

used in the calculation will be obtained for $\lambda=250$ A, $\mathcal{E}=10^7$ v/cm, and $E_0=4$ ev. Thus

$$\left(\frac{E}{W}\right)_{\min} = 4 \left(\frac{0.15}{10^7 \times 2.5 \times 10^{-6}}\right) \approx 10^{-3},$$

$$\left(\frac{E}{W} \frac{4E}{\hbar\omega}\right)_{\min} \approx 0.3.$$

The $(1+n/2)(\text{mfp}/\lambda)$ term, for that λ , a mfp of 15 A (the value estimated by Wolff) and an assumed value of $n \lesssim 4$, is $\lesssim 0.18$, and thus these terms are also less than the $4E/\hbar\omega$ term. At lower fields and λ 's the $(1+n/2)(\text{mfp}/\lambda)$ terms will, of course, be even less

significant. Further, since α is not proportional to Δ itself, any error due to the omission of these terms is even less in α than in Δ . For $\mathcal{E}=10^7$ v/cm, $\lambda=250$ A, $E_0=4$ ev one gets, neglecting these terms,

$$\alpha = 6.15 \times 10^5.$$

When these terms are included, and using a mfp of 30 A (i.e., twice the one estimated by Wolff) but with $n=0$, one has

$$\alpha = 7.32 \times 10^5.$$

The influence of these terms, in just about the worst case, is thus only about 16%, showing that the method is applicable to ZnS for fields up to at least 10^7 volts/cm.

Paramagnetic Resonance and Crystal Field in Two Nickel Chelate Crystals

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The splitting of the paramagnetic ground state of Ni^{++} in a cubic field perturbed by an axial and an orthorhombic term is calculated. The crystal field can be approximated by the electrostatic field of the surrounding ions, but the close contact of these ions with the impurity makes this an uncertain approximation. We have, therefore, measured the paramagnetic spectrum of Ni^{++} in a metal-organic crystal where the orthorhombic component of the crystal field is caused entirely by two far removed dioxane molecules. (Upon replacement of the dioxane by benzene, this component disappears.) A comparison between predicted and measured values is given.

A. INTRODUCTION

IT is well known that both the optical absorption spectra and the paramagnetic resonance spectra of $3d$ ions in nearly octahedral complexes can be understood in terms of a model, wherein the influence of the host crystal on the impurity ions is represented by a "crystal field." This field should make it possible to predict the orbital states of the impurity in the host lattice and hence explain the optical absorption spectrum to a good approximation. The spin-orbit interaction produces, then, small additional splittings, some of which can be observed in the paramagnetic resonance spectrum.

However, the quantitative prediction of paramagnetic spectra from this model has met with difficulties. An attempt at calculating the crystal field from the charge distribution of the surrounding ions was not successful.¹ Better results are obtained by representing the surrounding ions by point charges or point dipoles. But even if a crystal field is constructed so as to give the correct orbital levels, there occur new difficulties if the paramagnetic spectrum is to be derived from this field. Sugano and Tanabe² have found that the paramagnetic zero-field splitting of Cr^{+++} in AlO_3 , predicted

from optical absorption spectra, differs in magnitude and sign from the observed value.

In this paper we analyze a case where the crystal field contains a component of very low symmetry which is caused entirely by a set of relatively far removed charges. In this case, where overlap effects are minimized and the fields calculated from point charges and distributed charges are no longer very different, we expect to obtain a fair description by using an electrostatic crystal field.

The field in question is of orthorhombic symmetry, and the splitting of the ground state due to such a field is calculated. An example of such a field configuration is found in a metal-organic nickel salt, where the octahedral oxygen complex is of strictly trigonal symmetry and a lower symmetry field is provided by two distant dioxane molecules. The predicted splitting due to the orthorhombic electrostatic field caused by one of the four possible arrangements of the dioxane molecules is found to agree reasonably with the observed spectra.

B. CRYSTAL FIELD THEORY

The theory of the paramagnetic spectra of $3d$ ions has been reviewed by Abragam and Pryce.³ The energy

¹ W. H. Kleiner, *J. Chem. Phys.* **20**, 1784 (1952).

² S. Sugano and Y. Tanabe, *J. Phys. Soc. Japan* **13**, 880 (1958).

³ A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A205**, 336 (1951).

levels are given by the Hamiltonian

$$\mathcal{H} = \mathcal{H}_F + V + \mathcal{H}_{LS} + \mathcal{H}_{SS} + \mathcal{H}_M,$$

where \mathcal{H}_F is the free-ion Hamiltonian without spin-orbit and spin-spin interaction, V is the crystal field, \mathcal{H}_{LS} the spin-orbit interaction, \mathcal{H}_{SS} the spin-spin interaction, and $\mathcal{H}_M = g\beta\mathbf{H} \cdot (\mathbf{L} + 2\mathbf{S})$.

Only the lowest orbital multiplet (the 3F term in Ni^{++}) is considered (Pryce's approximation A). The effect of neglecting the higher orbital multiplets can be estimated with help of Fig. 4 of Tanabe and Sugano's article on the spectra of complex ions.⁴ The cubic part of V is found to split 3F into a 3A_2 orbital singlet ground level, and into two triplets, 3T_2 and 3T_1 . The higher multiplets will perturb mostly the 3T_1 level, whereas group theory shows that the paramagnetic spectrum depends mostly on the interaction of the ground level with 3T_2 . The same theory also shows that no interaction through \mathcal{H}_{LS} is possible between 3A_2 and the rather low-lying 1E level. Hence the omission of the higher orbital multiplets will not seriously distort the paramagnetic spectrum.

In this paper a complex of symmetry D_3 is considered to which a small rhombic distortion is added. The crystal field has therefore a cubic part V_c , a trigonal part V_d , and a rhombic part V_e , so that

$$V = V_c + V_d + V_e. \quad (1)$$

V_e is chosen in such a way that its z axis coincides with the trigonal axis of $V_c + V_d$, and its y axis with one of the twofold axes, C_2' . In the presence of V_e , the threefold axis is no longer a symmetry element, whereas the twofold symmetry along the y axis is preserved. This choice of axes is justified by the symmetry of the angular dependence of the observed paramagnetic spectrum. The spin Hamiltonian is now obtained by first diagonalizing the crystal field matrix and then adding $\mathcal{H}_{LS} + \mathcal{H}_M$ by perturbation theory. \mathcal{H}_{SS} is neglected.

Orbital states.—The crystal field is approximated by the electrostatic field from a distribution of point charges:

$$V = \sum_k (V_{ck} + V_{dk} + V_{ek}) = \sum_{i \neq k} \frac{e_i e_k}{r_{ik}}. \quad (2)$$

Here, e_i is the charge of the i th surrounding ion, $r_{ik} \equiv |\mathbf{r}_i - \mathbf{r}_k|$, where \mathbf{r}_i gives the position of the i th surrounding ion and \mathbf{r}_k the position of the k th electron on the central ion. (\mathbf{r}_i is given below by its polar coordinates, $r_i \equiv |\mathbf{r}_i|$, ϑ_i , φ_i .)

Next, $(r_{ik})^{-1}$ is expanded into two series of normalized spherical harmonics, one for $r_i > r_k$, the other for $r_i < r_k$. We find:

$$\begin{aligned} V_{ck} &= 28c(\pi)^{\frac{1}{2}} [Y_{40} - (10/7)^{\frac{1}{2}}(Y_{43} + Y_{4-3})], \\ V_{dk} &= -14d(5\pi)^{\frac{1}{2}} Y_{20}, \\ V_{ek} &= 28e(30\pi)^{\frac{1}{2}} (Y_{22} + Y_{2-2}). \end{aligned} \quad (3)$$

⁴ Y. Tanabe and S. Sugano, J. Phys. Soc. Japan 9, 766 (1954).

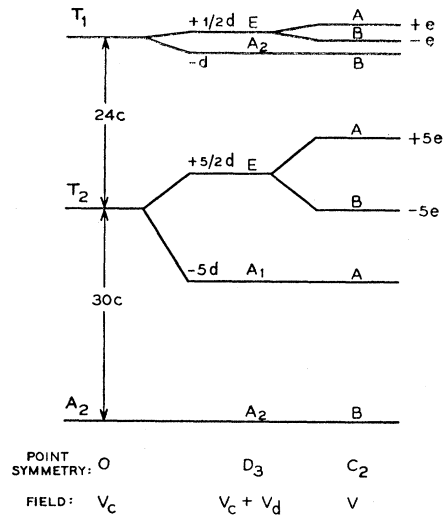


FIG. 1. Energies and symmetry properties of the F level under successive application of V_c , V_d , and V_e , assuming $c > d > e > 0$.

Terms of order Y_{4m} have been neglected in $V_d + V_e$. The coefficients c , d , and e contain integrals over the radial wave functions. Ballhausen has evaluated these integrals for Slater's (unnormalized) nodeless wave functions⁵ for the $3d$ electrons:

$$G_n = \int_{r_i}^{r_i} r_i^6 l^{-6} e^{-2r_i/l} \frac{r_i^n}{r_i^{n+1}} dr + \int_{r_i}^{\infty} r_i^6 l^{-6} e^{-2r_i/l} \frac{r_i^n}{r_i^{n+1}} dr, \quad (4)$$

$$l = 0.212 \text{ \AA for Ni}^{++}.$$

With these integrals, we get:

$$c = (4/405)(e_0 e_1 / l) G_4(r_1 / l), \quad (5a)$$

$$d = -(4/315) \sum_i (e_0 e_i / l) (3 \cos^2 \vartheta_i - 1) G_2(r_i / l), \quad (5b)$$

$$e = (1/1575) \sum_i (e_0 e_i / l) \sin^2 \vartheta_i \cos^2 \varphi_i G_2(r_i / l), \quad (5c)$$

where e_1 in (5a) stands for the charge of one of the six octahedrally coordinated oxygens, and r_1 for the Ni—O bond length.

The matrix of the crystal field, $V = V_c + V_d + V_e$, is now calculated for the 3F level with Stevens' method.⁶ V_c is first diagonalized, and V_d and V_e are added in two successive first order perturbation calculations, assuming $V_c \gg V_d \gg V_e$.

Terms of order ed/c^2 have also to be carried through the calculation in order to get the energies and wave functions correct to first order in d/c , e/c , and e/d .

Figure 1 shows the orbital level splitting obtained by successive application of V_c , V_d , and V_e .

The orbital problem has also been solved directly on the IBM 704 computer, and our expressions for the

⁵ C. J. Ballhausen, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. 29, No. 4 (1954); J. C. Slater, Phys. Rev. 36, 57 (1930).

⁶ K. W. H. Stevens, Proc. Phys. Soc. (London) A65, 209 (1952); B. Bleaney and K. W. H. Stevens, Reports on Progress in Physics (The Physical Society, London, 1953), Vol. 16, p. 108.

splittings of T_2 were found to be good to 2% for the e/d ratio used below.

Spin Hamiltonian.—With the help of the matrix for the angular momentum, \mathfrak{L} , we get now the spin Hamiltonian⁷:

$$\mathfrak{H}_S = D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) + \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H}, \quad (6)$$

$$D = -19\lambda^2 d / 270c^2, \quad (7a)$$

$$E = 19\lambda^2 e / 405c^2, \quad (7b)$$

$$g_x = 2\{1 - \lambda[(4/30)c - (19d/810c^2) - (19e/405c^2)]\}, \quad (7c)$$

$$g_y = 2\{1 - \lambda[(4/30)c - (19d/810c^2) + (19e/405c^2)]\}, \quad (7d)$$

$$g_z = 2\{1 - \lambda[(4/30)c + (19d/405c^2)]\}. \quad (7e)$$

In addition, we find that the z axis of the spin Hamiltonian tensor is tilted from the trigonal axis towards the x axis by a small angle: $\alpha \cong \sqrt{2}e/3d$. Yet another distortion is due to g_{xz} , an off diagonal element of the g tensor. Both α and g_{xz} are due to $\Lambda_{xz} = 19e\lambda^2/405c^2$, where Λ_{xz} is defined in reference 3. The seven real parameters D , E , g_x , g_y , g_z , g_{xz} , and α are all the constants that can possibly appear in our Hamiltonian for the symmetry C_2 as long as only terms linear in H are considered. This can be verified by the methods described by Koster and Statz.⁸ The terms quadratic in H are estimated to be smaller than one gauss in our problem and are neglected. The y axis coincides with the y axis of V_e for the symmetry reasons given above.

C. EXPERIMENTAL RESULTS

L. G. Van Uitert has grown single crystals of sodium-nickel triacetylacetonate·*p*-dioxane and sodium-nickel triacetylacetonate·benzene. The presence of the Ni^{++} paramagnetic spectrum in the *p*-dioxane crystals was discovered by Bowers and Mims.⁹ Extensive measurements were subsequently made on the millimeter wave spectrometer described earlier.¹⁰ The frequencies used varied from 50 kMc/sec to 80 kMc/sec, and the fields from 0.5 to 28 kilogauss. All measurements were taken at 4.2°K, except for the determination of the sign of D , which was made at 1.4°K. The spectrometer will be described in more detail elsewhere. The *p*-dioxane

⁷ Equation (7a) has been given previously by P. H. E. Meijer and H. J. Gerritsen, *Phys. Rev.* **100**, 742 (1955), and also by H. S. Jarrett, *J. Chem. Phys.* **27**, 1298 (1957). If one sets $5d=K$, $3\lambda=\xi'$, where K and ξ' are derived from the optical spectrum of Cr^{+++} in Al_2O_3 (Sugano and Tanabe, reference 2) one obtains from (7a) $D = +0.03 \text{ cm}^{-1}$, instead of the experimental value of $D = -0.1916 \text{ cm}^{-1}$ [J. E. Geusic, *Phys. Rev.* **102**, 1252 (1956)]. Better agreement can be expected for Ni^{++} because of the larger orbital admixture to the ground state. A simultaneous optical and paramagnetic study of Ni^{++} in a cubic field was made by W. Low, *Phys. Rev.* **109**, 247 (1958); a similar study of Ni^{++} in a field of lower symmetry would be desirable.

⁸ G. F. Koster and H. Statz, *Phys. Rev.* **113**, 445 (1959), and H. Statz and G. F. Koster, *Phys. Rev.* **115**, 1568 (1959).

⁹ K. D. Bowers and R. B. Mims (unpublished).

¹⁰ M. Peter, *Phys. Rev.* **113**, 801 (1959).

crystal showed a rhombically distorted spectrum, repeated three times around the c axis. Each of the three spectra could be fitted to the Hamiltonian \mathfrak{H}_S given in Eq. (6). The experimental values for sodium-nickel triacetylacetonate·*p*-dioxane are:

$$D = -56.0 \text{ kMc/sec}, \quad E = -2.5 \text{ kMc/sec}, \quad g_1 \cong g_{11} = 2.20.$$

The benzene crystals showed a similar axial distortion but no rhombic component:

$$D = -65.7 \text{ kMc/sec}, \quad E = 0, \quad g_1 \cong g_{11} = 2.20.$$

D. DISCUSSION: CRYSTAL FIELD AND STRUCTURE

From the measured g value and Eq. (7) we obtain $\lambda/c = -0.75$ and hence $d = 47 \text{ cm}^{-1}$ and $e = -3.2 \text{ cm}^{-1}$.

The angle α is then found to be -1.8 degrees, which is too small to be seen. Likewise, g_{xz} was not detected within our accuracy.

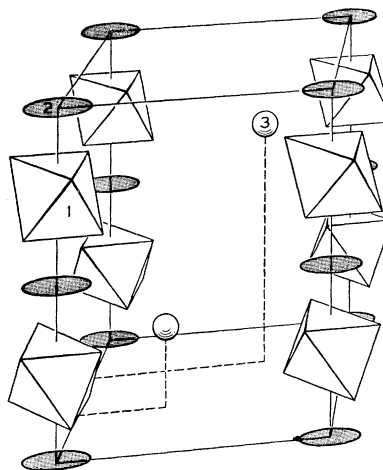


Fig. 2. Treuting's trial structure for sodium-nickel triacetylacetonate with *p*-dioxane or benzene. (1) The nickel chelate complex; (2) dioxane or benzene; (3) sodium.

λ and c could be obtained separately from $g_{11} - g_1$, but the accuracy of our measurements was not sufficient for this determination. The point charge approximation [Eq. (5)] gives, for the Ni—O bond length $r_1 = 2.06 \text{ \AA}$ ¹¹ the value $c'' = 200 \text{ cm}^{-1}$. This is too low, even though $|\lambda|$ should be smaller than the free-ion value, $|\lambda_F| = 335 \text{ cm}^{-1}$, because of the effects of covalent bonding.¹² Phillips¹³ has given a discussion of the limitations of the point charge approximation.

A better estimate of c can be derived from Maki's work.¹⁴ Maki finds for the four-coordinated nickel bi-

¹¹ G. S. Smith and J. L. Hoard, *Bulletin of the American Crystallographic Society Meeting June 23, 1958* (unpublished), p. 50.

¹² J. Owen, *Proc. Roy. Soc. (London)* **227**, 183 (1955); W. Low, *Phys. Rev.* **109**, 257 (1958); T. Murao, *Progr. Theoret. Phys. (Kyoto)* **21**, 657 (1959).

¹³ J. C. Phillips, *J. Phys. Chem. Solids* (to be published).

¹⁴ G. Maki, *J. Chem. Phys.* **29**, 162 (1958).

acetylacetonate dihydrate a ligand dipole field strength of 0.5 a.u. from optical measurements. From her prediction of the splittings for octahedral ligands of the same field strength, we obtain $c=380\text{ cm}^{-1}$. This leads to $\lambda=-285\text{ cm}^{-1}$.

Finally, the spectrum contains some information about the crystal structure of the *p*-dioxane crystal.

Treuting¹⁵ has found the space group of our crystals to be $P\bar{3}12/c$, and gives the trial structure shown in Fig. 2. The dioxane rings sitting on the threefold axes pose a problem, since they do not have the symmetry of their site.

The fact that the nickel spectrum is rhombically distorted and occurs every 60 degrees around C_3 indicates then that the dioxanes are oriented in some random way in each of three equivalent directions. (The cell dimensions given by Treuting, $a=10.2\text{ \AA}$ and $c=12.2\text{ \AA}$,

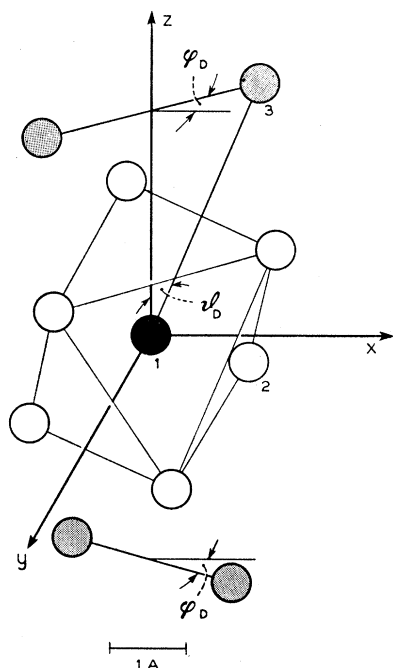
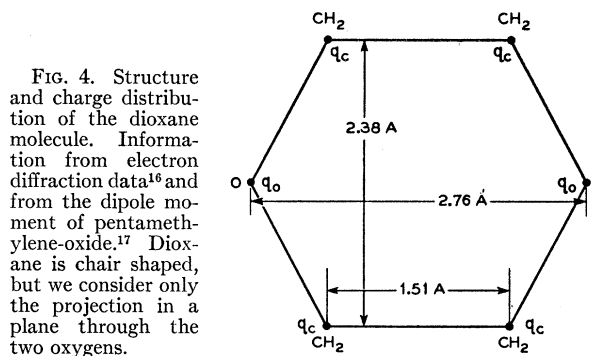


Fig. 3. Surroundings of the Ni^{++} ion. (1) Ni^{++} ion; (2) one of the 6 octahedral oxygens of the three acetylacetonate groups; (3) one of the two oxygens on each dioxane molecule.

are too small for a regular superstructure.) The fact that $E=0$ for the benzene crystal confirms that the rhombic distortion is caused by the dioxane molecules. The possible orientations of the dioxanes relative to the chelate complex are shown in Fig. 3. Since only one type of paramagnetic spectrum was observed, one of the

¹⁵ R. G. Treuting (private communication).



$$q_{\text{O}} = -2.3 \cdot 10^{-10} \text{esu}; \quad q_{\text{C}} = 1.15 \cdot 10^{-10} \text{esu}$$

FIG. 4. Structure and charge distribution of the dioxane molecule. Information from electron diffraction data¹⁶ and from the dipole moment of pentamethylene-oxide.¹⁷ Dioxane is chair shaped, but we consider only the projection in a plane through the two oxygens.

possible azimuths $\varphi_D = n\pi/6$ ($n=0, 1, 2, 3$) must be preferred.

From the point charge approximation [Eq. (5)], and the structural information on *p*-dioxane^{16,17} shown in Fig. 4, we can predict e for each value n . For $n=0, 1, 2, 3$, we find, respectively: $e = +2\text{ cm}^{-1}$, $+1\text{ cm}^{-1}$, -1 cm^{-1} , -2 cm^{-1} , and $e = -2\text{ cm}^{-1}$ ($n=3$) comes nearest to the experimental value, $e = -3.2\text{ cm}^{-1}$. It is understandable that the observed effect exceeds the calculated one, since we neglected the polarizability of the chelate group,¹⁸ but this effect would hardly more than double our calculated value. We conclude that our measurement can be brought into satisfactory agreement with our prediction if we assume that sodium-nickel triacetylacetonate·*p*-dioxane is macroscopically trigonal, with dioxane molecules that are aligned preferentially parallel to each other along the c axis, that the O—O direction of each dioxane is parallel to one of the two-fold crystal axes, and that each vertically aligned group is oriented in a random way with respect to its neighbors.

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¹⁶ W. Shand, private communication reported by P. W. Allen and L. F. Sutton, *Acta Cryst.* **3**, 46, (1950). For infrared data see D. A. Ramsay, *Proc. Roy. Soc. (London)* **190**, 562 (1947).

¹⁷ E. Hibbert and J. S. Allen, *J. Am. Chem. Soc.* **54**, 4115 (1932).

¹⁸ I. E. Coop and L. E. Sutton, *J. Chem. Soc.*, p. 1269 (1938).