

homogeneous deformation within the unit cell which cannot be measured by the strain gauge technique. While the analysis based on a rigid ionic model of the $(\text{Ni} \cdot 6\text{H}_2\text{O})^{2+}$ complex gives rough agreement between the magnitude and isothermal geometrical dependence of the splitting this static model should not be taken too seriously since the explicit temperature dependence indicates that the splitting is primarily determined by thermal vibrations. The magnitude of the explicit temperature dependence is consistent with torsional vibrations of the nearest-neighbor water molecules at a frequency close to 10^{12} cps. Since the elastic and thermal properties of this material are markedly anisotropic a more detailed analysis based on a dynamic model of the entire unit cell appears to be required if the splitting variations are to be understood in detail.

The monotonic, nonlinear variation of the PMR line widths with hydrostatic pressure provides qualitative evidence for the presence of appreciable indirect ex-

change coupling between the nickel spins in the fluosilicate. It appears that both isotropic and anisotropic exchange mechanisms make comparable contributions to the line widths. Though theoretically implausible this is consistent with earlier conclusions drawn from a variety of experimental data.

ACKNOWLEDGMENTS

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Pressure Dependence of the Paramagnetic Resonance Spectra of Two Dilute Chromium Salts*†

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The pressure dependences of the spin-Hamiltonian parameters of trivalent chromium in ammonium aluminum alum and potassium cobalticyanide have been measured up to 10 000 kg/cm² near room temperature. In the case of the alum, runs have been made at 0, 24 and 50°C. The g -value remains unchanged while the crystalline field splitting, δ , increases by $\sim 30\%$, $(\partial\delta/\partial P)_T$ decreasing with rising temperature and pressure.

Using an empirically determined equation of state the crystalline field splitting variations are converted to isothermal volume and explicit temperature dependences. These are discussed in terms of static and dynamic crystalline fields but are not satisfactorily

explained. This failure is attributed to inhomogeneous internal deformation of the unit cell as a function of stress and temperature.

A room temperature run on the covalent chromicyanide shows the g -value as well as the principal splitting parameter, D , to be nonmonotonic functions of pressure. The rhombic splitting parameter, E , increases quadratically with pressure. Since no attempt was made to determine the crystalline equation of state the resonance data are only qualitatively discussed. It is difficult to reconcile the results with the equivalent crystalline field model of the chromicyanide complex.

I. INTRODUCTION

IN order to distinguish between geometrical and explicit thermal contributions to the average crystalline electric field seen by paramagnetic ions it is necessary to measure the spin-Hamiltonian parameters over an appreciable range of stress and temperature. These results must then be combined with the equation of state of the particular crystal. In the preceding paper

we have reported the results of such an analysis of the crystalline field splitting of the paramagnetic resonance (PMR) spectrum of divalent nickel in the concentrated fluosilicate. Due to the trigonal symmetry of that crystal it was necessary to determine the effect of both volume and shape changes of the unit cell. In an effort to reduce the complexity of the problem we have examined the PMR spectrum of trivalent chromium in the cubic crystal, ammonium chromium alum diluted with diamagnetic ammonium aluminum alum, as a function of hydrostatic pressure and temperature.

In both the fluosilicate and the alum the magnetic ion is considered to form a primarily ionic complex with the six nearest-neighbor water molecules. It was, therefore, thought to be of interest to examine the covalent complex $[\text{Cr}(\text{CN})_6]^{3-}$ in potassium chromicyanide diluted with diamagnetic potassium cobalticyanide.

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‡ General Electric Company Predoctoral Fellow (1956-1958).

§ *Note added in proof.*—In the original abstract of this paper [Phys. Rev. Letters 2, 519 (1959)] the thermal expansion coefficient of ammonium aluminum alum was reported to be negative. This anomalous result is incorrect. The author is indebted to Dr. G. Burns of the IBM Research Center for bringing this error to his attention and for providing a reference to the thermal expansion of several alums.

1. Experimental Techniques

The spectrometer and pressure apparatus have been described previously.^{1,2} A water bath was inserted in the magnet gap for the alum runs and the bath temperature controlled to $\pm 1^\circ\text{C}$.

Single crystal samples of the alum, $\text{NH}_4(\text{Al}_{0.99}\text{Cr}_{0.01})(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and the cyanide, $\text{K}_3(\text{Co}_{0.99}\text{Cr}_{0.01})(\text{CN})_6$ were grown by slow evaporation of water solutions at room temperature by S. Shapiro of this Laboratory. Clear, homogeneous crystals with dimensions of roughly 1 cm may be obtained without special precautions though larger samples often show internal strain patterns. The diluted salts were used in order to obtain good resolution in the PMR experiments due to the absence of appreciable dipole-dipole or exchange interactions. Line widths in the alum were on the order of 10 to 20 gauss and 1 to 5 gauss in the cyanide.

II. Ammonium Chromium—Aluminum Alum

A. Experimental Results

In a recent paper Davis and Strandberg³ have discussed the PMR spectrum of this salt in detail. Earlier references to various chrome alums may be found in the review article of Bowers and Owen.⁴ The structure of this class of hydrated double sulphates has been the subject of x-ray⁵ and neutron diffraction⁶ analysis. The cubic unit cell contains four molecules. The trivalent metallic sites of interest lie on the four body diagonals and are surrounded by a slightly distorted octahedron of water molecules. The local crystalline potential thus has predominantly cubic symmetry with a much weaker trigonal component along the $[111]$ axis. The octahedral cubic electric field breaks up the 4F ground term of the free Cr^{3+} ion, leaving an orbital singlet well below two triplets. The ground spin quartet then acts as a free spin, $S = \frac{3}{2}$, save for a small orbital contribution to the magnetic moment due to spin-orbit interaction with the higher orbital states. The trigonal electric field component and the spin-orbit coupling split the ground quartet into two Kramers doublets. The lowest energy levels may be described by the spin Hamiltonian

$$\mathcal{H} = \beta[g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + D(S_z^2 - 5/4), \quad (1)$$

where the z -axis is the $[111]$ axis on which the Cr^{3+} ion of interest lies. The eigenvalue problem is most easily solved when the magnetic field is applied along this axis,

¹ W. M. Walsh, Jr., preceding paper [Phys. Rev. **114**, 1473 (1959)]. This paper will henceforth be referred to as I.

² W. M. Walsh, Jr., and N. Bloembergen, Phys. Rev. **107**, 904 (1957).

³ C. F. Davis and M. W. P. Strandberg, Phys. Rev. **105**, 447 (1957).

⁴ K. D. Bowers and J. Owen, Repts. Progr. in Phys. **18**, 304 (1955).

⁵ H. Lipson and C. A. Beevers, Proc. Roy. Soc. (London) **148**, 664 (1935); H. Lipson, Proc. Roy. Soc. (London) **151**, 347 (1935).

⁶ G. E. Bacon and W. E. Gardener, Proc. Roy. Soc. (London) **A246**, 78 (1958).

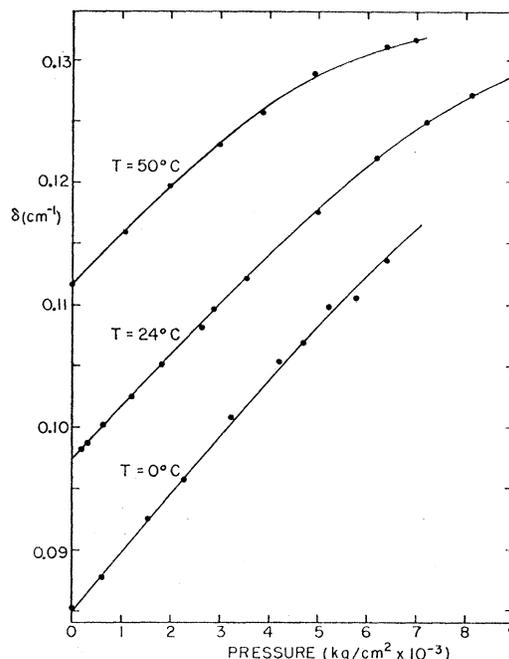


Fig. 1. Pressure dependence of the crystalline field splitting of Cr^{3+} in $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ at 0, 24, and 50°C .

i.e., a body diagonal of the cube. The energy levels then vary linearly with the applied field: $W_{\pm\frac{3}{2}} = \pm\frac{1}{2}g_{\parallel}\beta H - D$, $W_{\pm\frac{1}{2}} = \pm\frac{3}{2}g_{\parallel}\beta H + D$. Three first-order magnetic dipole transitions are observed and used to compute g_{\parallel} and D . Another spectrum is also seen due to the other three types of ions whose trigonal axes make equal angles of $\sim 70^\circ$ with the applied field.

Previous PMR investigations have shown the g -tensor to be isotropic within experimental error. D is found to be positive and to decrease with temperature. In the undiluted alum the crystalline field splitting, $\delta = 2D$, decreases linearly to zero at 90°K where a phase transition occurs, indicated by a sudden increase of δ to roughly twice its room temperature value.⁷

In the course of the pressure experiments the g -value remains constant within experimental error: $g = 1.976 \pm 0.002$. The crystalline field splitting increases rapidly with rising pressure and temperature as illustrated in Fig. 1. No hysteresis was observed upon raising and lowering the pressure.

Bridgman has determined the compressibility of ammonium aluminum alum up to $12\,000\text{ kg/cm}^2$ at 30 and 75°C .⁸ The original numbers must be slightly corrected in view of a later recalibration of the compressibility of iron which was used as a standard.⁹ The

⁷ B. Bleaney and R. P. Penrose, Proc. Phys. Soc. (London) **60**, 395 (1948).

⁸ P. W. Bridgman, Proc. Am. Acad. Arts Sci. **64**, 51 (1929).

⁹ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1952).

corrected fractional volume changes are

$$\Delta V/V_0 = -6.351 \times 10^{-6} P + 100.7 \times 10^{-12} P^2, \quad T = 30^\circ\text{C}, \quad (2)$$

$$\Delta V/V_0' = -6.195 \times 10^{-6} P + 98.2 \times 10^{-12} P^2, \quad T = 75^\circ\text{C},$$

where V_0 and V_0' are the initial volumes at 30 and 75°C, respectively and pressure is measured in kg/cm². Bridgman noted that the 2.5% decrease in the initial compressibility for a temperature increase of 45°C is quite anomalous.

X-ray diffraction measurements of the lattice constants of several alums from 20 to 50°C have been reported by Klug and Alexander.¹⁰ The volume thermal expansion coefficient of ammonium aluminum alum deduced from their data is

$$(\partial \ln V / \partial T)_P = 2.85 \times 10^{-5} (\text{°C})^{-1}. \quad (3)$$

The experimental equation of state of the ammonium aluminum alum may be expressed as

$$V(T, P) = V_0(24^\circ\text{C}, \text{kg/cm}^2) \{1 + 2.85 \times 10^{-5} (T - 24) - [6.372 - 0.00347 (T - 24)] \times 10^{-6} (P - 1) + [101.0 - 0.0556 (T - 24)] \times 10^{-12} (P - 1)^2\}. \quad (4)$$

Using Eq. (4) the data of Fig. 1 may be replotted versus relative volume and temperature. The result is shown in Fig. 2 where the points are computed at 1000 kg/cm² intervals from the smooth curves of Fig. 1. It may be seen in Fig. 2 that δ increases quite linearly for isothermal volume reductions of 2 to 3% and that this volume dependence decreases as the temperature is raised. The weak positive curvature of the δ versus V/V_0 isotherms observable in the 0 and 24°C plots is probably spurious since the experimental determination of $(\partial^2 V / \partial P^2)_T$ is not very precise. The negative curvature of δ versus volume as the splitting reaches its largest values (~ 0.14 cm⁻¹) is genuine, however.

It is evident from Fig. 2 that δ is an explicit and fairly linear function of temperature at constant unit cell volume. In fact the temperature dependence of the splitting observed at atmospheric pressure, $(\partial \delta / \partial T)_P = 5.4 \times 10^{-4}$ cm⁻¹/°C is almost entirely due to the

TABLE I. Explicit volume and temperature dependences of the crystalline field splitting of Cr³⁺ in ammonium aluminum alum.

T°	$(\partial \delta / \partial \ln V)_T$ cm ⁻¹	V/V ₀	$(\partial \delta / \partial T)_V$ cm ⁻¹ × 10 ⁴ /°C
50	-0.66	1.00	5.6
24	-0.70	0.99	5.4
0	-0.80	0.98	5.0
		0.97	4.3
		0.96	3.3

¹⁰ H. P. Klug and L. Alexander, J. Am. Chem. Soc. 64, 1819 (1942).

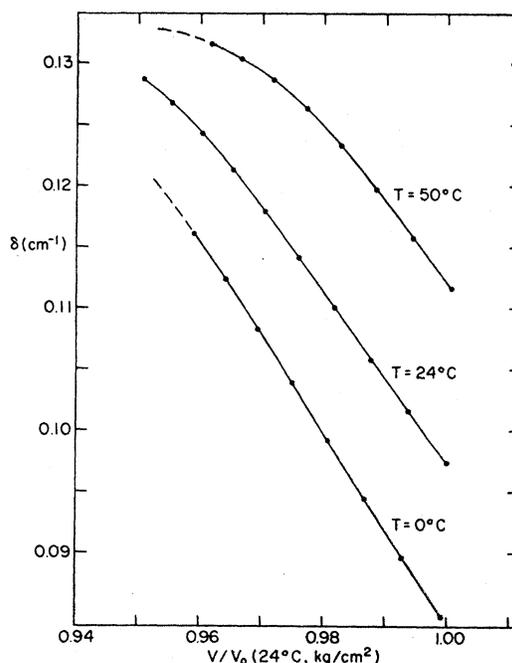


Fig. 2. Volume dependence of the crystalline field splitting of Cr³⁺ in NH₄Al(SO₄)₂ · 12H₂O at 0, 24, and 50°C.

explicit temperature effect, $(\partial \delta / \partial T)_{V_0} = 5.6 \times 10^{-4}$ cm⁻¹/°C. The latter is markedly sensitive to volume as indicated in Table I which lists various numerical results.

B. Discussion

Divalent nickel and trivalent chromium behave very similarly under the influence of the crystalline electric field¹¹; therefore much of the discussion of the nickel fluosilicate results qualitatively applies to the chrome alum. Broer¹² and Weiss¹³ have obtained formulas for the g-value and the crystalline field splitting of Cr³⁺ in distorted octahedral surroundings which closely resemble the corresponding expression for Ni²⁺ due to Becquerel and Opechowski¹⁴ [Eqs. (18) and (20) of I] though the fourth-order axial potential has been neglected in the chromium calculations. Certain differences between the two cases are to be expected because of the different ionic spins, spin-orbit couplings and radii. These numerical details are not important, however, since the qualitative arguments concerning the geometrical dependences of the spin-Hamiltonian parameters which have been made for (Ni · 6H₂O)²⁺ in I apply equally well to (Cr · 6H₂O)³⁺.

The orbital contribution to the magnetic moment of Cr³⁺ is inversely proportional to the cubic component of the electric potential at the chromium site. This potential is predominantly due to the electric dipole

¹¹ J. H. Van Vleck, Phys. Rev. 41, 208 (1932).

¹² L. J. F. Broer, Physica 9, 547 (1942).

¹³ P. R. Weiss, Phys. Rev. 73, 470 (1948).

¹⁴ J. Becquerel and W. Opechowski, Physica 6, 1039 (1939).

moments of the nearest-neighbor water molecules. On this basis one would expect $\Delta g \equiv g - 2.0023 = -0.026 \pm 0.002$ to vary as V^2 [see Eqs. (17a) and (21) of I]. Since the alum volume is reduced $\sim 5\%$ by application of 9000 kg/cm² we should hope to observe a decrease of Δg of $\sim 10\%$. Unfortunately the experimental uncertainty is roughly $\pm 8\%$ of the g -shift so that the lack of a measurable pressure dependence is not surprising. It is also quite conceivable that the $(\text{Cr} \cdot 6\text{H}_2\text{O})^{3+}$ complex is significantly less compressible than is the unit cell as a whole in which case the estimated pressure dependence of Δg is too large.

The crystal field splitting, δ , is proportional to the square of the g -shift and to the axial component of the crystalline potential. If lattice vibration effects are ignored for the moment and it is assumed that all interionic distances vary simply as $V^{1/3}$ (homogeneous deformation within the unit cell) then we may expect $\delta \propto V^n$ where $n \lesssim 8/3$ (see Sec. V.A. of I). Over an appreciable range, however, the observed isothermal volume dependence is of the form $\delta \propto (1 - KV)$, where K is a function of temperature. It is quite evident that the simple geometrical model cannot be used to explain even the isothermal data.

The explicit temperature dependence of δ and the inadequacy of the static model suggest that the effect of lattice vibrations must be taken into account. A general method of expanding the splitting in terms of normal modes of vibration has been outlined in I and is discussed more fully in the literature for the case of nuclear quadrupole resonance.^{15,16} It is, of course, formally possible to fit the linear portions of the data of Fig. 2 to an equation of the form $\delta = \delta_0(1 + BT)$ where δ_0 and B are functions of volume only and to formally assign some physical meaning to these parameters [see Eq. (30) of I]. The strong volume dependence of $(\partial\delta/\partial T)_V$ displayed in Table I implies, however, that δ_0 and B vary implausibly rapidly with volume so that the representation cannot be considered acceptable.

The major weakness of the attempted analysis probably lies in the assumption that the internal dimensions of the unit cell scale homogeneously with volume, i.e., that the internal coordinates vary as $V^{1/3}$. Unfortunately the alum structure is sufficiently complex that many atomic positions are not uniquely specified by the unit cell volume. For example, the water octahedron surrounding the chromium ion is required to have trigonal symmetry about the $[111]$ axis but no other restrictions are imposed by the space group of the alum lattice. As the stress state or temperature of the lattice changes it is possible that "shape" changes of this octahedron occur which account to a large extent for the observed variations of δ .

It is thus apparent that the uncertainty as to the internal coordinates nullifies the presumed advantage

of the cubic alum over the trigonal fluosilicate as a suitable crystal in which to study the effect of stress and temperature on the paramagnetic resonance spectrum. A somewhat better understanding could be obtained in the case of the fluosilicate, despite the relatively lower macroscopic symmetry, because it has but one molecule per unit cell. Experiments now in progress with iron group impurities in the much simpler MgO and ZnS lattices may prove more amenable to interpretation.

Despite the difficulties of detailed interpretation an interesting corollary experiment may be performed with the alum. The quadrupole splitting of the Al²⁷ nuclear magnetic resonance in ammonium aluminum alum (the host lattice in the present PMR experiments) may be determined as a function of temperature and pressure and compared with the crystalline field splitting results. If we neglect the contribution of the fourth-order axial potential to the splitting, δ , as discussed in I, then both δ and the nuclear quadrupole splitting are proportional to the gradient of the crystalline electric field. The main distinction lies in the polarizability of the paramagnetic charge cloud. The nuclear quadrupole moment is a permanent property of the given nucleus which cannot be significantly deformed by crystalline electric fields¹⁷ whereas the paramagnetic ion is deformed or polarized by the cubic and axial electric field components. This is reflected in the dependence of δ on the inverse square of the strength of the cubic field component. Segleken and Torrey¹⁸ have found the ratio of the quadrupole splittings in the ammonium aluminum and potassium aluminum alums to be equal to the ratio of the crystalline field splittings in the corresponding undiluted chrome alums as determined by Bagguley and Griffiths.¹⁹ These data, as well as the invariance of Δg in our experiments, indicate that the time average cubic electric field strength at the trivalent metallic sites is quite constant in these alums; therefore the variations of the Al²⁷ nuclear quadrupole splitting and the Cr³⁺ crystalline field splitting should be directly comparable. If this proves to be the case the T and P dependences of the Al²⁷ splitting would, to our knowledge, be much larger than any previously measured in nuclear magnetic resonance.²⁰

III. Potassium Chromi-Cobalticyanide

A. Experimental Results

The iron group cyanides differ from the hydrated ionic complexes in that the magnetic ion is covalently

¹⁷ The possibility of stress or temperature-induced changes in the antishielding factor of an ion is presumed negligible for present purposes.

¹⁸ W. G. Segleken and H. C. Torrey, *Phys. Rev.* **98**, 1537 (1955).

¹⁹ D. M. S. Bagguley and J. H. E. Griffiths, *Proc. Roy. Soc. (London)* **A204**, 188 (1950).

²⁰ In a private communication Professor T. Kushida indicates that this suggested experiment will be performed at Hiroshima University.

¹⁵ T. Kushida, *J. Sci. Hiroshima University* **A19**, 327 (1955).

¹⁶ Kushida, Benedek, and Bloembergen, *Phys. Rev.* **104**, 1099 (1956).

TABLE II. Comparison of room temperature and low temperature values of the spin Hamiltonian parameters of dilute potassium chromicyanide.

	$T \cong 297^\circ\text{K}$	$T = 20^\circ\text{K}^a$
g_y	1.9826 ± 0.0005	1.991 ± 0.001
D	0.0824 ± 0.0005	0.0831 ± 0.001
E	0.00765 ± 0.0005	0.0108 ± 0.001

^a From reference 24.

bonded to six $(\text{CN})^-$ groups. This compact octahedron may be considered to produce a particularly strong cubic electric field with weaker components of lower symmetry if the structure is not regular. The magnetic behavior of the complexes can be explained by assuming that the effective crystalline field interaction is stronger than the Russel-Saunders coupling of the magnetic electrons of the free ion. A modification of Hund's rule is then required in order to predict the ground state of the ion.²¹ In the particular case of Cr^{3+} the "strong crystalline field" ground state is equivalent to that in the ionic case: $S = \frac{3}{2}$, $L = 0$. The crystal investigated, $\text{K}_3(\text{Cr}_{0.01}\text{Co}_{0.99})(\text{CN})_6$, has a monoclinic unit cell containing four $[\text{Cr}(\text{CN})_6]^{3-}$ complexes which are equivalent in pairs as is discussed in more detail by Baker *et al.*²² and Bowers and Owen.⁴ The spin Hamiltonian required to describe the PMR spectrum of each pair of equivalent complexes includes a rhombic as well as an axially symmetric splitting term:

$$\mathcal{H} = \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + D(S_z^2 - 5/4) + E(S_x^2 - S_y^2). \quad (5)$$

The spectrum is particularly simple when the magnetic field is applied along the crystalline c -axis which coincides with the \hat{y} spin-Hamiltonian axes of both types of magnetic complex. The somewhat involved eigenvalue expressions are given by Bowers and Owen.⁴ Using the three first-order transitions the parameters g_y , D and E may be evaluated. The crystalline field splitting, δ , of the two Kramers doublets is not exactly $2D$ due to the rhombic component of the effective crystalline field; instead $\delta = 2(D^2 + 3E^2)^{1/2}$.

The results of a hydrostatic pressure run to 10 000 kg/cm^2 at room temperature are plotted in Fig. 3. The slight hysteresis is within the experimental error. The atmospheric pressure values of the parameters differ somewhat from those found by Baker, Bleaney, and Bowers²⁴ at 20°K as shown in Table II. It is of interest to note that the orbital moment contribution changes by almost 100% ($\Delta g = -0.020$ at 297°K , -0.011 at 20°K) over this temperature range though the parameters D and E vary relatively little. This sensitivity of Δg is also observed in the pressure data: $|\Delta g|$ increases by 17% to 7300 kg/cm^2 then decreases,

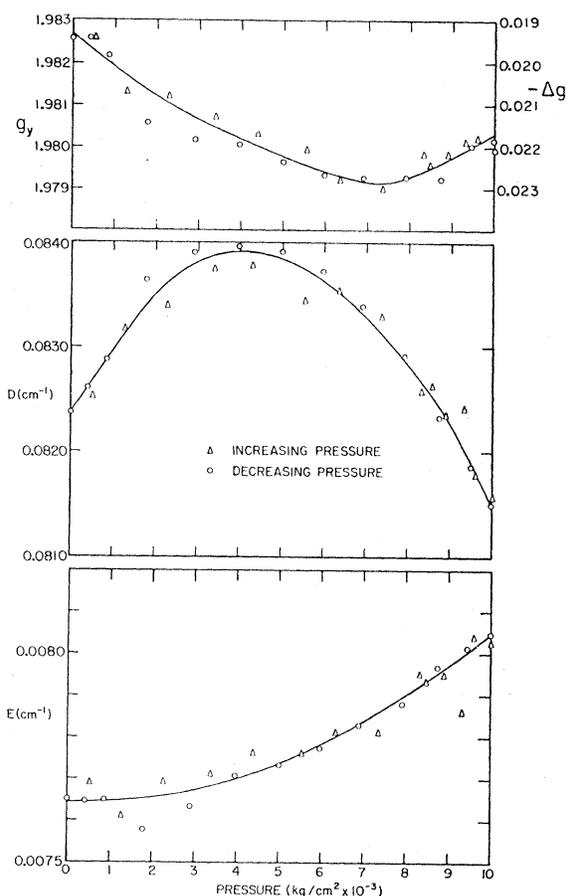


FIG. 3. Pressure dependence of the spin-Hamiltonian parameters of Cr^{3+} in $\text{K}_3\text{Co}(\text{CN})_6$ at room temperature.

whereas the maximum variations of D and E are 3% and 5%, respectively. Within experimental error the data of Fig. 3 could be represented by quadratic functions of pressure but no evident correlation exists between the expressions nor is there any obvious physical significance in such a representation.

No attempt has been made to measure the (probably anisotropic) compressibility or thermal expansion coefficients of this crystal due to its complexity. These quantities are expected to be somewhat smaller in magnitude than those of the fluosilicate or the alum. The covalent cyanide complex itself is probably relatively incompressible whence inhomogeneous deformation within the unit cell may be expected.

B. Discussion

In analyzing the data of Baker *et al.*²² Bleaney and O'Brien²³ found that the functional dependences of the parameters Δg , D , and E on the effective crystalline field components in the cyanide complex are identical to those in ionic surroundings. The spin-orbit coupling

²¹ J. H. Van Vleck, *J. Chem. Phys.* **3**, 807 (1935).

²² Baker, Bleaney, and Bowers, *Proc. Phys. Soc. (London)* **B69**, 1205 (1956).

²³ B. Bleaney and M. C. M. O'Brien, *Proc. Phys. Soc. (London)* **B69**, 1216 (1956).

is expected to be reduced relative to the ionic case due to charge transfer from the Cr^{3+} ion to π bonds with the neighboring cyanide groups.^{24,25} Since the effective cubic electric field component is larger in the cyanide and the spin-orbit coupling reduced $|\Delta g|$ is expected to be appreciably smaller for $[\text{Cr}(\text{CN})_6]^{3-}$ than for $(\text{Cr}\cdot 6\text{H}_2\text{O})^{3+}$. This difference is indeed observed, the g -shift for the chromicyanide at 20°K being only ~40% of that found in the dilute alum. The distinction is less manifest in our room temperature cyanide data, however, where $|\Delta g|$ is about 80% of the alum value.

The percentage variations of the cyanide g -shift with pressure and temperature are considerably larger than would be expected from simple ionic volume dependence of the cubic crystalline field component. This suggests that the spin-orbit coupling may vary quite rapidly with volume. However, a decrease of $|\Delta g|$ upon volume reduction should result from either of these mechanisms whereas the opposite effect is observed up to 7300 kg/cm². A qualitative explanation of this anomaly may be that the cyanide octahedron is relatively incompressible but "intermolecular hybridization" or bond sharing increases with decreasing volume due to the decreasing distance between the chromium and its *next*-nearest neighbors. This would tend to make the Cr^{3+} ion see more isotropic surroundings, i.e., reduce the effective cubic electric field. Nuclear quadrupole resonance experiments indicate just such an effect in the case of the covalent C-Cl bond in *para*-dichlorobenzene.¹⁶ The decrease of $|\Delta g|$

with volume above 7300 kg/cm² could be attributed to reduced spin-orbit coupling since this interaction might vary sufficiently rapidly with interatomic distance to eventually dominate the bond sharing mechanism.

It is surprising that the pressure and temperature variations of D and E are markedly smaller than the corresponding changes of Δg since both D and E are proportional to $(\Delta g)^2$ in the equivalent crystalline field model. Since D and E are also proportional to the axial and rhombic electric field components, respectively, it appears that changes in these components roughly compensate for the variations of $(\Delta g)^2$. Such a high degree of correlation is unlikely, though not impossible, and suggests that the equivalent crystalline electric field representation of the $[\text{Cr}(\text{CN})_6]^{3-}$ complex may not be valid.

CONCLUSION

The PMR experiments on dilute ammonium chrome alum demonstrate that the crystalline field splitting is a sensitive probe for determining variations of the average electric field at the Cr^{3+} sites. Detailed interpretation of the results is difficult, however, since the equation of state does not provide sufficient information concerning the positions of all ions within the unit cell.

The chromicyanide results show that the orbital contribution to the magnetic moment is a more sensitive function of stress and temperature than are the crystalline field splitting parameters. It is difficult to reconcile such behavior with the equivalent crystalline field model of the covalently bonded cyanide complex.

ACKNOWLEDGMENTS

The author wishes to thank Professor N. Bloembergen for his encouragement and guidance in the course of these experiments. Discussions with Professor G. B. Benedek, Professor T. Kushida, and Dr. W. Marshall have been of great assistance.

²⁴ K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 542 (1953).

²⁵ It should be noticed that spin-orbit interaction is quite strongly reduced in nominally ionic iron-group complexes relative to free ion values (see Sec. V.A of I). While such an effect might be attributed to partially covalent bonding detailed considerations indicate that this cannot be the case in iron group oxides, for example. A theoretical treatment of the problem will be given in a paper to be published by Dr. W. Marshall.

Some Selection Rules for Band-Band Transitions in Wurtzite Structure

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Optical selection rules at $\mathbf{k}=(0,0,0)$ in the wurtzite structure are discussed. These rules suggest an interpretation of recently reported work on CdS by Dutton and Lempicki on reflection spectra, and the excitation spectrum of edge emission in polarized light. Assuming band-band transitions at $\mathbf{k}=(0,0,0)$ are involved, a valence band spin-orbit splitting of 0.0167 eV and crystal field splitting of about 0.070 eV (at liquid N₂ temperature) are obtained for CdS. Other predictions of the model and other possible interpretations of the data are discussed.

WITH the increasing attention being given to optical and other properties of compounds with wurtzite structure, e.g., ZnO, ZnS, CdS, it is of importance to have available the proper optical selection rules for this structure. These rules may help in the

identification of the levels involved in optical transitions in the pure, or activated materials. A recently published paper¹ correctly drew attention to the importance

¹ G. Dresselhaus, Phys. Rev. **105**, 135 (1957).