

*Supported in part by the U. S. A. E. C., Contract No. AT(11-1)-1054.

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PHYSICAL REVIEW B

VOLUME 3, NUMBER 11

1 JUNE 1971

EPR and Optical Studies of Cu^{2+} in Dodecahedral Configuration

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(Received 31 July 1970)

The EPR and polarized optical spectra of copper calcium acetate hexahydrate and Cu^{2+} doped in isomorphous cadmium calcium acetate hexahydrate have been investigated in the range of temperature 300–77°K. g values in both concentrated and doped crystals are found to be the same, indicating the identical ligand fields. The spin-Hamiltonian parameters remain unchanged throughout the temperature range. The parameters are $g_{\parallel} = 2.360 \pm 0.005$, $g_{\perp} = 2.060 \pm 0.005$, $|A_{\parallel}| = 0.0119 \pm 0.0002 \text{ cm}^{-1}$, $|A_{\perp}| = 0.0013 \pm 0.0002 \text{ cm}^{-1}$. Detailed study of the linewidth has established the important contributions of the exchange, hyperfine, and crystal fields. The observed optical bands at 12 800 and 14 000 cm^{-1} exhibit polarization and have intensities characteristic of ligand field bands. With the knowledge of relative magnitudes of g ($g_{\parallel} > g_{\perp}$), assignments of the bands have been made, consistent with the D_{2d} symmetry of the ligand field. The analysis has revealed that the $3d^9-3d^84p$ configuration interaction is rather small (at most 2%) in these noncentrosymmetric complexes, and the covalent metal-ligand interaction is more pronounced in the ground state than in the excited states.

I. INTRODUCTION

X-ray structure investigations¹ of isomorphous copper calcium acetate hexahydrate and cadmium calcium acetate hexahydrate reveal that in these crystals, M^{2+} ions (Cu^{2+} and Cd^{2+}) are coordinated with oxygen ligands in an irregular dodecahedral configuration (Fig. 1), the distortion being more pronounced in the former case. Preliminary EPR^{2,3} and magnetic studies^{2,4} only in the case of copper calcium acetate have appeared in the literature. Detailed EPR and optical studies of Cu^{2+} in copper calcium acetate hexahydrate and Cu^{2+} in

cadmium calcium acetate have been undertaken with the following objectives: (i) to see whether the observed distortions are solely due to solid-state forces or whether the configurational stability of the molecular complex $[\text{MO}_6]$ has a positive role, (ii) to obtain an understanding of the relative magnitudes of various dynamical interactions and to assess the contribution from an anisotropic hyperfine coupling tensor, if any, to the anisotropic EPR linewidth, and (iii) to probe into the nature of the Stark pattern of a Cu^{2+} ion in the metal acetate hexahydrate crystal environments.

The paramagnetic complex has approximate D_{2d}

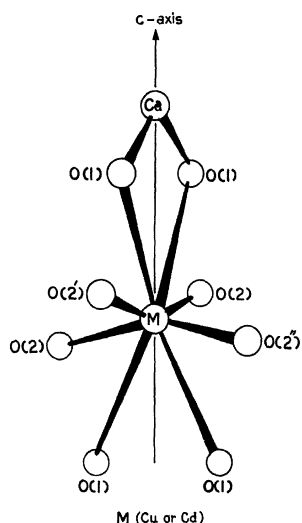


FIG. 1. M (Cu or Cd) coordination in copper calcium acetate hexahydrate and its isomorph cadmium calcium acetate hexahydrate (Ref. 1).

symmetry, so it is expected that a certain percentage of excited configuration $3d^84p$ may be admixed with the $3d^9$ ground configuration of Cu^{2+} . Further, the possible presence of a covalent-type metal-ligand interaction cannot be ignored. To estimate these configurational admixture and covalency effects, an analysis of "g" and hyperfine tensors and optical data has also been made on the basis of the existing ligand field theory.⁵

II. EXPERIMENTAL AND CRYSTALLOGRAPHIC DATA

The samples were prepared following the method⁶ of Holden and Singer. The crystals chosen for measurements were previously checked by x rays and by a polarizing microscope for any possible twinning or any occluded material.

The EPR spectra in the temperature range 300–77 °K were recorded in an x -band reflection-type spectrometer using a 100-kHz magnetic field modulation. Optical spectra were taken in the same temperature interval with a single-beam Zeiss spectrophotometer.

Both copper and cadmium crystals belong to the tetragonal system having space group $I4/m$ (No. 87) and contain four magnetically equivalent molecules per unit cell.¹ $M(\text{Cu}, \text{Cd})$ are coordinated with two types of oxygen ligands O(1) and O(2) (see Fig. 1). The interatomic distances and angles are given in Table I.

III. EPR OBSERVATIONS

A. g Factors and Hyperfine Coupling Constants (A)

Since all the four paramagnetic molecules in the unit cell are magnetically equivalent, the crystal-

line g 's and A 's correspond to the molecular values. Both g and A tensors show axial symmetry about the symmetry axis (c) of the crystal. Principal values of g tensors (g_{\parallel} and g_{\perp}) are identical in both concentrated and diluted salts ($\text{Cu}:\text{Cd} = 1:200$). The underlying implication of this result will be discussed in Sec. V. No variation of g and A values is observed in the temperature range 300–77 °K. The two outer lines of the four-line hyperfine pattern show noticeable doublet structure near the symmetry axis, because of Cu^{63} and Cu^{65} nuclei. Any unevenness in the spacing of hyperfine lines has not been detected in any direction whatsoever, which suggests the quadrupole coupling is negligibly small. The spin-Hamiltonian parameters are given below:

$$g_{\parallel} = 2.36 \pm 0.005, \quad g_{\perp} = 2.06 \pm 0.005,$$

$$|A_{\parallel}| = 0.0119 \pm 0.0002 \text{ cm}^{-1},$$

$$|A_{\perp}| = 0.0013 \pm 0.0002 \text{ cm}^{-1}.$$

B. Linewidth and Line Shape

In order to estimate various types of interactions present in the concentrated paramagnetic solid copper calcium acetate, a study of linewidth, in various directions of the single crystal at different temperatures, was carried out. No change in linewidth has been observed in the temperature interval 300–77 °K, so it is quite reasonable to assume that the spin-phonon interaction has negligible contribution to the linewidth. The observed maximum and minimum linewidth between half-power points are 250 ± 5 and 40 ± 5 G along the c and a (or b) axes, respectively. Assuming Gaussian line shape and using Van Vleck's well-known expression⁷ for the mean-square width

$$H_p^2 = \frac{3}{4} S(S+1) \mu_B^2 \sum_j \frac{g^2(1+3\cos^2\theta_{ij})^2}{r_{ij}^6},$$

the linewidths for dipolar interactions have been estimated to be 256 and 112 G along the c and a (or b) axes, respectively. The disagreement between the observed and theoretical values of line-

TABLE I. Metal-ligand distances and angles in copper calcium acetate hexahydrate and cadmium calcium acetate hexahydrate. The O(2) atoms describe a tetrahedrally distorted square plane, while O(1) atoms describe an elongated tetrahedron about the variable metal ion (see Fig. 1).

	$M = \text{Cu}$	$M = \text{Cd}$
$M\text{-O}(1)$	2.79 Å	2.68 Å
$M\text{-O}(2)$	1.97 Å	2.29 Å
$\text{O}(1)\text{-}M\text{-O}(1)$	65.7°	66.3°
$\text{O}(2)\text{-}M\text{-O}(2'')$	90.6°	90.7°

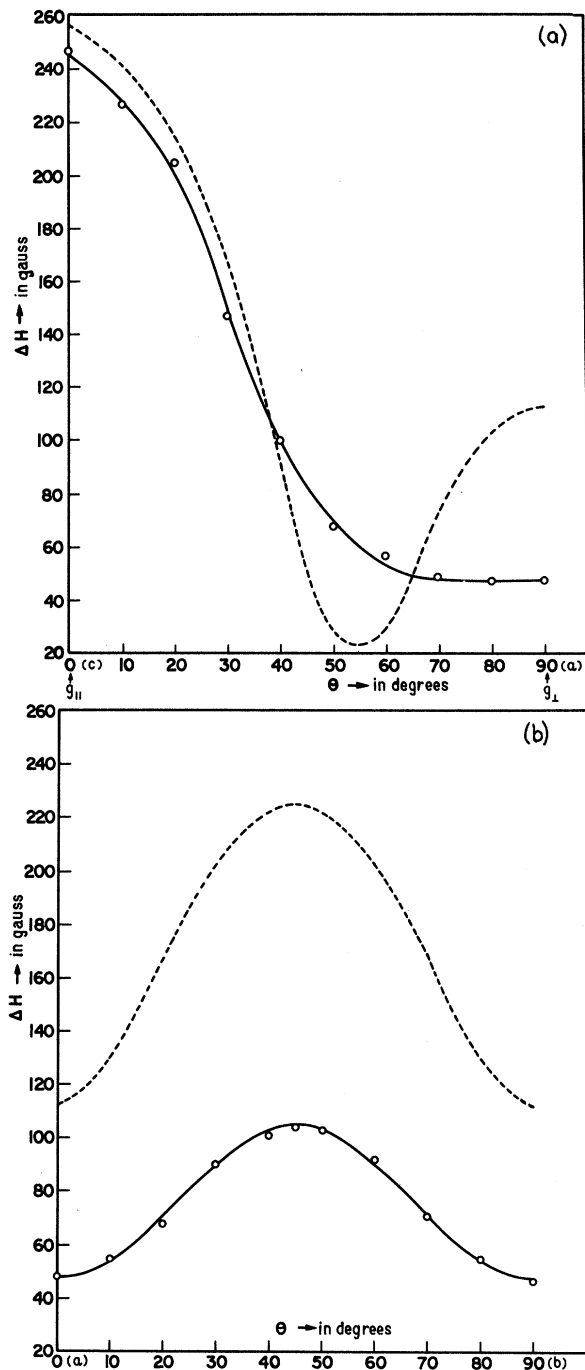


FIG. 2. (a) Linewidth (ΔH) vs angular orientation (θ) in (010) plane of copper calcium acetate hexahydrate. Open circles are the experimental linewidth, the dashed curve represents the theoretical curve, considering only dipolar contribution, and the solid curve, the theoretical curve, considering dipolar, exchange, hyperfine, and crystal field contributions. (b) Linewidth (ΔH) vs angular orientation (θ) in (001) plane of copper calcium acetate hexahydrate. Open circles are the experimental linewidth, the dashed curve represents the theoretical curve, considering only dipolar contribution, and the solid curve, the theoretical curve, considering dipolar, exchange, hyperfine, and crystal field contributions.

width along the a (or b) axis, as well as the nature of its variation in the (010) plane [Fig. 2(a)], clearly indicates the presence of other interactions. The observed line shape shows that the width between half-power points (ΔH) and that between maximum slopes of the derivative curve (δH) are related by $\Delta H = 0.832 \delta H$, thereby suggesting⁸ the existence of exchange interactions. However, even if an exchange term is incorporated, the observed orientational dependence of linewidth cannot be accounted for. The importance of anisotropic contribution from unresolved hyperfine structure towards linewidth has been previously shown⁹ in the case of octahedrally coordinated copper fluosilicate tetrahydrate. Assuming this to be prevalent in the present case, a hyperfine term H_F^2 has been included in Anderson and Weiss's formula¹⁰ for the calculation of linewidth:

$$\Delta H = 2 \left(\frac{10}{3} H_D^2 + H_F^2 \right) / H_{ex}$$

where H_F is given by¹¹

$$H_F = K' (1 + 3 \cos^2 \alpha),$$

$$H_{ex} = [2.83 S(S+1)]^{1/2} 2J / g\mu_B.$$

H_{ex} is the exchange field, J the exchange integral; α is the angle between the molecular symmetry axis and the magnetic field directions, and K' is some function of the hyperfine field and the crystal field. The theoretical values of ΔH are found to be in excellent agreement with the experimental results as regards their magnitudes and the nature of their variations in both (010) and (001) planes [Figs. 2(a) and 2(b)], if we assume the values of $K' = 1.15 \times 10^4 \text{ G}^2$ and $J = 0.02 \text{ cm}^{-1}$. Such a small value of exchange integral is quite consistent for the large separation between Cu^{2+} ions (shortest Cu-Cu distance is about 8 Å).

It may be mentioned in this context that the linewidth of an individual hyperfine line of copper-doped cadmium crystal (Cu: Cd = 1 : 200) is almost isotropic as regards the angular variation and is about 7 G at temperatures 300 and 77 °K. The residual linewidth may be attributed to the random magnetic fields of protons of water of the crystallization and acetate groups.

IV. ANALYSIS OF POLARIZED OPTICAL SPECTRA

The observed optical bands of single crystals of cadmium calcium acetate hexahydrate in which Cu^{2+} is doped (1 : 200) have intensities (extinction coefficient $\epsilon \approx 8-11$) characteristic of a $d-d$ transition^{12,13} and exhibit polarization properties. The 12 800- cm^{-1} band exhibited with electric vector $\vec{E} \parallel c$ axis is absent when \vec{E} lies in the (a, b) plane, and a new band at 14 000 cm^{-1} appears instead (Fig. 3). When the crystal is cooled down to 77 °K no resolution of the bands occur except some sharpening of the

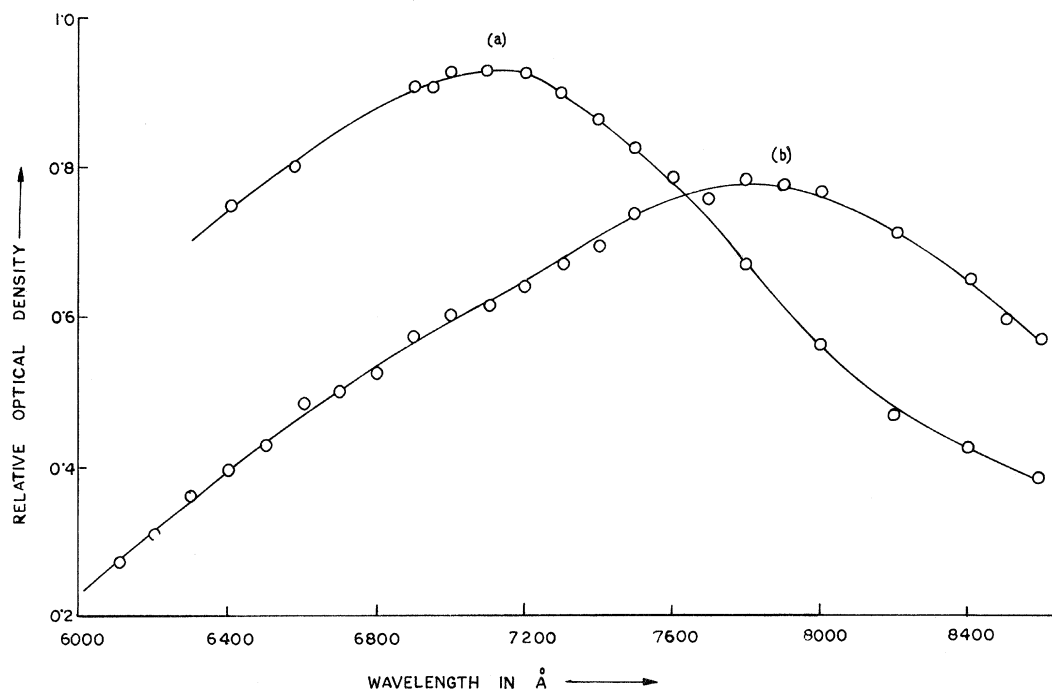


FIG. 3. Polarized optical spectra of Cu^{2+} -doped cadmium calcium acetate hexahydrate ($\text{Cu}:\text{Cd}=1:200$) single crystal at room temperature, for the cases: (a) electric vector $\vec{E} \perp c$ axis, and (b) electric vector $\vec{E} \parallel c$ axis.

peaks. A very broad band centered at about $13\,500\text{ cm}^{-1}$ is observed with a very thin section of a single crystal of copper calcium acetate hexahydrate.

For proper assignment of the bands observed in the doped crystal, unique determination of the ground state is essential. The 2D state of a Cu^{2+} free ion is split into four levels of symmetry, 2A_1 , 2B_1 , 2B_2 , and 2E , by the crystal field having D_{2d} symmetry.¹⁴ From the consideration of relative values of g_{\parallel} and g_{\perp} ($g_{\parallel} > g_{\perp}$), 2A_1 is excluded from being the ground state. Then the bands at $12\,800$ and $14\,000\text{ cm}^{-1}$ can only be reconciled as due to ${}^2B_2 \rightarrow {}^2A_1$ and ${}^2B_2 \rightarrow {}^2E$ transitions, respectively, so that 2B_2 is the ground level corresponding to a hole in the d_{xy} orbital. The ${}^2B_2 \rightarrow {}^2B_1$ transition normally forbidden should appear in (a, b) polarization because it mixes with the Γ_7 component of the 2E state through spin-orbit coupling. It most probably remains hidden within the envelope of the band due to the ${}^2B_2 \rightarrow {}^2E$ transition ($12\,000\text{--}16\,000\text{ cm}^{-1}$) and cannot be resolved in the temperature interval $300\text{--}77\text{ }^\circ\text{K}$.

V. EVALUATION OF LIGAND FIELD PARAMETERS FROM EPR AND OPTICAL DATA

The ligand field theory of magnetic properties of dodecahedrally coordinated copper salts for tetragonal site symmetry (D_{2d}) has been developed by Pal and Pal.⁵ This is based on the following con-

siderations: (i) Abragam and Pryce's spin-Hamiltonian technique¹⁵ is applied; this is appropriate because the excited ligand field levels are well-separated from the ground state, and the spin-orbit interaction has no effect in first order on the ground orbital singlet. (ii) Perturbation calculations have been carried out up to third order. (iii) Admixture of $4p$, $4s$ orbitals into primarily $3d$ orbitals has been considered in accordance with D_{2d} symmetry requirements.¹⁴ (iv) Effect of covalent overlap of $3d$ and $4p$ orbitals with the ligand orbitals ($2s$, $2p$) has been introduced semiempirically in the calculation of the following matrix elements connecting antibonding molecular orbitals (ψ) and atomic orbitals (ϕ) in a manner similar to that of Stevens,¹⁶ Owen,¹⁷ and Tinkham¹⁸:

$$\langle \psi_i | \hat{L} | \psi_j \rangle = k_{ij} \langle \phi_i | \hat{L} | \phi_j \rangle,$$

$$\langle \psi_i | (\xi, P)\hat{L} | \psi_j \rangle = R_{ij} \langle \phi_i | (\xi, P)\hat{L} | \phi_j \rangle,$$

where k_{ij} and R_{ij} are the orbital and spin-orbit reduction parameters. (v) Equal admixture of $4p(4p_x, 4p_y, 4p_z)$ orbitals into each member of primarily ${}^2T_2(3d_{xy}, 3d_{yz}, 3d_{zx})$ has been admitted, which is a fairly good approximation.

The expressions for g factors (g_{\parallel} , g_{\perp}) and hyperfine coupling coefficients (A_{\parallel} , A_{\perp}) obtained by adopting the above procedure are

$$g_{||} = 2 \left(1 - \frac{4p^2 R_{14} k_{14} \zeta_d}{\Delta_{41}} - \frac{p^4 R_{12}^2}{\Delta_{21}^2} (\zeta_d^2 - 2\gamma^2 \zeta_p \zeta_d + \gamma^4 \zeta_p^2) - \frac{p^6 R_{12}^2 k_{22}'}{2\Delta_{21}^2} (\zeta_d - \gamma^2 \zeta_p) \right. \\ \left. \times (\zeta_d - \gamma^2 \zeta_d - \gamma^2 \zeta_p + \gamma^4 \zeta_p) - \frac{2p^4 R_{12} R_{24} k_{14}}{\Delta_{21} \Delta_{41}} (\zeta_d^2 - \gamma^2 \zeta_d \zeta_p) \right),$$

$$g_{\perp} = 2 \left(1 - \frac{p^4 R_{12} k_{12}}{\Delta_{21}} (1 - \gamma^2) (\zeta_d - \gamma^2 \zeta_p) - \frac{p^4 R_{12}}{2\Delta_{21}^2} (\zeta_d^2 - 2\gamma^2 \zeta_p \zeta_d + \gamma^2 \zeta_p^2) [R_{12} - p^2 R_{22}' k_{12} (1 - \gamma^2)] \right. \\ \left. + \frac{p^4 R_{14}}{\Delta_{21} \Delta_{41}} [R_{12} k_{24} (\zeta_d^2 - \gamma^2 \zeta_p \zeta_d) - R_{24} k_{12} (1 - \gamma^2) \zeta_d^2] - \frac{2p^2 R_{14} \zeta_d^2}{\Delta_{41}^2} \right),$$

$$A_{||} = -k_0 R_{11} p^2 (P_d + \gamma^2 P_p) - R_{11} p^2 \left(\frac{4}{7} P_d - \frac{4}{5} \gamma^2 P_p \right) + (g_{||} - 2) \frac{R_{14}}{k_{14}} P_d + (g_{\perp} - 2) \frac{R_{12}}{k_{12} (1 - \gamma^2)} \left(\frac{3}{7} P_d + \frac{3}{5} \gamma^2 P_p \right),$$

$$A_{\perp} = -k_0 R_{11} p^2 (P_d + \gamma^2 P_p) + R_{11} p^2 \left(\frac{2}{7} P_d - \frac{2}{5} \gamma^2 P_p \right) + \frac{(g_{\perp} - 2) R_{12}}{k_{12} (1 - \gamma^2)} \left(\frac{11}{14} P_d - \frac{13}{10} \gamma^2 P_p \right),$$

where $\Delta_{ij} (= E_i - E_j)$ are ligand field splittings corresponding to i th and j th ligand field levels.

$p^2 = 1/(1 + \gamma^2)$; γ^2 represents the average $4p$ contribution towards ${}^2T_2(3d)$ orbitals. ζ_p and ζ_d are spin-orbit coupling coefficients of $\text{Cu}(4p)$ and $\text{Cu}(3d)$ orbitals, related as¹⁹

$$\zeta_p/\zeta_d = P_p/P_d = (925 \pm 40) : 829 \quad \text{for a free Cu}^{2+} \text{ ion.}$$

The parameter k_0 takes account of the isotropic Fermi-type interaction and has a value of about 0.43 ± 0.02 for free Cu^{2+} .²⁰

It comes out clearly from an inspection of the above explicit expressions for g factors that the latter are dependent on the separation of "ligand field" levels (Δ_{ij}), " $3d^8 4p-3d^9$ " admixture (p^2) and covalency reduction parameters (k_{ij}, R_{ij}). It can be shown that $g_{||}$ should be different in copper calcium acetate and in cadmium calcium acetate single crystals (provided the $[\text{CuO}_6]$ copper complex doped in the latter crystal has the same geometry as that of the host cadmium complex) from the following facts: (i) The crystal field calculation of Golding²¹ for regular dodecahedral geometry can be readily extended to derive the following expression for Δ_{41} :

$$\Delta_{41} = E_4 - E_1 = \frac{5}{3} e q \langle r^4 \rangle (\sin^4 \theta_1 / a_1^5 + \sin^4 \theta_2 / a_2^5),$$

where q is the charge on each ligand, e is the electronic charge, $\langle r^4 \rangle$ is the radial integral given by $\langle r^4 \rangle = \int [f(r)]^2 r^6 dr$, $f(r)$ is the radial function of the d orbital. a_1 and a_2 are the respective distances of O(1)- and O(2)-type ligands from the central metal atom, and θ_1 and θ_2 are the angles the radius vectors \vec{a}_1 and \vec{a}_2 make with the symmetry axis S_4 of the distorted dodecahedron (i. e., the c axis of the crystal). Considering metal-ligand distances and angles given in Table I, it follows that Δ_{41} will be greater for the copper crystal.

(ii) Covalency is very much dependent upon the metal-ligand orbital overlap, and so it will primarily be determined by O(2)-type ligands. Also, since the angular orientations of O(2)-type ligands around the metal sites are the same but the metal-ligand distances are different, covalency effects will be more in copper calcium acetate, i. e., covalency reduction parameters k_{ij} and R_{ij} will be less.

(iii) Angular parameters associated with the dodecahedral metal clusters are almost identical for copper and cadmium crystals. The necessary consequence is that the " $d-p$ " admixture parameter p^2 , which gives a measure of deviation from the center of symmetry, should be identical for both.

Hence, it is evident from the respective occurrence of the " $d-p$ " admixture that the covalency parameters (p^2, k_{14}, R_{14}) and the energy separation in the numerator and denominator of the second-order contribution to $g_{||}$ (which is the main component responsible for deviation from the free spin value 2) that $g_{||}$ should be less in the copper crystal. On the other hand, EPR measurements show that the g values are identical in both cases; this

TABLE II. Results of theoretical fitting of spin-Hamiltonian parameters.

Parameters	Theoretical value	Experimental value
$g_{ }$	2.36	2.36
g_{\perp}	2.07	2.07
$A_{ }$	-0.01185 cm^{-1}	-0.0119 cm^{-1}
A_{\perp}	-0.0017 cm^{-1}	-0.0015 cm^{-1}
$k_0 = 0.41$	$\gamma^2 = 0.02$	
$\zeta_p = -885 \text{ cm}^{-1}$	$\zeta_d = -829 \text{ cm}^{-1}$	
$N_1^2 = 0.76$	$N_2^2 = 0.90$	
	$N_4^2 = 0.88 \text{ to } 1.0$	

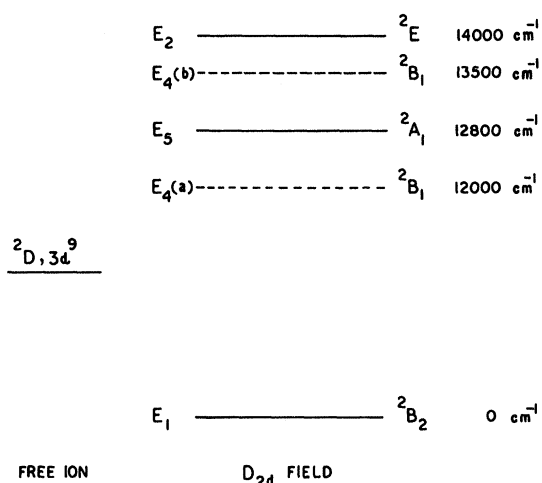


FIG. 4. Proposed ligand field scheme of Cu^{2+} doped in cadmium calcium acetate hexahydrate.

establishes the identity of the configuration of the $[\text{CuO}_8]$ complex in both of these crystals. In other words, the crystalline forces (long range) do not affect the molecular geometry (determined by the short-range forces); so one concludes that the observed distorted dodecahedral coordination of Cu^{2+} which is quite distinct from that of Cd^{2+} is essentially a consequence of Jahn-Teller interaction.²² The constancy of g and A values and of the optical spectrum (see Secs. III and IV) in the temperature interval 300–77 °K demonstrates further that the anisotropic thermal vibration of the lattice does not perturb the molecular framework of the $[\text{CuO}_8]$ complex in the given temperature interval.

Since third-order contributions are rather small (about 1%), we can assume the average values of reduction parameters for their estimation. Even then, and taking for granted that the energy separations $\Delta_{41}(=E_4 - E_1)$ and $\Delta_{21}(=E_2 - E_1)$ are known, the number of theoretical parameters ($p^2, k_{14}, R_{14}, k_{12}, R_{12}, R_{11}$) clearly outnumber the

number of observables ($g_{\parallel}, g_{\perp}, A_{\parallel}, A_{\perp}$). Further, there is uncertainty in the value of the energy separation Δ_{41} . In view of these facts, some simplifying assumptions are necessary for the unique evaluation of relevant ligand field parameters. Since the spin-orbit coupling of the oxygen ligands is small compared to that of Cu^{2+} , it seems reasonable²³ to take the spin-orbit reduction parameter $R_{ij} \approx N_i N_j$ (where N_i and N_j are normalization constants connected with i th and j th levels, respectively) and also to assume, to a good approximation, equality of the reduction parameters k_{ij} and R_{ij} . It may be noted that for a fixed value of the $4p$ admixture, no improvement in the fitting of hyperfine coupling constants is achieved by taking k_{ij} and $N_i N_j$ to be different. The results for the different parameters obtained through this analysis are given in Table II.

It is found that the $4p$ admixture in 2B_2 and 2E states is small (at most 2%), whereas the covalencies of these states are quite appreciable (about 25% and 10%, respectively). It is further realized that a ${}^2B_1 \leftrightarrow {}^2B_2$ separation cannot exceed 13 500 cm^{-1} because of the restriction that the covalency parameter N_4^2 connected with the 2B_1 level can at most be equal to unity for purely ionic cases. The 2B_1 state lies somewhere between 13 500 and 12 000 cm^{-1} above the ground state. Maximum covalency that can be assigned to this state is about 12%. The proposed ligand field level scheme is shown in Fig. 4.

ACKNOWLEDGMENTS

The authors are grateful to Professor A. K. Saha for his keen interest and helpful discussions. Sincere gratitude is also due Professor A. Bose for his inspiration and advice. Thanks are also due R. Shaha for his assistance in the optical measurements and Dr. P. K. Ghosh for his active co-operation.

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Calculations of the Spectra of $\text{SrF}_2:\text{Gd}^{3+}$ in a Tetragonal Crystal Field*

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(Received 4 September 1970)

A theoretical calculation by means of parameter fitting to the experimentally observed crystal-field splittings of $\text{SrF}_2:\text{Gd}^{3+}$ for a tetragonal symmetry site is presented. The calculation uses free-ion wave functions which include spin-orbit, spin-other-orbit, spin-spin, and configuration interactions as basis vectors. The Stark splittings are calculated to all orders of the crystal field within the space defined by the first 15 free-ion states as basis. The tetragonal crystal-field coefficients were found to be $B_0^2=205.9$, $B_0^4=-1715.2$, $B_4^4=-1224.5$, $B_0^6=1874.6$, and $B_4^6=-499.5$ in cm^{-1} with a mean error of 7.0 cm^{-1} for 37 experimentally observed levels.

I. INTRODUCTION

The optical spectra of Gd^{3+} in crystals consist of transitions between the ground state ${}^8S_{7/2}$ and the nearest excited multiplets ${}^6(P, I, D)_J$. Theoretical calculations of the crystal-field spectra of Gd^{3+} in various MF_2 ($M = \text{Ca}, \text{Sr}, \text{or Ba}$) hosts and site symmetries have been the subject of recent investigations.¹⁻⁵ In Refs. 1 and 2, the cubic crystal-field splittings of the ${}^8S_{7/2}$ and ${}^6(P, I, D)_J$ multiplets of Gd^{3+} in MF_2 were determined by including all interactions between these multiplets to all orders throughout the crystal field. Nerenberg and Schlesinger³ and Nerenberg *et al.*⁴ have examined the tetragonal and trigonal sites of the 6P_J and 6I_J multiplets of Gd^{3+} in CaF_2 . Gilfanov *et al.*⁶ have experimentally observed tetragonal sites of the 6P_J and ${}^6I_{7/2}$ levels of Gd^{3+} in CaF_2 and SrF_2 , and Ivoilova⁵ has done some theoretical calculations on these levels. Recently, Detrio *et al.*⁷ have experimentally identified many of the tetragonal 6P_J , 6I_J , and 6D_J levels of Gd^{3+} in SrF_2 , thereby making it possible to do a detailed calculation to determine the tetragonal crystal-field coefficients of that system.

A number of calculations will be presented here in order to show the importance of including the interactions between all the ${}^8S_{7/2}$, ${}^6(P, I, D)_J$ free-

ion states when determining the crystal coefficients for any one of these multiplets. Firstly, the calculations were done for the 6P_J and 6I_J multiplets independently; that is, the matrix of the free ion plus the crystal-field interaction for the 6P_J multiplets was set up and diagonalized. By iterating this process, the eigenvalues were fitted to the experimental levels, with a similar procedure for the 6I_J multiplets. Next the splittings of the 6P_J multiplets were calculated by fitting the 6P_J eigenvalues of the matrix of the free-ion energy levels plus the crystal-field interaction between the ${}^8S_{7/2}$, ${}^6(P, I, D)_J$ free-ion states to the experimentally observed levels of 6P_J ; again the same calculation was done for the 6I_J and the 6D_J multiplets. Finally, in order to examine the possibility of fitting all of these levels simultaneously—that is, finding one set of crystal-field coefficients for all of these multiplets—the eigenvalues of the matrix of the free-ion energy levels and the crystal-field interaction between the ${}^8S_{7/2}$, ${}^6(P, I, D)_J$ free-ion states were fitted to the 6P_J and 6I_J experimental levels. The calculation was again repeated but with the addition of the ${}^6D_{9/2, 7/2}$ to the experimental lines included in the fitting procedure. No attempt to fit the ${}^8S_{7/2}$ levels was made; rather, it was of more interest to include them in the diagonalization and see how much ground-state splitting was produced by fitting the excited states.