$	$2\bar{C}_2$ $2C_2$	$2\bar{\sigma}d$ $2\sigma d$
Γ_1	A_1	1	1	1	1	1	1	1
Γ_2	A_2	1	1	1	1	1	−1	−1
Γ_3	B_1	1	1	1	−1	−1	1	1
Γ_4	B_2	1	1	1	−1	−1	−1	1
Γ_5	E	2	−2	−2	0	0	0	0
Γ_6	E	2	−2	0	$\sqrt{2}$	$-\sqrt{2}$	0	0
Γ_7	E	2	−2	0	$-\sqrt{2}$	$\sqrt{2}$	0	0

With $\Gamma_6 = \Gamma 1/2$

a and b polarizations but very weak in c polarization may be ascribed as a $^2B_2(\Gamma_7) \rightarrow {}^2B_1(\Gamma_7)$ transition. Two transitions at 7400 and 5970 cm^{-1} are allowed in a, b, and c polarizations and can be assigned in accordance with the above selection rule as follows:

$$^2B_2(\Gamma_7) \rightarrow {}^2A_1(\Gamma_6) : 7400 \text{ cm}^{-1} ,$$

$$^2B_2(\Gamma_7) \rightarrow {}^2E(\Gamma_6) : 5970 \text{ cm}^{-1} .$$

This assignment is also based on the consideration that $^2A_1$ lies higher than ^2E levels as in similarly constituted tetrahedral copper salts Cs_2CuCl_4 (Ferguson 1964)[8] and Cs_2CuBr_4 (Morosin and Lingafelter 1960).[16]

III. CONCLUSION

Since no X-band EPR signal could be detected in T_2CuBr_4 diluted with isomorphous $T_2ZnBr_4[T_2(Cu:Zn)Br_4]$ in the temperature range 77–300 K, it can be concluded that the nature of the ligand fields in similarly constituted T_2CuBr_4 and $T_2(Cu:Zn)Br_4$ are quite different. Under the circumstances, it is not possible to throw much light on the ligand field behavior in T_2CuBr_4 as will be evident from the following:

The relevant ligand field calculation of the magnetic properties of Cu^{2+} ion in tetragonally distorted tetrahedral conformation may be briefly discussed in this connection. The ground state for Cu(II) in tetrahedral (Ferguson 1964)[8] configuration is $^2B_2$. The resulting states after "d-p, s" admixture under D_{2d} symmetry are:

$$(^2B_2)\psi_1 = P_1|xy\rangle + \gamma_1 P_1|Z\rangle ,$$

$$\psi_2 = P_2|xz\rangle + \gamma_2 P_2|Y\rangle ,$$

$$(^2E)\psi_2' = P_2|yz\rangle + \gamma_2 P_2|X\rangle ,$$

$$(^2B_1(\psi_3 = |x^2 - y^2\rangle ,$$

$$(^2A_1)\psi_4 = Q|z^2\rangle + \alpha Q|S\rangle ,$$

where

$$P_1 = 1/(1+\gamma_1^2)^{1/2} , \quad P_2 = 1/(1+\gamma_2^2)^{1/2} , \quad Q = 1/(1+\alpha^2)^{1/2} ,$$

and $|Z\rangle$, etc. and $|S\rangle$ denote the $4p$ and $4s$ orbitals of the Cu(II) and p and s orbitals of the ligands, respectively, and $\gamma_1 P_1$, etc. and αQ represent their respective combined admixtures in the composite representations ψ_1, ψ_2, ψ_2', ψ_3, ψ_4.

The well-known spin-Hamiltonian technique of Abragam and Pryce (1951)[21] has been adopted in calculation of g_i^s. Following the perturbation calculations up to third order and taking due care of covalent bonding of metal orbitals with ligand orbitals in the evaluation of the matrix elements of $\mathbf{L}$ and $\lambda\mathbf{L}$ in a manner similar to that of Stevens (1953),[22] Owen (1955),[23] and Tinkham (1956)[24]

$$\langle\psi_i|\mathbf{L}|\psi_j\rangle = K_{ij}\langle d_i|\mathbf{L}|d_j\rangle ,$$

$$\langle\psi_i|(\lambda_d, \lambda_p)\mathbf{L}|\psi_j\rangle = R_{ij}\langle d_i|(\lambda_d, \lambda_p)\mathbf{L}|d_j\rangle ,$$

where K_{ij} and R_{ij}^s are orbital and s.o. reduction parameters, respectively. The following expression for g's are obtained for a Cu^{2+} ion in a distorted tetrahedral (D_{2d}) symmetry:

$$g_{\parallel} = 2\Bigg[1 - \frac{4P_1^2R_{14}K_{14}\lambda_d}{E_{4,1}} - \frac{P_1^2P_2^2}{E_{2,1}^2}\Bigg\{R_{12}\lambda_d^2 - 2\gamma_1\gamma_2R_{12}\lambda_d\lambda_p + \gamma_1^2\gamma_2^2\lambda_p^2 - \frac{P_1^4P_2^4}{2E_{2,1}^2}(K_{22}R_{12}\lambda_d$$
$$-K_{22}\gamma_1\gamma_2\lambda_p - \gamma_1^2R_{12}\lambda_d + \gamma_1\gamma_2^3\lambda_p)(R_{12}\lambda_d - \gamma_1\gamma_2\gamma_p)\Bigg\} - \frac{2P_1^2P_2^2}{E_{2,1}E_{4,1}}\{(R_{12}\lambda_d - \gamma_1\gamma_2\lambda_p)R_{24}K_{14}\lambda_d\}\Bigg] , \tag{5}$$

$$g_{\perp} = 2\Bigg[1 - \frac{P_1^2P_2^2}{E_{2,1}}\{(R_{12}\lambda_d - \gamma_1\gamma_2\lambda_p)(K_{12} - \gamma_1\gamma_1)\} + \frac{P_1^2P_2^4}{2E_{2,1}^2}\{(R_{12}R_{22}\lambda_d^2 - \gamma_1\gamma_2R_{22}\lambda_d\lambda_p - \gamma_2^2R_{12}\lambda_d\lambda_p$$
$$+\gamma_1\gamma_2^3\lambda_p^2)(K_{12} - \gamma_1\gamma_2)\} + \frac{P_1^2P_2^2}{E_{4,1}E_{2,1}}\{(R_{12}\lambda_d - \gamma_1\gamma_2\lambda_p)K_{24}R_{14}\lambda_d\} - \frac{P_1^2P_2^2}{E_{2,1}E_{4,1}}\{(K_{12} - \gamma_1\gamma_2)R_{24}R_{14}\lambda_d^2\}$$
$$-\frac{P_1^2P_2^2}{2E_{2,1}^2}\{R_{12}^2\lambda_d^2 - 2\gamma_1\gamma_2R_{12}\lambda_d\lambda_p + \gamma_1^2\gamma_2^2\lambda_p^2\} - 2\frac{P_1^2R_{14}^2\lambda_d^2}{E_{4,1}^2}\Bigg] , \tag{6}$$

$E_{2,1}$ and $E_{4,1}$ being the ligand field splitting between $^2B_2 - {}^2E_1$ and $^2B_2 - {}^2B_1$ states.

It is evident from Eqs. (5) and (6) that if we ignore terms of higher order other than second order the ligand field parameters (p_1, p_2, R_{12}, R_{14}, K_{12}, K_{14}, and $E_{2,1}$, $E_{4,1}$) outnumber the observables ($g_{\parallel}$, $g_{\perp}$). If we assume the isotropy of R_{ij} and K_{ij}s and equality of p_1 and p_2, i.e., $p_1 = p_2$, it is not possible to calculate the covalency parameters and d-p admixture parameters from the above expressions even on the additional assumption that $R_{ij} = K_{ij}$ because $E_{4,1}$ and $E_{2,1}$ are unknown for T_2CuBr_4 and further that $E_{4,1}$ and $E_{2,1}$ obtained from polarized optical study in $T_2(Cu:Zn)Br_4$ cannot be used because the ligand field behaviors of the two systems are found to be quite different from our EPR studies.

In Table VI are listed principal ionic g values in several halogen coordinated pseudotetrahedral copper(II) compounds. It is seen that the value of $g_{\parallel}$ is less in T_2CuBr_4 compared to those in Cs_2CuCl_4, $Cs_2(Cu:Zn)Cl_4$, $T_2(Cu:Zn)Cl_4$. Moreover, in T_2CuBr_4 values of $g_{\parallel}$ is found to be temperature dependent. From magnetic studies Lahiry *et al.*[10] (1971) showed in these pseudotetrahedral copper halide compounds, reductions of orbital moment and spin orbit coupling constant are quite high (reduction parameters lie in the range 0.60–0.66 in Cs_2CuBr_4) and the amount of reduction increases with the increased axial distortion of the coordination tetrahedron. A low value of $g_{\parallel}$ might arise due to two factors: (i) a large value of ligand field splitting $E_{4,1}$; (ii) large covalency, i.e., a small value of the product $K_{14}R_{14}$ because the corresponding term is multiplied

TABLE VI. Principal ionic g values in several halogen coordinated pseudotetrahedral copper (II) compounds.

	300 K	250 K	220 K	200 K	77 K	References
Cs_2CuCl_4 : $g_{11}=g_3=2.384\pm0.006$					2.404	4
$g_\perp=1/2(g_1+g_2)=2.094\pm0.003$					2.083	
$Cs_2(Cu:Zn)Cl_4$: $g_{11}=2.446\pm0.002$					2.461 ± 0.005	4
$g_\perp=1/2(g_1+g_2)=2.092\pm0.002$					2.083 ± 0.005	
$T_2(Cu:Zn)Cl_4$: $g_{11}=2.462\pm0.002$					2.481	13
$g_1=1/2(g_1+g_2)=2.078\pm0.002$					2.078	
T_2CuBr_4	$g_{11}=$	2.31 ± 0.01	2.28 ± 0.01	2.24 ± 0.01	2.24 ± 0.01	Present work
	$g_1=$	2.09 ± 0.01	2.06 ± 0.01	2.06 ± 0.01	2.06 ± 0.01	
$T_2(Cu:Zn)Br_4$	EPR spectra unobserved					Present work
Cs_2CuBr_4	EPR spectra unobserved					Present work

four times in the expression for $g_{\parallel}$ [Eq. (5)]. We have no definite knowledge about the ligand field splitting. But considering the possible presence of largest distortion in T_2CuBr_4 as discussed in the Introduction and the findings of Lahiry *et al.*,[9,10] it may be concluded that lowest g value in T_2CuBr_4 corresponds to largest covalency in this compound. From Table VI it is further noted that the value of g is decreasing with temperature in the temperature range 250–200 K and becomes constant down to 77 K whereas decrease in $g_\perp$ value occurs in the interval 250–200 K. Lahiry *et al.* observed in T_2CuBr_4 a sharp discontinuity in the ΔK. $\Delta K=K_{\parallel}-K_\perp$, the difference of the principal susceptibilities. ($K_{\parallel}$ and $K_\perp$ are principal ionic magnetic susceptibilities) vs T curve at about 238 K at which temperature the value of $\cos^{-1}\gamma$ suddenly changes from 34.4° to 62.6°. $\cos^{-1}\gamma$ (which defines the orientation of magnetic susceptibility/g ellipsoids in this orthorhombic crystal), as derived from our EPR study, is found to change from 12° to 70.8° as the temperature is lowered from 250 to 200 K and constant down to 77 K. Further from inspection of Table IV, following facts emerge: (i) Ionic g and susceptibility ellipsoids are noncoincident in T_2CuBr_4. (ii) Although the ionic g ellipsoid experiences a large change in orientation in passing through the phase transition temperature (238 K) ($\cos^{-1}\gamma$ is 12° and 65.5° at 250 and 220 K, respectively), the change is continuous down to 200 K unlike the sharp change that occurs for the ionic magnetic susceptibility ellipsoid, only near the phase-transition point. (iii) A continuous decrease in $g_{\parallel}$ value down to 200 K indicate certainly a continuous change in the ligand field. Complete structural analysis by x-ray and reflectance spectroscopic studies in the temperature range 300–77 K are however essential to have a clear understanding about the nature of the temperature dependent ligand field in T_2CuBr_4.

ACKNOWLEDGMENTS

The author wishes to acknowledge support from CSIR (India) during the work. He also expresses thanks to Marilyn Glessner for typing the manuscript.

[1]N. S. Gill and R. S. Nyholm, J. Chem. Soc. 3997 (1959).
[2]C. A. Bates, W. S. Moore, K. J. Standley, and K. W. H. Stevens, Proc. Phys. Soc. 79, 73 (1962).
[3]A. Bose, R. Rai, and S. Mitra, Indian J. Phys. 39, 357 (1965).
[4]M. Sharnoff, J. Chem. Phys. 41, 2203 (1964); 42, 3383 (1965).
[5]C. A. Bates, Proc. Phys. Soc. 83, 465 (1964); 91, 359 (1967).
[6]A. G. Karipides and T. S. Piper, Inorg. Chem. 1, 970 (1962).
[7]C. Furlani and G. Morpugo, Theor. Chem. Acta (Berlin) 1, 102 (1963).
[8]J. Ferguson, J. Chem. Phys. 40, 3406 (1964).
[9]S. Lahiry, D. Ghosh, and D. Mukhopadhyay, Indian J. Phys. 40, 671 (1966).
[10]S. Lahiry, D. Ghosh, and D. Pal, Indian J. Phys. 45, 312 (1971).
[11]R. M. Golding, *Applied Wave Mechanics* (Van Nostrand, New York, 1969).
[12]L. L. Lohr and W. N. Lipscomb, Inorg. Chem. 2, 911 (1963).
[13]L. Helmholz and R. F. Kruh, J. Am. Chem. Soc. 74, 1176 (1952).
[14]M. Sharnoff and C. W. Reiman, J. Chem. Phys. 43, 2993 (1965).
[15]B. Morosin and K. Lawson, J. Mol. Spectrosc. 12, 98 (1964).
[16]B. Morosin and E. C. Lingafelter, Acta Crystallogr. 13, 807 (1960).
[17]B. Morosin and E. C. Lingafelter, J. Phys. Chem. 65, 50 (1961).
[18]Van Vleck, Phys. Rev. 57, 426 (1940); 59, 724 (1941).
[19]*Spin-Lattice Relaxation in Ionic Solids*, edited by A. A. Manenkov and R. Orbach (Harper and Row, New York, 1966), pp. 174–201.
[20]G. Felsenfeld, Proc. R. Soc. London Ser. A 236, 506 (1956).
[21]A. Abragam and M. H. L. Pryce, Proc. R. Soc. London Ser. A 205, 135 (1951).
[22]K. W. H. Stevens, Proc. R. Soc. London Ser. A 219, 542 (1953).
[23]J. Owen, Proc. R. Soc. London Ser. A 227, 183 (1955).
[24]M. Tinkham, Proc. R. Soc. London Ser. A 236, 536 (1956).