

The corresponding values of c_2 , c_4 and c_6 are then

$$c_2 = -3.68 \times 10^{-1} \text{K},$$

$$c_4 = 1.24 \times 10^{-5} \text{K},$$

$$c_6 = -5.63 \times 10^{-10} \text{K}.$$

It was pointed out earlier that the Hamiltonian used

for computing the energy levels was written in the form

$$\mathcal{H} = \lambda(\mathbf{n}_i \cdot \mathbf{J}) + (1 - \lambda)c_4'[(c_2/c_4)\mathcal{H}_2 + \mathcal{H}_4 + (c_6/c_4)\mathcal{H}_6].$$

c_4' was taken arbitrarily to be 1.97×10^{-7} . As pointed out in the earlier text, when values of c_2/c_4 and c_6/c_4 are mentioned they are expressed in terms of the values of c_2/c_4 and c_6/c_4 calculated above.

Paramagnetic Resonance of Chromic Ions in Double Nitrate Crystals and Frozen Solution*

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(Received June 12, 1961; revised manuscript received August 21, 1961)

Chromic ions are shown to enter double nitrate crystals in two different interstitial sites, and the spin Hamiltonian parameters for these ions have been determined. It is also shown that cloudy double nitrate crystals contain occluded solution and the amount of solution contained in a number of crystals has been measured. The paramagnetic resonance properties of frozen samples of the solution from which the chromium-doped double nitrate crystals were grown have been investigated. The results reported in this paper are compared with the nuclear orientation results for Cr^{51} in cerium magnesium nitrate obtained by Kaplan and Shirley. The utility of frozen solutions for nuclear orientation experiments is discussed.

I. INTRODUCTION

CERIUM magnesium and cerium zinc nitrate crystals have been used extensively in nuclear orientation experiments¹ because very low temperatures may be obtained by adiabatic demagnetization of the salt, and the small value of g_{11} for the cerium ion permits the application of rather large external fields without a large rise in temperature. Nuclei of several of the rare-earth trivalent ions and iron-group divalent ions can be oriented in these crystals. Recently, Kaplan and Shirley (KS)² have shown that cerium magnesium nitrate crystals grown from solutions containing chromic ions do contain some chromium and that Cr^{51} nuclei thus included in the crystal can be oriented. These authors suggest that their method may be extended to a wide variety of paramagnetic ions, and this possibility enhances the interest in the clarification of the nuclear orientation mechanism or mechanisms which were operative in their experiment.

KS concluded that the chromic ions were trapped in tiny pockets of solution—"brine holes"—rather than in crystal sites. In Sec. II of this paper, electron paramagnetic resonance data are described which show that chromic ions go into two different interstitial sites of the

double nitrate crystals. However, proton resonance measurements described in Sec. III show that cloudy double nitrate crystals may be grown with at least as much as 10% occluded solution by volume without any large-scale occlusions. On the other hand, clear crystals do not contain an appreciable amount of solution. In Sec. IV, the electron paramagnetic resonance properties of frozen solutions of chromic ions are discussed and qualitative estimates are made of their utility in nuclear orientation experiments.

In Sec. V, the orientation experiments reported by KS are compared with the paramagnetic resonance results. In the last section, the use of interstitial sites and occluded solution for nuclear orientation is discussed as a general method for the orientation of the nuclei of paramagnetic ions.

Note added in proof. While this paper was in press, the author found that the presence of two paramagnetic complexes in chromium-doped lanthanum zinc has been reported by Pastor and Devor [J. Chem. Phys. **31**, 1145 (1959)]. The spin-Hamiltonian parameters obtained by those authors agree with those reported in the present paper. Their results for the ratio of the concentration of chromic ions relative to rare-earth ions in the crystal to the ratio in the solution is much smaller than reported in this paper. Subsequent investigation by the author has shown that the origin of this discrepancy is the fact that the concentration of chromic ions in the crystal does not increase in direct proportion to the concentration of chromic ions in the solution.

* Research supported in part by the National Science Foundation and the Office of Naval Research.

¹ R. P. Hudson, *Progress in Cryogenics* (Academic Press, Inc., New York, 1961), Vol. III, p. 97.

² Morton Kaplan and D. A. Shirley, Phys. Rev. Letters **6**, 361 (1961).

II. PARAMAGNETIC RESONANCE OF CHROMIC IONS IN INTERSTITIAL SITES

The Spin Hamiltonian

Lanthanum magnesium and cerium zinc nitrate crystals have been grown from aqueous solutions containing chromic nitrate in a concentration such that the ratio of chromic ions to rare-earth ions was 3:100. For good growth conditions, very clear crystals were obtained which were slightly colored by the chromic ions. For less favorable conditions, the crystals were sometimes very cloudy. The paramagnetic resonance results reported in this section were independent of the optical quality of the crystals.

The paramagnetic resonance measurements were made at $\nu=16$ kMc/sec. When the static field was applied in a direction perpendicular to the symmetry axis, six narrow lines are observed which can be interpreted as the spectrum of two different magnetic complexes each with spin $\frac{3}{2}$ and very large fine-structure splittings. The angular variation of the spectrum was investigated as fully as possible although the large values of the fine-structure splittings precluded the observation of all six lines when the field was along the symmetry axis.

The spectrum of the two complexes was fitted with the spin Hamiltonian:

$$\mathcal{H} = g\beta(H_z S_z + H_x S_x + H_y S_y) + D(S_z^2 - 5/4) + E(S_x^2 - S_y^2) + A(\mathbf{I} \cdot \mathbf{S}).$$

For either complex, the effective spin is $\frac{3}{2}$, the z axis is the symmetry axis of the crystal, and E is less than 0.001 cm^{-1} . The values of g and D are given in Table I for chromic ions in lanthanum magnesium nitrate at temperatures of 290° , 77° , and 4.2°K . The sign of D was determined from the relative intensity of the transitions at 1.2°K where $kT \sim D$. The hyperfine interaction constant for Cr^{53} was determined at 4.2° only and is also listed in the Table. The spectrum of the two complexes have intensities that are equal within ten percent. Within experimental error, the same parameters were obtained for cerium zinc nitrate.

Linewidths

In the lanthanum salt, the rms magnetic field widths for all transitions of complex I are 4.0 gauss, and 4.9 gauss for complex II, at all temperatures. For the cerium salt, the linewidths are very nearly the same as those for the lanthanum salt at 290°K and 77°K . However, at 4.2°K the rms magnetic field widths of the transitions of complex I and II are 120 gauss and 150 gauss, respectively. The temperature dependence of the linewidth is caused by the temperature dependence of the spin-lattice relaxation time for the cerium ion. At 77°K and higher, the cerium ions have such a rapid spin-lattice relaxation time that the Ce-Cr interactions do not broaden the levels of the chromic ions. The large rms width observed at 4.2°K in the cerium salt excludes

TABLE I. Spin-Hamiltonian parameters for chromic ions in cerium zinc nitrate.

Temperature ($^\circ\text{K}$)	g	$D \text{ (cm}^{-1}\text{)}$	$A \text{ (cm}^{-1}\text{)} - \text{Cr}^{53}$
(a) Complex I			
290	1.98 ± 0.01	-0.159 ± 0.005	
77	1.97 ± 0.01	-0.184 ± 0.001	
4.2	1.98 ± 0.01	-0.186 ± 0.001	0.0018 ± 0.0002
(b) Complex II			
290	1.98 ± 0.01	-0.232 ± 0.006	
77	1.98 ± 0.01	-0.260 ± 0.003	
4.2	1.97 ± 0.01	-0.272 ± 0.003	0.0018 ± 0.0002

the possibility that either of the chromic ion sites is the same as the rare-earth ion site. The rms width calculated for ions in the rare-earth sites, assuming dipole-dipole interactions, is only 33 gauss. If the chromic ions were in the site occupied by the divalent cobalt Y ion, the rms width would be only 72 gauss.³ If the ions were in the sites occupied by the divalent cobalt X ion, the rms width would be 107 gauss and the line would show a resolvable structure due to very large nearest neighbor effects when the magnetic field is applied in certain directions.³ This structure was not observed and, unless there is a Ce-Cr interaction in addition to the dipole-dipole interaction, the chromic ions cannot occupy any of the usual metal-ion sites in the crystal.

Concentration of Chromic Ions

The intensity of the chromic ion resonances were compared with that of cupric ions in a copper sulfate crystal. This comparison showed that the ratio of the number of chromic ions to the number of rare-earth ions in the crystal was smaller by a factor of 15 than the ratio which existed in the solution from which the crystal was grown.^{3a}

III. OCCLUDED SOLUTION IN DOUBLE NITRATE CRYSTALS

In the next section, it is shown that the electron paramagnetic resonance lines for a frozen solution are very broad, and the signal is far more difficult to detect than for an equal number of chromic ions in crystal sites. A much more sensitive test for occluded solution is provided by the proton resonance spectrum of the crystals at room temperature. The absorption spectrum of the protons in the crystal water is very broad (10–20 gauss, depending upon the direction of the applied field relative to the crystal axes) whereas the resonance spectrum of the protons in the solution is motionally narrowed. Because of the narrow line, the proton resonance of a very small fraction of solution can be observed. The volume fraction of solution was determined by comparison of the intensity of the narrow

³ J. W. Culvahouse, W. Unruh, and R. C. Sapp, Phys. Rev. **121**, 1370 (1961).

^{3a} See Sec. I, Note added in proof.

component of the proton spectrum obtained for the crystal with that obtained from an equal volume of saturated solution.

In very clear crystals, it has been possible to establish that the volume of occluded solution is less than 0.5% of the crystal volume. At the other extreme, one large crystal which had well-formed crystal faces and no macroscopic pockets but which was chalk-white, had very nearly 10% occluded solution. The fraction of solution determined by the proton resonance measurements correlated well with the optical quality of the crystal.

The importance of occluded solution in the double nitrate crystals in magnetic, thermal, and nuclear measurements is enhanced by the high density of ions in the saturated solution. The saturated aqueous solution without added nitric acid and at room temperature has an ionic density about one-half that of the crystal. Thus, a crystal containing 10% occluded solution will have 5% of its ions in solution rather than in the crystal. Since the chromic ions are preferentially excluded from the crystal, as many chromic ions may be trapped in the solution as are in the crystal sites if ~13% of the crystal is occluded solution.

IV. PARAMAGNETIC RESONANCE OF CHROMIC IONS IN FROZEN SOLUTION

Small pockets of solution occluded in a cerium double nitrate crystal would be readily cooled to a low temperature by self-cooling and by heat transfer to the crystalline material. The value of the frozen solution for orientation of chromium nuclei will depend upon the structure of the low-lying energy levels of the chromic ions in the frozen solution. Paramagnetic resonance measurements such as those described in Sec. II can provide the required information rather easily for ions in crystalline sites. In principle, equally complete information could be obtained from the paramagnetic resonance spectrum of a frozen solution. One expects that each ion in the frozen solution will have six waters of hydration with a wide range of distortions from octahedral symmetry. Thus the problem is similar to that for ions in crystal sites; but, in the frozen solution, there are a very large number of sites, and distributions of the values of the spin-Hamiltonian parameters will usually be required to fit the observed spectrum. In addition, the principal axes for the Hamiltonian will probably have an isotropic distribution of directions.

Figure 1 shows the paramagnetic resonance spectrum near $H_0 = h\nu/g\beta$ for chromic ions in a saturated lanthanum magnesium nitrate solution which was rapidly frozen and brought to 77°K. The curve was obtained by integration of the derivative of paramagnetic absorption. This curve may not include parts of the spectrum which are even broader and were not detected.

It should be possible to fit the observed spectra by assuming a distribution of D and E values and an isotropic distribution of principle axes for the Hamil-

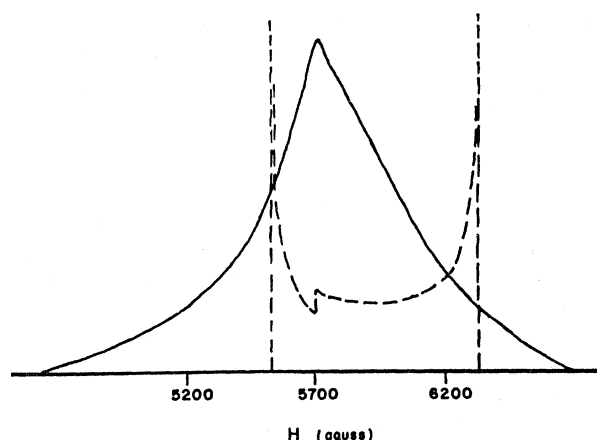


FIG. 1. The solid curve is the paramagnetic resonance absorption spectrum of a small concentration of chromic ions in a frozen solution of lanthanum magnesium nitrate at 77°K. The dashed curve is the theoretical line shape for ions which are axially symmetric with a single value 0.15 cm^{-1} for the fine structure constant and an isotropic distribution of directions for the axis of symmetry.

tonian written in Sec. II. The g factor for chromium is not sensitive to the crystal field and should be about 1.98 for all ions. We have calculated the line shape to be expected for a single D value of 0.15 cm^{-1} for ions which have an axis of symmetry, the directions of which are distributed isotropically. The $(\frac{3}{2}, -\frac{1}{2})$ transition leads to the line shape shown as a dashed curve in Fig. 1. For this model, the $(\pm\frac{3}{2}, \pm\frac{1}{2})$ transitions are too broad to observe. The lack of agreement is not surprising and shows that a more complicated model is required.

A less complete analysis than that suggested above permits one to make some semiquantitative conclusions. The Hamiltonian for a particular chromic ion may be written in the form

$$\mathcal{H} = g\beta HS_z + \sum_{m=0}^{m=2} G_m(Q_{2m} + Q_{2-m}),$$

where the operators Q_{2m} are irreducible tensor operators of rank two which have the transformation properties of spherical harmonics.⁴ Explicitly:

$$\begin{aligned} Q_{20} &= \left(\frac{3}{2}\right)(S_z^2 - 5/4), \\ Q_{21} + Q_{2-1} &= \left(\frac{3}{16}\right)^{1/2}(S_z S_+ + S_+ S_z + S_z S_- + S_- S_z), \\ Q_{22} + Q_{2-2} &= \left(\frac{3}{16}\right)^{1/2}(S_+ S_+ + S_- S_-). \end{aligned}$$

With the operators in this form, matrix elements are easily calculated. If the frozen solution has a nonordered structure, the distribution of the values of the coefficients should be independent of the direction of the axis chosen for the description. For an axis with a polar angle $\theta = \cos^{-1}(1/\sqrt{3})$ and an azimuthal angle $\phi = \frac{1}{2}\pi$ relative to the axis used above, the coefficient of the diagonal part of the fine-structure interaction becomes $G_1/\sqrt{12}$ instead of G_0 . For another direction, it becomes $G_2/\sqrt{12}$. Thus the distribution of values for $(12)^{1/2}G_0$ is

⁴ M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), Chap. V, p. 76.

the same as the distribution for G_1 and G_2 . If the magnetic field interaction is considered large in comparison with the fine-structure interaction the zero-order perturbation theory result for the energy levels except for an unimportant constant is given by $E_M = g\beta HM + \frac{3}{2}G_0M^2$, where M is the azimuthal quantum number for the electron spin. The linewidth of the $(\pm\frac{3}{2}, \pm\frac{1}{2})$ transitions will give the spread of values for G_0 . The frequency splitting of the $(\frac{1}{2}, -\frac{1}{2})$ transition is not affected in zero order and will lead a more narrow line than the other transitions. This transition will thus be emphasized in a derivative of paramagnetic absorption. The field at which the $(\frac{1}{2}, -\frac{1}{2})$ transition will be observed is given in terms of the Hamiltonian parameters by first-order perturbation theory to be

$$H = H_0 + (\frac{3}{2})^2(2G_1^2 - G_2^2)/H_0(g\beta)^2,$$

where $H_0 = h\nu/g\beta$. The exact shape of the line arising from this transition will depend not only on the distribution of values for G_1 and G_2 but also upon the correlations between them. The linewidth of the $(\frac{1}{2}, -\frac{1}{2})$ transition will yield the spread of values for the second term of the preceding equation. If ΔH is the full width at half maximum intensity for the line due to $(\frac{1}{2}, -\frac{1}{2})$ transition, a measure of the spread of nondiagonal matrix elements is given by

$$\Sigma = g\beta(H_0\Delta H)^{\frac{1}{2}}.$$

The field H_P that would be required to begin to exceed the effect of nondiagonal interactions for an appreciable fraction of the ions in the frozen solutions is $H_P = (H_0\Delta H)^{\frac{1}{2}}$. For chromic ions in solution, this field is about 1800 gauss. This result is probably better than an order of magnitude estimate, but it is intended only as an indication of the difficulty of establishing an orientation axis for the frozen solution.

It is interesting to note that not all ions in frozen solution show such a large spread of nondiagonal interactions. We have found that manganous ions ($S = \frac{5}{2}$) have a spectrum with a resolved hyperfine structure for the $(\frac{1}{2}, -\frac{1}{2})$ transition. The value of ΔH for these lines is approximately 20 gauss, which yields a value of about 100 gauss for the field required to begin to suppress the nondiagonal fine structure interactions.

V. NUCLEAR ORIENTATION OF CHROMIC IONS IN DOUBLE NITRATE CRYSTALS

Bleaney⁵ has discussed the nuclear orientation produced in crystals for which the fine-structure splitting is much larger than the hyperfine splitting. When D is large and negative for an ion of spin S and having the hyperfine interaction constants A and B , the states with $S_z = \pm S$ lie lowest. For this case, the hyperfine structure in zero field is the same as that for an ion with spin $\frac{1}{2}$ and the effective hyperfine interaction constants $A' = 2SA$ and $B' = 0$ and the orientation produced will be axial. If D is positive and the spin of the ion is integral, the lowest level will have $S_z = 0$ and there will be no hyperfine splitting. If D is positive and the ionic spin is half-

integral, the lowest level will have $S_z = \pm\frac{1}{2}$ and the hyperfine structure is the same as that for an ion of spin $\frac{1}{2}$ and the effective hyperfine interaction constants $A' = A$ and $B' = (S + \frac{1}{2})B$. This situation will lead to a planar orientation if $A = B$.

For both types of chromic ions in the double nitrate crystals, D is large and negative. The orientation produced by these sites in zero field will therefore be axial. The alignment produced at a fixed temperature is not affected at all by the application of a magnetic field in the direction of the symmetry axis. The alignment is affected by a field perpendicular to the symmetry axis only when that field is sufficiently large that $g\beta H$ is of the order of D . For the same reasons that applied fields have no effect if $g\beta H$ is small compared with D , spin-spin interactions can affect the nuclear alignment produced by these sites only if those interactions are of the same order of magnitude as the fine structure splitting. The linewidth due to the Ce-Cr interactions discussed in Sec. II show that this is not the case. We expect, therefore, that the chromic ions in the crystal sites will produce an axial alignment in zero field which is not complicated by spin-spin interactions and which will not be affected by the application of fields along the symmetry axis.

The chromic ions in frozen solution are expected to produce no nuclear orientation in zero field. From the discussion in Sec. IV, one would expect that an applied field of the order of 1000 gauss would produce some axial orientation.

The gamma radiation from the Cr^{51} nuclei oriented by KS showed a small anisotropy in zero field for temperatures of the order of 0.003°K . A much larger anisotropy of the same sign was observed at temperatures of the order of 0.009°K when a field of 400 gauss was applied along the symmetry axis of the crystal. These results might be interpreted as follows: In zero field, the anisotropy due to those chromic ions in the crystal sites is observed and the increase with applied field is due to orientation produced by the chromic ions in the solution pockets. It is not unreasonable to assume that 400 gauss will produce some effect on the frozen solution. One difficulty with this interpretation is that a very large amount of frozen solution is required to explain the small size of the zero-field orientation observed by KS. At 0.003°K and in zero field, the difference between the gamma-ray emission probability along the symmetry axis and perpendicular to it is $\Delta W = \{W(0) - W(90)\} = 0.05$. This difference for an applied field of 400 gauss and a temperature of 0.009°K was 0.12, and there was no indication of a saturation effect as the temperature was lowered. One would expect that the orientation produced by chromic ions in the crystal sites in zero field and at 0.003°K would lead to a value for ΔW much in excess of 0.12. Assuming that the value of ΔW for these sites is only 0.12 and that the observed value is caused by the isotropic background from the chromic ions in solution, then approximately equal amounts of chromium must be present in solution pockets and in

⁵ B. Bleaney, Phil. Mag. 42, 441 (1951).

crystal sites. Using our data for the relative density of chromic ions in the crystal and in frozen solution, we require that more than 13% of the crystal used by KS be occluded solution. As this is really an underestimate of the fraction of solution, we conclude that the crystal used by KS probably had a lower density of chromium in the crystal relative to that in the solution than existed for the crystals which we have grown. (See Sec. I, Note added in proof.)

VI. CONCLUSIONS

Chromic ions and possibly many other trivalent ions can be put into two different sites of cerium double nitrate crystals which are not any of the sites usually occupied by the metal ions. Such crystals provide an excellent method for the orientation of chromium nuclei because the large negative value of D should prevent complications due to Ce-Cr interactions. The very small value of $g_{||}$ for cerium ions in this compound permits the application of a field along the symmetry axis so to produce a large polarization of the chromium nuclei. If complications due to occluded solution are to be avoided only very clear crystals should be used and they should be checked for solution content by the proton resonance method described in Sec. III.

Rather large amounts of solution may be trapped in small pockets within the double nitrate crystals. If the pockets are sufficiently small, they will be cooled by contact with the crystalline material. The small value of $g_{||}$ for cerium ions in the double nitrate permits one to apply a field to the crystal so to establish an orientation axis for the electron spins.

The amount of orientation which can be established by a given field will depend critically upon the distribution of nondiagonal interactions present for the ions in the solution. The nature of the distribution of non-

diagonal interactions can often be inferred from the paramagnetic resonance spectrum. For ions of spin greater than $\frac{1}{2}$, the off diagonal interactions will usually be most severe. If the spin is half integral and greater than one, the width of the $(\frac{1}{2}, -\frac{1}{2})$ transition gives a measure of the nondiagonal interactions. When the spin is integral, it may be necessary to observe the forbidden transitions in order to obtain a relatively sharp line from which the nondiagonal interactions can be estimated. For ions with an effective spin of $\frac{1}{2}$, the only nondiagonal interactions are the magnetic and electric hyperfine interactions and, of course, the spin-spin interactions which should never be very severe. If the g factor is highly anisotropic, it will be almost impossible to determine the spread of off diagonal interaction as most of the linewidth observed in paramagnetic resonance measurements would be due to the variation of the effective g value. If the hyperfine interaction constants are sensitive to the distortions of the hydrated complex, a spread of values will be encountered. Chromic ions are probably more difficult to orient in frozen solution than most ions because of the large fine structure interactions which are encountered. However, the frozen solution might be useful for the orientation of the nuclei of paramagnetic ions which do not enter the crystal sites. If the ion does enter the crystal sites, nuclear orientation experiments with good quality crystals will be more easily interpreted. If the ion enters the crystal very readily, the presence of occluded solution will be relatively unimportant.

ACKNOWLEDGMENTS

The author wishes to thank Mr. Wesley P. Unruh who made many of the measurements reported here. This investigation was stimulated by numerous discussions with Dr. R. C. Sapp.

Inverted Nature and Significance of Negative-Mass Landau Levels*

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(Received April 14, 1961)

Quantum-mechanical considerations on negative-effective-mass carriers in crystals show the following: The energy-level structure of particles with negative effective mass, in the presence of a magnetic field, consists of a system of *inverted* Landau levels. A simple derivation of the level inversion is given. Sharp contradistinctions are found on the behavior of the levels by comparison to that of positive-mass regions of momentum space. The significance of this type of level structure for cyclotron resonance transitions, in particular in the case of the observed small negative-mass branch of heavy holes in Ge is discussed.

INTRODUCTION

THE inverted nature of the harmonic oscillator-like Landau levels for carriers (electrons or holes) with negative effective mass has already been pointed

out^{1,2} and the implications of such a quantum level structure for nonequilibrium cyclotron resonance work

¹ G. C. Dousmanis, in *Quantum Electronics*, edited by C. H. Townes (Columbia University Press, New York, 1960), p. 458; J. Appl. Phys. **32**, 2005 (1951).

² H. Kroemer, International Solid-State Circuit Conference, 1960, University of Pennsylvania (unpublished), p. 81.

* This work has been supported in part by the U. S. Air Force, Air Research and Development Command, Air Force Cambridge Research Center under contract.