

TABLE III. The reduced bulk modulus for the three alkaline-earth fluorides.

	CaF ₂	SrF ₂	BaF ₂
K*	34.0	34.4	36.3

in the repulsive lattice energy term, and q the electronic charge. Since all the three alkaline-earth fluorides, CaF₂, SrF₂, and BaF₂ have the same crystalline structure, A and δ are the same for all three. It is also reasonable to assume that the value of n is the same for all the three. If this model, therefore, is rigorously applicable to all three alkaline earth fluorides, then the

reduced bulk modulus K^* , defined as $K/(q^2r_0^{-4})$, would be equal for all three materials. In Table III, K^* for the three alkaline-earth fluorides is shown. As can be seen, K^* is nearly equal for CaF₂ and SrF₂, while for BaF₂ the discrepancy is much larger. This is not surprising, since the rigid ion model is least applicable to barium fluoride.⁴

ACKNOWLEDGMENTS

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Electron Spin Resonance of Concentrated Copper Phthalocyanine Crystals

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An electron-spin-resonance study of pure copper phthalocyanine single crystal reveals a highly anisotropic environment. There are strong exchange and dipolar interactions between equivalent sites. However, the exchange interactions between the two nonequivalent sites are small enough to permit detection and separation of the two individual resonances. Values of g and the linewidth have been measured as a function of angle in the three crystallographic planes. The variation of ΔH is discussed in terms of the exchange narrowing, exchange broadening, dipolar broadening, and hyperfine interaction.

I. INTRODUCTION

ELECTRON-spin-resonance (ESR) measurements on single crystals of copper phthalocyanine magnetically diluted in metal-free phthalocyanine have been reported previously.¹ ESR spectra of Cu²⁺ ion in a dilute crystal, in which the interactions between neighboring ions are negligible, consists of four copper hyperfine lines. Each of the copper lines is further split into nine lines by the nitrogen nuclear interaction.¹ In this paper we report measurements on undiluted copper phthalocyanine crystals, which were found to have extremely anisotropic magnetic properties.

In the copper complex the spin-lattice relaxation time is long compared with the spin-spin relaxation time. Therefore, we find no temperature dependence of the linewidth in our analysis, and consequently we concern ourselves solely with the ion-ion interactions and ignore the spin-lattice interaction. In concentrated paramagnetic crystals, the magnetic interactions between neighboring ions cause considerable overlapping of the hyperfine lines, and only one broad resonance line is usually found. The breadth of the resonance line depends on the relative magnitude of the spin-spin dipolar interaction, exchange narrowing between equivalent

ions, and exchange broadening between nonequivalent ions. Although the physical nature of these interactions is understood, complete theoretical and quantitative treatment is lacking at present. Nevertheless, it is of interest to study these interactions by investigating the angular dependence of the ESR spectra and comparing it with computed theoretical curves.²⁻⁴

II. CRYSTALLOGRAPHY

The phthalocyanine compounds form a monoclinic series, in which the crystallographic axes a , b , and c are closely related by the ratio 4:1:3. The b axis is normal to the ac plane, and the a axis makes an angle of 120°36' with the c axis in the copper crystal. Robertson⁵ has determined the crystal dimensions of the copper phthalocyanine by x-ray measurements. The cell dimensions of the monoclinic crystal are $a=19.6$ Å, $b=4.79$ Å, and $c=14.6$ Å, and $\beta=120^\circ36'$. The unit cell contains two molecules with parameters (0,0,0) and ($\frac{1}{2}, \frac{1}{2}, 0$). One molecule is translated into the second by a screw rotation of 180° about the b axis. The two mole-

² D. M. S. Bagguley and J. H. E. Griffiths, Proc. Roy. Soc. (London) **201**, 366 (1950).

³ H. Kamagai, K. Ôno, I. Hayashi, H. Abe, and J. Shimada, J. Phys. Soc. (Japan) **9**, 369 (1954).

⁴ B. Bleaney, R. P. Penrose, and B. I. Plumptre, Proc. Roy. Soc. (London) **A198**, 406 (1949).

⁵ J. M. Robertson, J. Chem. Soc. **1935**, 615 (1935); 1105 (1935).

¹ S. E. Harrison and J. M. Assour, J. Chem. Phys. **40**, 365 (1964).

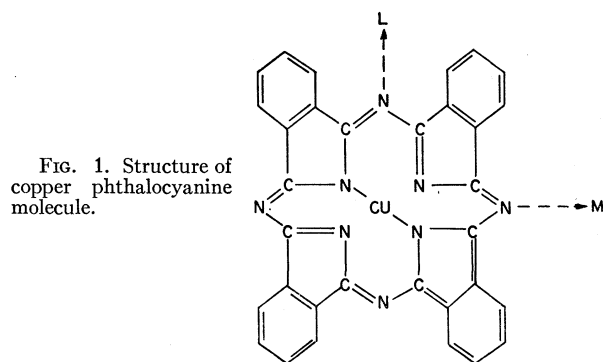


FIG. 1. Structure of copper phthalocyanine molecule.

cules per unit cell are similar in the ac plane, while in the ab and bc planes they are dissimilar. This property will be considered later. The molecule is square planar and it is often convenient to characterize it by a set of three Cartesian axes L , M , and N . The perpendicular to the plane of the molecule, designated as N , and the other two axes in the molecular plane, designated as L and M , are shown in Fig. 1. The axes of symmetry of the two molecules in the unit cell are almost at right angles ($\angle N_1 N_2 = 88.4^\circ$). The two molecular symmetry axes N_1 and N_2 in the unit cell are equally inclined to the ac plane by an angle $\delta = 45.8^\circ$. The orientation of the principal susceptibility axes⁴ K_1 , K_2 , and K_3 can be elucidated with reference to the molecular and crystal axes. The axes K_1 and K_2 lie in the ac plane containing K_1 , N_1 , and N_2 . The third axis K_3 lies along the b axis as shown in Fig. 2. K_2 is in the plane of the molecule and affords an easily accessible direction for the determination of g .

The crystal grows in the shape of a long flat needle with typical dimensions of $1.0 \times 0.1 \times 0.01$ cm. The longest dimension is along the b axis and the largest flat face corresponds to the ab plane. The angles between the crystal axes and the molecular symmetry axis N are: $\alpha(a, N) = 131.4^\circ$, $\beta(b, N) = 44.2^\circ$, and $\gamma(c, N) = 77.3^\circ$, where the c^* axis forms an orthogonal set of axes with a and b . The angles that the copper complex makes with the crystal axes are such that the relationship between the applied magnetic field H and the magnetic axes of the molecule is quite complex for the easily accessible orientations utilizing the natural crystal habit. Since the angle θ between H and N is not directly accessible in our ESR measurements, we have selected an angle ϵ which represents the angle between H and one of the crystal axes in the plane of rotation. The relationships between θ and ϵ when H is rotated in the ab , bc , and ca planes, respectively, are given by

$$\begin{aligned} \cos\theta_{ab} &= \cos\alpha \cos\epsilon - \cos\beta \sin\epsilon, & \epsilon &= \angle H, a; \\ \cos\theta_{bc} &= \cos\beta \cos\epsilon - \cos\gamma \sin\epsilon, & \epsilon &= \angle H, b; \\ \cos\theta_{ca} &= \cos\gamma \cos\epsilon - \cos\alpha \sin\epsilon, & \epsilon &= \angle H, c. \end{aligned} \quad (1)$$

It is easily seen that θ never reaches the zero value (N

parallel to H) in any of the three easily accessible planes.

III. EXPERIMENTAL RESULTS

The crystals were grown by a sublimation method similar to that first used by Linstead.⁶ Crystals with well defined faces were mounted on sample holders made of Plexiglas. The microwave equipment used was a Varian spectrometer. The magnetic-field modulation was 100 kc/sec, while the microwave frequency was 9500 Mc/sec. The magnetic field was determined by a Harvey-Wells nuclear-magnetic-resonance gaussmeter used in conjunction with a Hewlett-Packard 524 D counter. In all measurements reported here, the derivative of the absorption was recorded at room temperature and the linewidth was taken between two points of extrema. The ESR spectra were determined for each plane over a region of 180° in steps of 10° each.

The spectra recorded in the ac plane consisted of one resonance line, since both ions are similar in this plane. Anisotropic values for g and the linewidth ΔH as a function of ϵ are shown in Figs. 3 and 4. The maximum value of $g = 2.166 \pm 0.003$ occurred at $\theta = 45^\circ$. At this maximum value one determines the position of the susceptibility axis K_1 , which makes an angle of $\approx 101^\circ$ with the c axis. The minimum value $g = 2.050 \pm 0.003$ occurred at $\theta = 90^\circ$ which is the position of the second axis K_2 . This minimum value of g is identical to the value of g_1 obtained for the dilute crystal.¹ From the polar plot shown in Fig. 4 $\Delta H_{\max} = 333 \pm 5$ G at $\theta = 45^\circ$ and $\Delta H_{\min} = 147 \pm 5$ G at $\theta = 90^\circ$.

In the ab plane, where the two ions per unit cell are dissimilar, just one resonance was originally found. However, upon amplification of the signal, a weak

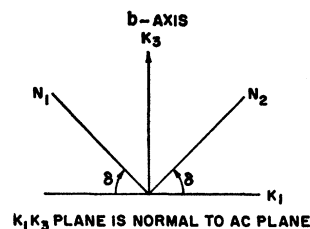
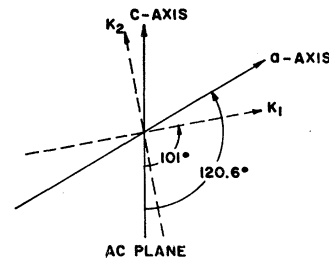
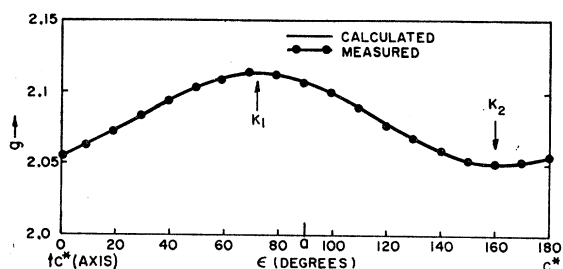


FIG. 2. Crystallographic (a, b, c) and susceptibility (K_1, K_2, K_3) axes.



⁶ R. P. Linstead, P. A. Barrett, and C. E. Dent, J. Chem. Soc. 1936, 1719 (1936).

FIG. 3. Plot of g versus ϵ in ac plane.

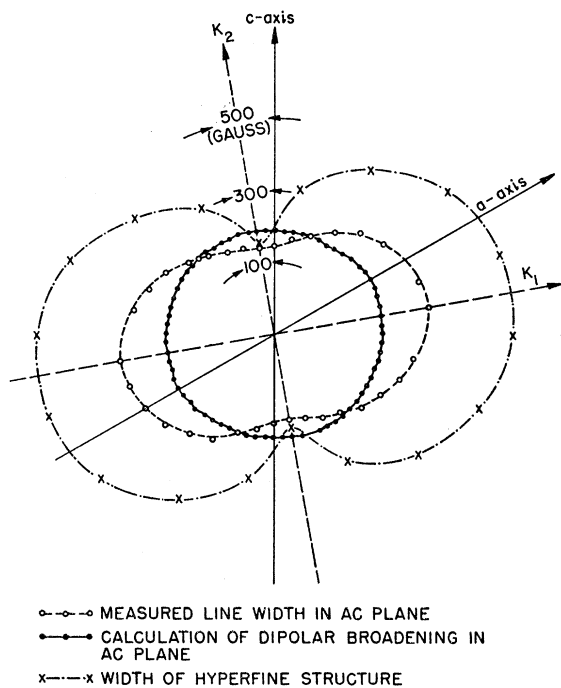
additional resonance also made its appearance, which corresponded to the second ion. This is shown in Fig. 5 for $\epsilon=45^\circ$ ($\theta=167.5^\circ$ and 87.7°). The two resonances are not always observed because the separation of the two signals occurs only if the g values are sufficiently different that the signals do not overlap. Also, as shown in Fig. 5, the intensity of the signal depends on the value of θ (see Sec. IV).

The linewidth ΔH and the g values in the ab and bc planes are highly anisotropic. Figures 6 and 7 show these variations for the bc plane. Results for the ab plane are shown in Fig. 8.

IV. DISCUSSION

A. Variation of g

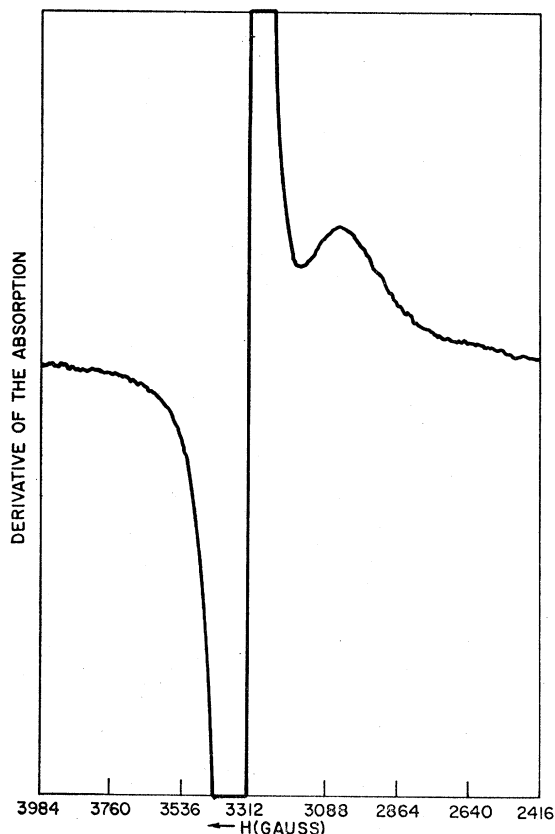
The values of g_{11} and g_1 had been previously determined from the ESR spectra of dilute crystals¹ and these are $g_{11}=2.1797\pm 0.0002$ and $g_1=2.050\pm 0.0002$. For all

FIG. 4. Experimental and theoretical linewidth in ac plane.

three planes, values of $g(\theta)$ were calculated for each ion using the relation

$$g^2 = g_{11}^2 \cos^2 \theta + g_1^2 \sin^2 \theta. \quad (2)$$

The experimental results were fitted to theoretical curves as shown in Figs. 3, 7, and 8. In the ac plane, the theoretical and experimental values are in good agreement. In the ab plane the two theoretical curves g_1 and g_2 for each ion intersect at $\theta=49^\circ$ and at $\theta=131^\circ$, which corresponds to the position of the third susceptibility axis K_3 . The experimental values for g are found to

FIG. 5. ESR of copper phthalocyanine crystal in ab plane, $\angle(H, a) = 45^\circ$.

agree with the theoretical values in the lower portions of the curves g_1 and g_2 , i.e., θ close to 90° . As the angle between H and a axis is varied from $\epsilon=0^\circ$ to $\epsilon=90^\circ$, the magnetic-resonance transitions of ion No. 2 are predominant and values of g_2 are recorded. From $\epsilon=90^\circ$ to $\epsilon=180^\circ$, the resonance transitions of ion No. 1 become stronger and values of g_1 are obtained. When the resonance fields of the two ions are well separated (Fig. 5), we obtain experimental values of g_1 and g_2 which are in good agreement with the predicted theoretical values.

In the bc plane, the dissimilarity of the two ions also most clearly manifests itself. In this plane, several

experimental values of g were found to be lower than the theoretical values. The causes of these differences are rather obscure. However, these small discrepancies have no effect on our conclusions.

B. Variation of Linewidth

In copper phthalocyanine crystals the two predominant types of interaction between the Cu^{2+} ions which influence the resonance linewidth are the dipole-dipole and the exchange interaction. These two interactions were fully discussed by Van Vleck⁷ and Bleaney

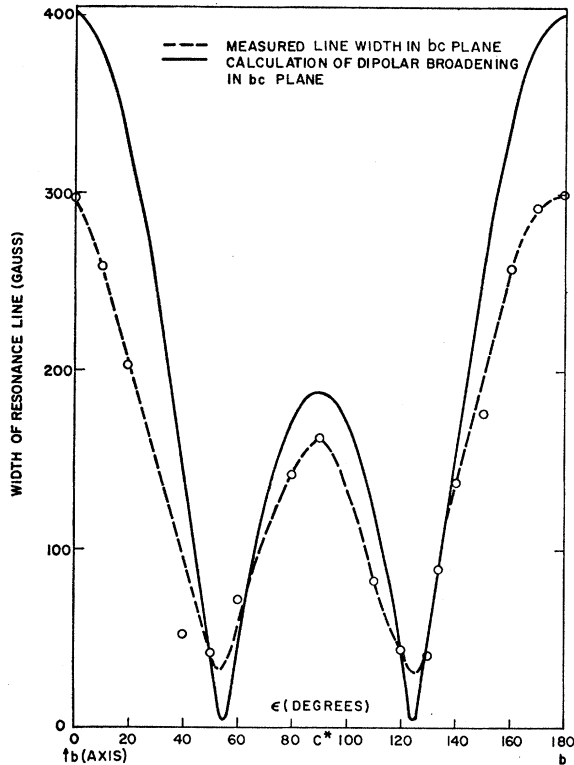


FIG. 6. Experimental and theoretical linewidth in bc plane.

and Stevens.⁸ Van Vleck⁷ has shown that the mean square width of a line for the case of free spins, assuming dipole-dipole interaction only, is given by

$$H_{av}^2 = \frac{3}{4}s(s+1)g^4\beta^4 \sum_k (1 - 3\cos^2\phi_{jk})^2 r_{jk}^{-6} + \frac{1}{3}s'(s'+1)g'^2g'^2\beta^4 \sum_{k'} (1 - 3\cos^2\phi_{j'k'})^2 r_{j'k'}^{-6}, \quad (3)$$

where ions of type j , spin s , and factor g are in resonance and the dissimilar ions are of type k' (s', g'); ϕ_{jk} denotes the angle between the applied magnetic field and the line joining the two ions; β is the Bohr magneton; and r_{jk} is the distance between two dipoles. Since in the ac plane the two magnetic ions are similar,

⁷ J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

⁸ B. Bleaney and K. W. H. Stevens, Rept. Progr. Phys. 16, 108 (1953).

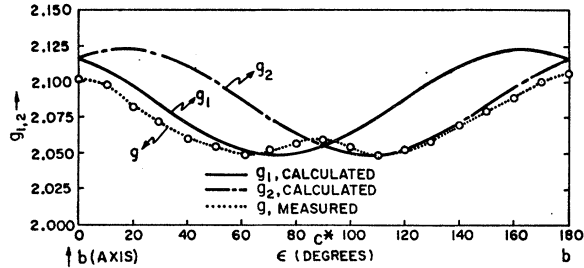


FIG. 7. Plot of g_1 and g_2 versus ϵ in bc plane.

the second term in Eq. (3) vanishes. In all calculations only second-neighbor interactions were considered. Ions at distances greater than 12.14 Å were neglected. The position and distance of neighbors relative to the ion at (0,0,0) in the ac plane is given in Table I. The values for the dipolar linewidth were calculated every 5° and are plotted in Fig. 4. Note that in this plane, ions a and b of Table I are independent of the angle ϕ_{jk} and con-

TABLE I. Position and distance of neighbors relative to the ion at (0,0,0) in the ac plane.

	No. of similar ions	Position	Distance (Å)
a	2	(0, ±1, 0)	4.79
b	2	(0, ±2, 0)	9.58
c	4	(±½, ±½, 0)	10.08
d	4	(±½, ±1½, 0)	12.14

tribute a constant term to the linewidth as H is rotated in the plane. Since these ions have the shorter distances to the central ion, the contribution of this resulting constant term will be predominant. The theoretical curve is shown to vary slightly around a base line of magnitude ~200 G.

In the ab and bc planes the two ions are dissimilar, with both spins s and s' of Eq. (3) equal to ½. In these planes an angular dependence exists between all neighboring ions and the magnetic field, and as expected, the

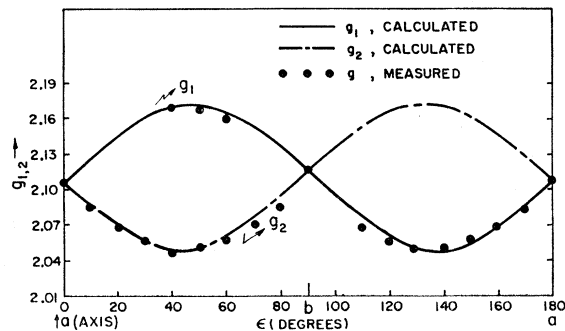


FIG. 8. g_1 AND g_2 vs. ϵ IN ab PLANE

FIG. 8. Plot of g_1 and g_2 versus ϵ in ab plane.

linewidth varies considerably, as shown, for example, in Fig. 6.

Exchange interactions in concentrated paramagnetic crystals have a far more complex nature than the dipolar interaction. Basically, there are two kinds of exchange interaction which contribute to the resonance linewidth. The first kind is an isotropic interaction which depends only on the relative orientation of the spins provided the spin-orbit interaction is neglected. This interaction can be reduced to a scalar product given by

$$\mathcal{H}_{\text{ex}} = -2J_{ij}(\mathbf{S}_i \cdot \mathbf{S}_j) \quad (4)$$

summed over all nearest neighbors. The second kind is an anisotropic exchange interaction and is given by

$$\mathcal{H}_{\text{ex}}' = \sum_{i>j} c_{ij}(r_{ij})[(\mathbf{S}_i \cdot \mathbf{S}_j) - 3(\mathbf{S}_i \cdot \mathbf{r}_{ij})(\mathbf{S}_j \cdot \mathbf{r}_{ij})/r_{ij}^2]. \quad (5)$$

Because of the complexities involved, we shall only consider the isotropic exchange interaction. If the ions precess about the same axis, i.e., they are equivalent, there is exchange narrowing and the line diminishes in width. If the ions are nonequivalent, then the resultant contribution to the mean square width is proportional to $J^2(\sin \mathcal{E}/2)^4$, when the ions have the same precessional frequencies, and proportional to $J^2(\cos \mathcal{E})^2$ when they have different precessional frequencies⁹; \mathcal{E} is the angle between the axes of precession. For dissimilar ions, the absorption line depends on whether the exchange frequency is greater or less than the difference in precessional frequencies. For weak exchange, the spectrum of the two dissimilar ions in the unit cell consists of two distinct resolved lines having different g values (Fig. 5). As the exchange increases, the lines broaden and eventually overlap. For $J > (g_1 - g_2)\beta H$, the lines coalesce into one line at $h\nu = \frac{1}{2}(g_1 + g_2)\beta H$, where g_1 and g_2 are the g factors of the dissimilar ions. This effect has been observed in copper sulfate.^{2,10,11}

A third contribution to the variation of ΔH with angle is the variation of the hyperfine structure with θ . The width of the spectrum of the isolated molecule is given approximately by $3(A^2g_{11}^2 \cos^2\theta + B^2g_1^2 \sin^2\theta)^{1/2}/g$, where A and B are the copper hyperfine structure constants. This factor ranges from 600 to about 60 G and is plotted for the ac plane for further reference in Fig. 4. In addition, we have noted that the superhyperfine structure of the four nitrogen ligands splits each of the copper lines into nine components with an average nitrogen splitting of about 16 G. So the width of the spectrum of the isolated molecule extends from about 200 to 800 G.¹ To obtain a relative magnitude of these exchange interactions, we compare the calculated contribution to broadening with the experimental linewidth.

V. COMPARISON WITH EXPERIMENTAL RESULTS

Before we compare the experimental and theoretical results, some assumptions must be made concerning the line shape. For concentrated crystals, the shape of the resonance line is found to resemble a Gaussian distribution. The width of the line at the half-power point is then given by

$$\Delta H_{1/2} = 1.18(\Delta H^2)_{\text{av}}^{1/2}. \quad (6)$$

In our experiments the linewidth ΔH of the derivative of the absorption is recorded. The relation between ΔH and $\Delta H_{1/2}$ is given by

$$\Delta H = 0.852\Delta H_{1/2}, \quad (7)$$

again assuming a Gaussian distribution. Combining Eqs. (5) and (6) we obtain

$$\Delta H \approx (\Delta H^2)_{\text{av}}^{1/2}. \quad (8)$$

We first compare the sum of the half-width due to the hyperfine structure (ΔH_P) and the dipolar broadening (ΔH_D) with the experimental half-width (ΔH_E). Then, qualitative evidence of exchange interaction will be examined.

The calculated anisotropy due to dipolar broadening in the ac plane differs markedly from the value of ΔH_E as shown in Fig. 4. The values of ΔH_E plotted in the ac plane closely follow the variation of ΔH_P (Fig. 4), so that the width of the hyperfine structure as a function of θ is prominent in determining ΔH_E in this plane. At $\theta = 90^\circ$, i.e., along the susceptibility axis K_2 , we obtain a minimum value for ΔH_E . This value of θ corresponds to a minimum value of ΔH_P . Similarly the maximum value for ΔH_E occurs at a minimum value for ΔH_P . Exchange narrowing is clearly in evidence in the ac plane since the values of ΔH_E fall approximately 50 G below ΔH_D even without considering ΔH_P . Note that the maximum value of $\Delta H_E = 330$ G at $\theta = 47^\circ$ (i.e., along the K_1 axis) is less than what one might expect from a consideration of ΔH_D and ΔH_P ($\theta = 46^\circ$) ~ 560 G. Thus, in the ac plane the angular variation of ΔH_E follows the form of ΔH_P , but it is strongly diminished by exchange narrowing.

In Fig. 6, where we have compared ΔH_E with ΔH_D in the bc plane, the sharp minimum in the experimental curve corresponds to the vanishing of the term $(\cos^2\phi - \frac{1}{3})$ for the most prominent contribution of Eq. (3) for dipolar broadening. The minimum value for ΔH_P occurs at $\epsilon = 72^\circ$ (or $\theta = 90^\circ$). Unlike the ac plane, in the bc plane the ΔH_E curve does not seem to strongly reflect the anisotropy of ΔH_P in the experimental half-width. When $H \parallel b$ (or K_3 axis) ΔH_E is ~ 100 G greater than ΔH_D . This is probably due to the fact that in this direction ΔH_P assumes its largest value in the bc plane. The symmetry about $\epsilon = 90^\circ$ shown in Fig. 6 (i.e., compare the difference between Figs. 4 and 6) results from the fact that in the bc plane the two ions are not equivalent

⁹ M. H. L. Pryce and K. W. H. Stevens, Proc. Phys. Soc. (London) **63**, 36 (1950).

¹⁰ M. H. L. Pryce, Nature **162**, 539 (1948).

¹¹ K. Yoshida, Progr. Theoret. Phys. (Kyoto) **5**, 1047 (1950).

and experimentally one sees for the most part only the ion which has the narrowest and strongest resonance line. Therefore, from $0 \leq \epsilon \leq 90^\circ$ we are observing the resonance of one molecule and from $90^\circ \leq \epsilon \leq 180^\circ$ the second is being recorded. Consequently, we have not recorded a maximum for ΔH_E in this plane.

In the ab plane the minima in ΔH_E are determined primarily by ΔH_P and shifted somewhat (about 5°) toward the calculated minima of ΔH_D .

Thus, the general features of the variation of ΔH_E as a function of direction in the three planes may be summarized in the following way. In the ac plane ΔH_E follows the variation of ΔH_P , in the bc plane that of ΔH_D , and in the ab plane it is influenced by both ΔH_P and ΔH_D .

By noting that ΔH_E consistently falls well below the amount $(\Delta H_P^2 + \Delta H_D^2)^{1/2}$, it is apparent that there is exchange narrowing in all three planes. This is due to the interaction between nearest-neighbor identical ions. If one calculates the difference between $(\Delta H_D^2 + \Delta H_P^2)^{1/2}$ and ΔH_E , the apparent exchange narrowing is highly anisotropic. The anisotropic exchange interaction is due to the spin-orbit interaction. The spins sense the departure of the wave functions from spherical symmetry through the agency of the spin-orbit coupling.¹² We note that in the ac plane, where the two ions per unit cell are resonating at the same frequency but about different axes, ΔH_E never falls below 150 G. This is due to the fact that there are exchange broadening contributions such that $\Delta H_{ex} \sim \sin^2(\mathcal{E}/2)$, where $\mathcal{E} = 88.4^\circ$. In the other two planes, where the two ions do not resonate at the same frequency, the additional width from exchange broadening is $\Delta H_{ex} \sim \cos^2 \mathcal{E}$, i.e., the exchange broadening should be negligible by comparison. Accordingly, in the ab and bc planes our minimum values of ΔH_E are approximately 20 and 35 G, respectively.

A. Magnitude of J

From the resonance data (Fig. 5) it is apparent that the exchange integral J for nonequivalent ions is smaller than the microwave quantum ($\frac{1}{3} \text{ cm}^{-1}$). A rough estimate of J can be obtained from the resonance data in Fig. 5. For the case of weak exchange coupling, two resonance peaks should be observed according to the relations

$$\begin{aligned} h\nu_1 &= g_1\beta H, \\ h\nu_2 &= g_2\beta H, \end{aligned} \quad (9)$$

where g_1 and g_2 are the g values of the two nonequivalent ions. The difference in Zeeman energies of these ions is

$\Delta W_z = (\Delta g)\beta H$, where $\Delta g = g_1 - g_2$. Since the separation between the resonance lines is observed, as a first approximation we let $2J \approx \Delta W_z$. In our experiments the frequency ν is kept constant while the magnetic field is varied. Therefore, $2J \approx \Delta g h\nu / g_m$, where $g_m = 2.118$ is the mean value of g_1 and g_2 , and $\nu = 9500.5 \text{ Mc/sec}$. An approximate value for $J \sim 9.8 \times 10^{-3} \text{ cm}^{-1}$ is obtained.

For the case of exchange interaction between *equivalent* ions which are only 4.72 \AA apart, an approximate value of J' can be calculated from the susceptibility measurements of copper phthalocyanine made by Klemm and Klemm¹³ and Ray and Sen.¹⁴ Unfortunately, the temperature range in the two experiments is not clearly specified in the literature. Nevertheless, based on their experimental results, an approximate value for the paramagnetic Curie temperature $\theta = -12.8^\circ \text{K}$ is obtained. The relation between the exchange integral and the Curie point¹⁵ is given by

$$3K\theta = 2J'ZS(S+1), \quad (10)$$

where $S = \frac{1}{2}$ for CuII and Z , the number of nearest neighbors is equal to 2; $J' \sim 10 \text{ cm}^{-1}$.

The exchange constant of 10 cm^{-1} is a significant interaction from the point of view of conductivity of phthalocyanines.¹⁶ In metal-free phthalocyanine the width of the conduction band was estimated to be less than $100\text{--}150 \text{ cm}^{-1}$.¹⁷ According to Fröhlich and Sewell,¹⁸ the mobility is roughly proportional to the square of the bandwidth in a narrow-band semiconductor. As a consequence of this relation, any broadening of the bands by the magnetic interaction between the equivalent ions along the b axis will give rise to a higher mobility. In copper phthalocyanine the mobility of the electronic carriers¹⁹ has been shown to be 10^2 times as large as in metal-free phthalocyanine.²⁰ Thus, the conduction bands will undoubtedly be broader in the copper phthalocyanine derivative. Nevertheless, it is anticipated that even in the compounds that have the wider energy band, this exchange interaction may affect the mobility of the carriers through the alteration of the shape of the bands, especially at the edges.

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