

extensive calculation would be desirable in order to make a more detailed comparison.

There is a simple device which seems to reproduce the calculated level order within a given band very well in this case. Let ψ_k^i represent the wave function for the i th irreducible representation of the wave vector \mathbf{k} . ψ_k^i is expanded in orthogonalized plane waves

$$\psi_k^i = \sum_{\mathbf{h}} \beta_{\mathbf{k}, \mathbf{h}}^i M_{\mathbf{k}+\mathbf{h}}, \quad (9)$$

where $X_{\mathbf{k}+\mathbf{h}}$ is given by (3). The vector \mathbf{h} runs over all reciprocal lattice vectors. The levels at symmetry points may be ordered accordingly to the quantity $(\mathbf{k}+\mathbf{h})^2$ where $(\mathbf{k}+\mathbf{h})'$ characterizes the OPW of lowest energy belonging to ψ_k^i . Since this is an ordering according to kinetic energy, there is a vague resemblance to the principle of maximum smoothness.³²

This prescription says in essence, that the order of levels at symmetry points in a given band is what would be expected for free-electron bands. It is not surprising that it gives the correct results for potassium. It is more interesting that it seems to work reasonably well in iron. Even in potassium, however, one must not suppose that the numerical energy values of the levels will be in good agreement with a free-electron model. Inspection of Fig. 2 will reveal that some levels will connect by bands which must depart severely from the free electron form.

The successful comparison of these results with other calculations for the various bands suggests that at least the relative order of levels within a given band is not very sensitive to details of the potential. It is

possible, then, that the general forms of individual S , P , and D bands are now well understood for the body-centered cubic lattice. It is important to note, however, that the situation in regard to overlap of these bands is much less clear because the overlap is much more sensitive to the potential.¹⁷ It is interesting to note that there is apparently a very considerable degree of overlap in potassium.

Since there is evidence that the general form of a band is reasonably independent of potential, it is interesting to consider the form of the F band. It is a little difficult precisely to define the F band since some representations (Γ_{15} , H_{15} , P_4 , $N_{1'}$, $N_{3'}$, and $N_{4'}$) also contain P functions. At $k=0$, the states Γ_{25} , $\Gamma_{2'}$, and Γ_{15} contain F functions. At P we have P_4 , P_5 , and P_1 , and at N we have $N_{2'}$, $N_{1'}$, $N_{4'}$, $N_{3'}$. The lowest predominantly F -like state is Γ_{25} , and the top of the band also appears to occur at Γ with $\Gamma_{2'}$. This order is reversed at H : $H_{2'}$ lies below H_{25} . We find Γ_{15} intermediate between Γ_{25} and $\Gamma_{2'}$ and H_{15} intermediate between $H_{2'}$ and H_{25} . At P , the order is apparently P_5 , P_4 , and P_1 .

ACKNOWLEDGMENTS

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Absorption Spectra, Zeeman Effects, and Magnetic Properties of Neodymium Salts*†

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The absorption spectra of nine neodymium salts were obtained in single crystals at liquid helium temperature and high dispersion. The Zeeman effect of the lines was observed in a field of about 37 000 gauss with different orientations of the crystals, so that the magnetic splitting of the ground and excited states could be measured. This provides valuable clues for the interpretation of the spectra and quantitative data for the derivation of the crystal field. The results are related to those obtained in paramagnetic resonance measurements.

1. INTRODUCTION

IT is well known that the salts of the rare earths may give sharp absorption lines particularly at low temperatures and that often these lines are split in a

magnetic field. It is also known since the work of Bethe¹ and Kramers² that the crystal field splits the

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† In order to conserve journal space, this paper has been considerably condensed. More details can be found in a technical report [U. S. Atomic Energy Commission Report NYO-3977 (unpublished)] of which a limited number of copies are available to interested persons. This report contains in particular the complete wavelength measurements of the field-free absorption spectra of most of the salts and the Zeeman effects of all lines which

show resolved patterns. This supplementary material has also been deposited as Document No. 4886 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$13.75 for photoprints or \$4.50 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

¹ H. Bethe, *Ann. Physik* **3**, 133 (1929); *Z. Physik* **60**, 218 (1930).

² H. A. Kramers, *Proc. Acad. Sci. Amsterdam* **32**, 1176 (1929); **33**, 960 (1930).

TABLE I. Symmetry and Stark splitting of ground states of investigated salts.

Salt	Symmetry	a_2	a_3	a_4	a_5	Previous work
$\text{Nd}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	hexagonal C_{3v} ^a	33.13 ^b				(20°) ^c
$\text{Nd}_2\text{Zn}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	hexagonal C_{3v} ^a	36.6				(20°) ^c
$\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	hexagonal C_{6h} ^d	149.64 ^b				
$\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$	hexagonal C_{6v} ^{d,e}	115.	184	363	384 ^f	(20°) ^c (77°) ^f
$\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$	monoclinic ^g	61.5	250			(20°) ^c (77°) ^h (83°) ⁱ
$(\text{La}+\text{Nd})\text{Cl}_3 \cdot 7\text{H}_2\text{O}$	triclinic ^j	103.91				
$\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	monoclinic ^k	76	226	263	301 ^l	(20°) ^c (20°, 77°) ^m (83°) ^{n,l}
$(\text{La}+\text{Nd})_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	hexagonal ^k	26.48 ^b				
$\text{Nd}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$	unknown	83.15 ^b				

^a Determined by Hellwege for the corresponding Pr-salts which are isomorphic with the neodymium salts.^b Measurements of this paper.^c See reference 8.^d Point group determined by x-ray diffraction [J. D. H. Donnay and W. Nowacki, *Crystal Data* (Geological Society of America, New York, 1954)].^e There is evidence that the surroundings of the Nd-ion has lower symmetry.^f See reference 6.^g A crystal was measured by Donnay and the monoclinic structure confirmed.^h F. H. Spedding and H. F. Hamlin, *J. Chem. Phys.* 5, 429 (1937).ⁱ P. C. Muhherji, *Indian J. Phys.* 11, 123 (1937).^j A crystal was measured by Donnay and found to be triclinic. The number of molecules of water is not certain.^k Crystal system as reported in the literature.^l See reference 7.^m Spedding, Hamlin, and Nutting, *J. Chem. Phys.* 5, 191 (1937).ⁿ H. Gobrecht, *Ann. Physik* 28, 673 (1937).

salts in the literature except that Brochard and Hellwege³ mention that they have obtained the splittings in $\text{Nd}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ without, however, giving the measurements. Chow⁵ attempted to obtain the Zeeman effect of NdF_3 but achieved only broadening of the lines because he used crystal powder. Clear splittings can be obtained only in single crystals as the Zeeman effect is very sensitive for the orientation of the crystal.

The magnetic resonance method also measures the Zeeman effect, but can do this only for the lowest state of each ion, whereas the optical spectra give also the Zeeman effects of the excited states. For the ground state the results of the two methods should be the same (see later on).

2. EXPERIMENTAL TECHNIQUE

The necessity of having the crystals in the restricted space between the pole pieces of a magnet at liquid helium temperature required a Dewar vessel of special construction. We are indebted to Dr. H. Meissner for the design of a metal Dewar vessel which was built in our machine shop under his supervision and proved very effective (Fig. 1). The crystals were mounted on a plastic holder and immersed directly into liquid helium. Under the intense illumination necessary for obtaining the absorption spectra in a reasonable time the helium lasted for 12–15 hours. The general optical arrangement is shown in Fig. 2.

Most exposures were made with a 21-foot concave grating spectrograph in a Paschen mounting with a dispersion of about 1.2 Å/mm. While the high resolution and dispersion were not necessary in all cases except for very sharp lines, it proved convenient to obtain all spectra under uniform conditions. The light source was a tungsten ribbon filament and the exposures were from

10 minutes to two hours. An iron hollow cathode discharge tube furnished the comparison spectrum. The spectral range covered was from about 3500 Å, the short-wavelength cutoff of the spectrum, to about 9000 Å. The light was polarized with a large calcite rhomb. In general the two polarizations were obtained in two different exposures as the varying astigmatism of the spectrograph made simultaneous exposures of the two polarizations inadvisable. The whole spectral range could be covered in two sets of exposures and the spectrum between 3500 and 9000 Å was contained on eleven 16-inch-long plates. The magnetic field with a distance between the pole pieces of about 20.6 mm was between 35 000 and 37 000 gauss.

Table I gives the salts which were investigated with particulars about the crystals and references to the literature where previous data on the particular compound can be found. The figures between parentheses in the last column indicate the temperature at which the cited measurements were made. Only observations at the temperature of liquid air or lower have been quoted and in general only those papers where a substantial amount of experimental data is given. The Stark splitting of the ground level is completely known only for two salts^{6,7} and the first and second levels for most of the remaining salts. The elucidation of the complete splitting requires observations at varying temperatures up to room temperature. At 4°K only the lowest level is occupied and at 77°K also the second one, but the higher ones have negligible probabilities at that temperature.

The compounds were prepared by conventional chemical methods with Nd_2O_3 as starting product. The crystals were obtained by evaporation from aqueous solutions.

⁶ R. A. Satten, *J. Chem. Phys.* 21, 637 (1953).⁷ R. A. Satten and D. J. Young, *J. Chem. Phys.* 23, 404 (1955).⁵ Y. K. Chow, *Z. Physik* 124, 52 (1947).

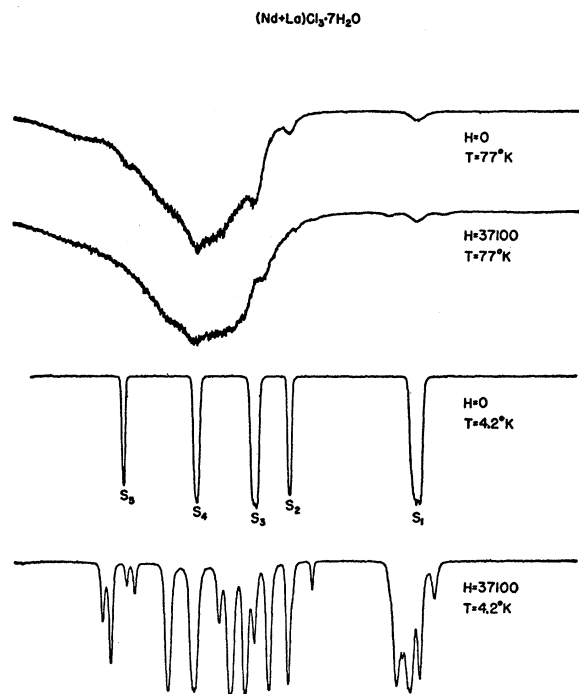


FIG. 3. The *S* group (near 9750 Å) of $(\text{Nd}+\text{La})\text{Cl}_3 \cdot 7\text{H}_2\text{O}$, showing the increased resolution at 4°K.

The crystals were examined under a polarizing microscope and the optical axes determined. These determine the index ellipsoid, the three axes of which are, the acute bisectrix, the obtuse bisectrix, and the axis perpendicular to the plane of the optical axes. The

index ellipsoid is related in the well-known manner to the structural symmetry of the crystal.

In all cases measurements were made with the acute bisectrix (chief axis) parallel and perpendicular to the magnetic field, and the direction of observation perpendicular to the plane of the optical axes and to the lines of force. This is sufficient to derive the behavior for all other orientations for uniaxial crystals, except that observations parallel to the magnetic lines of force would be required to determine whether the lines have right or left circular polarization. For biaxial crystals observations with other additional crystal orientations are also desirable. Measurements have been made for monoclinic neodymium chloride with all the axes parallel to the magnetic field. The feasibility of such measurements depends on whether crystals can be grown which can be cut so that the light can pass in the desired direction.

We have used the term "chief axis" in this paper for the optical axis of uniaxial crystals or the acute bisectrix of biaxial crystals.

The choice of the compounds was chiefly determined by the fact that reasonably good crystals could be obtained with relative ease. We considered it desirable to have crystals of as divergent symmetry properties as possible in order to be able to study the neodymium ion in widely varying surroundings. The crystal structure is not known for all crystals. The crystal system can be determined with relative ease from the shape of the crystals. Knowledge of the point group requires usually a careful x-ray analysis which is lacking in most cases. Eventually the evidence from the absorption spectra

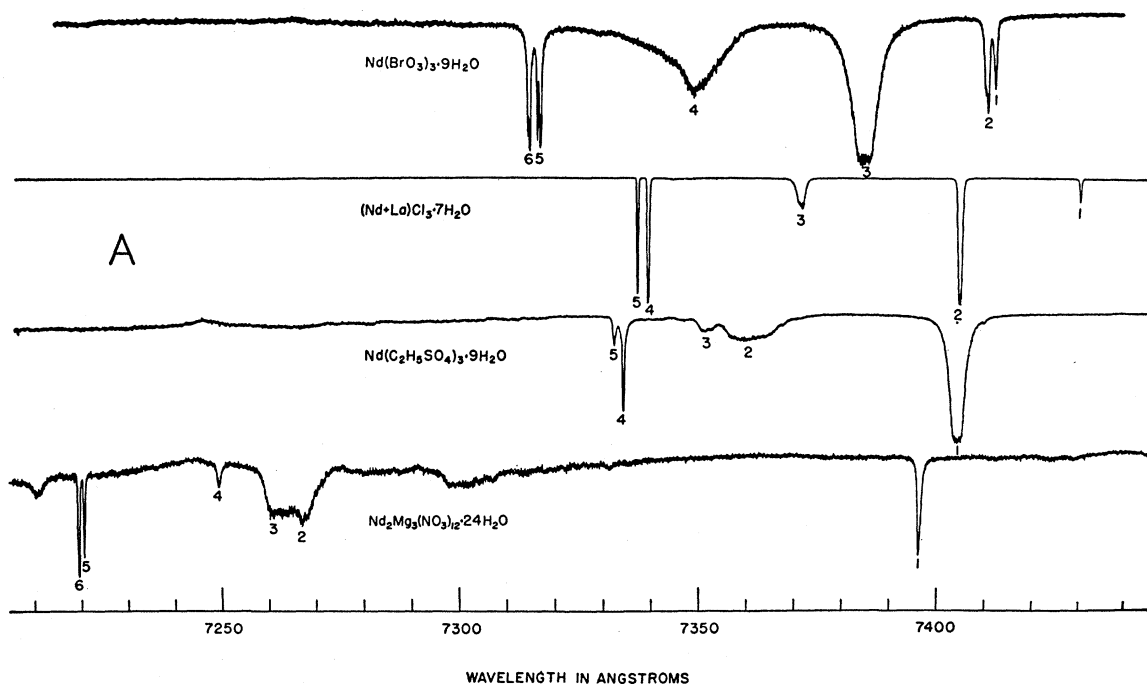


FIG. 4. The *A* group (near 7400 Å) for five neodymium salts.

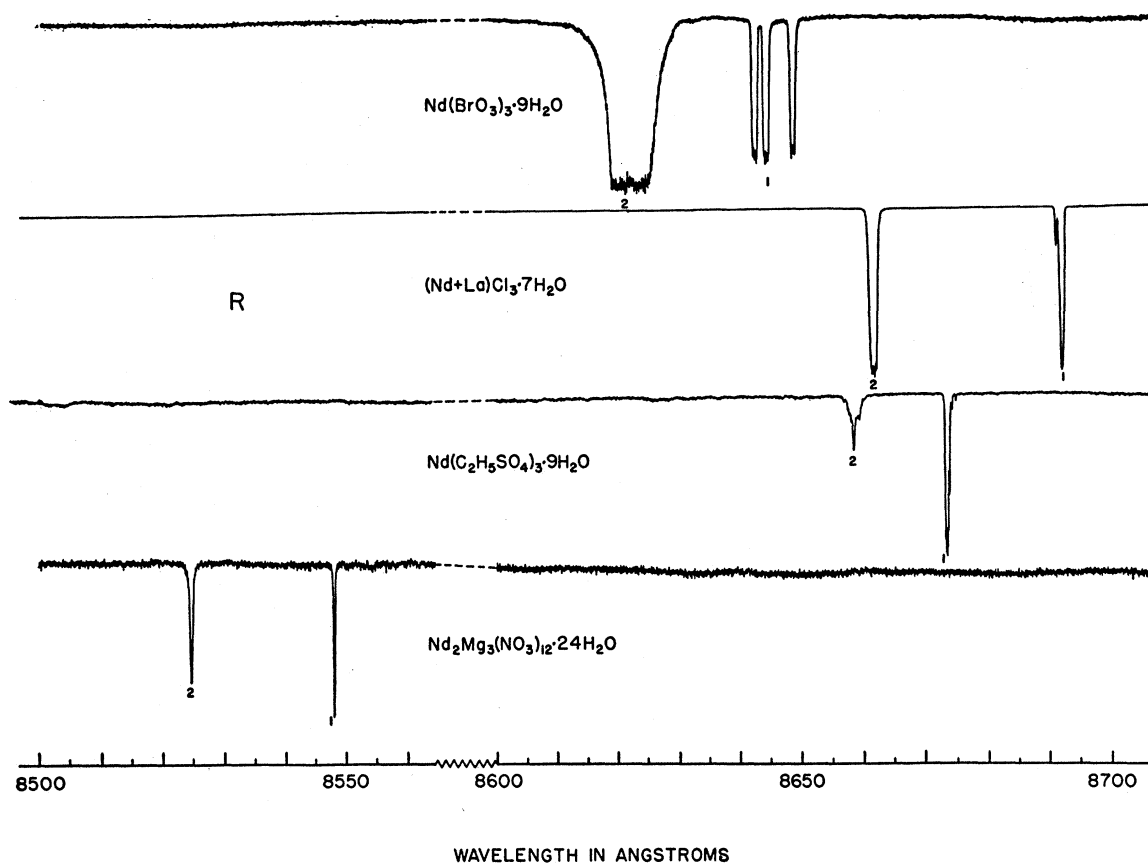


FIG. 5. The *R* group (near 8700 Å) of five neodymium salts. Note the satellite structure in some salts.

will determine the point group reliably in each case. It should be kept in mind however that the point group obtained from the absorption spectra and that obtained from x-ray data are not necessarily the same. The former gives the symmetry of the force field at the neodymium ion, the latter the symmetry of the geometrical arrangement of the atoms in the unit cell.

The chloride and sulfate were diluted with lanthanum because the lines of the pure salt were too strong and not sharp enough. It turned out, however, that the lanthanum salts are not isomorphic with the corresponding neodymium salts and that the structure of the mixed crystals for the Nd concentrations used (up to 50% Nd for the chloride, 10% for the sulfate) was that of the lanthanum salt. This offered an interesting possibility to study salts of practically the same chemical composition (they differ only by one molecule of water of crystallization) but with different arrangement of the ions and therefore different symmetry of the force field. A more detailed investigation of mixed crystals is under way.

3. GENERAL DESCRIPTION OF THE SPECTRA

In the absorption spectra of all neodymium salts (and of the ion in solution as well), some of which are shown in Figs. 3–6, certain groups of lines can be recognized

which vary very little in wavelength from salt to salt. These have been labeled empirically, partly following Ewald,⁸ by letters: *R*(8667), *S*(7955), *A*(7409), *B*(6740), *C*(6266), *D*(5796), *E*(5227), *F*(5109), *G*(4730), *H*(4454), *I*(4280), *K*(3806), and *L*(3542). The wavelengths given in parentheses are those of the longest wavelength components for the bromate. The corresponding values for the other salts vary only little. Below 5000 Å, the separation into groups is not always clear.

The accepted interpretation is that in general each group at 4°K corresponds to a transition from the ground state to another state, also of the $4f^3$ configuration, characterized in the free ion among other quantum numbers by the value J of the total angular momentum. The upper state is split into $J + \frac{1}{2}$ levels for all crystals of less than cubic symmetry and each level is doubly degenerate.⁹ It should therefore be possible to determine the J value of the upper state by merely counting the lines in the corresponding group. Attempts to do this (see for instance Chow⁵) have been unsuccessful. The number of components actually observed may be smaller than $J' + \frac{1}{2}$ if there are selection rules

⁸ H. Ewald, Ann. Physik 34, 209 (1939).

⁹ Exceptions are *S* levels which may have higher degeneracy.

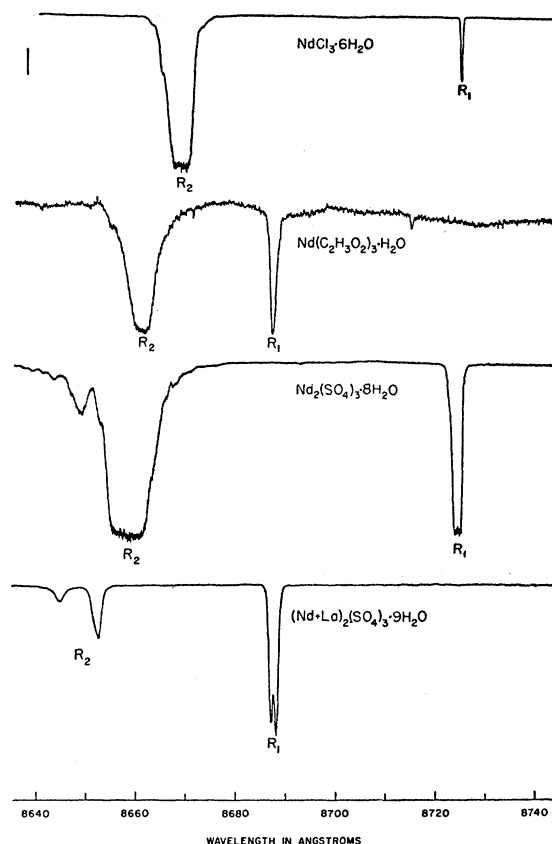


FIG. 6. The R group (near 8700 Å) of four neodymium salts.

forbidding some transitions. Furthermore, if two levels of the free ion fall closely together, they interact in the crystal field and both together will be responsible for one group. In observations at the temperature of liquid nitrogen or higher, there is the additional complication that transitions from other than the ground level may confuse the structure of a group.

The first task in the interpretation of the spectra is the identification of the levels between which transitions occur, that means, assignment of values for J , L , and S , as far as this is possible, and correlation with the theoretically expected levels for a f^3 configuration which are $^2(P, D, D, F, F, G, G, H, H, I, K, L)$ and $^4(S, D, F, G, I)$. According to Hund's rule 4I should be the ground state. All available evidence confirms $^4I_{9/2}$ as the ground state.

Satten⁶ has taken the approach of calculating the approximate positions of the levels by making reasonable assumptions about the interactions and thus has come to a tentative identification of the upper levels.¹⁰ The nature of the calculations makes only a

¹⁰ See also C. K. Jørgensen, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. 29 No. 11 (1955) and R. A. Satten, J. Chem. Phys. 23, 400 (1955). Satten and Jørgensen agree on the approximate position of the quartet levels but, because they assume different values for some perturbation parameters, come to different conclusions about the doublet levels.

rough approximation possible but even this is very helpful. The situation is of course complicated by the fact that for the heavy atoms L , S coupling is not a good approximation so that particularly for the excited levels where the density of interacting levels is high, Russell-Saunders symbols like $^4D_{3/2}$ may lose their meaning because neither the resultant spin S nor the orbital angular momentum L are even approximately constants of the motion. The total angular momentum J for the free ion remains, of course, well defined for any kind of interaction.

This complex state of affairs in the free ion complicates greatly the evaluation of the influence of the crystal field on the levels of the free ion. The crystal field causes further interactions and in general destroys J and M as good quantum numbers. At the present state of affairs all that can be done is to work tentatively with a reasonable Russell-Saunders approximation for the free ion, keeping in mind the possibilities for departures from this approximation and estimate the influence of the crystal field. This analysis eventually should give a quantitative evaluation of the crystal field in great detail. With rare earths we are in the fortunate position that the crystal field can be varied with the same rare earth ion, and also that the rare earth ion can be changed with a constant or almost constant crystal field (comparison of isomorphic crystals of different elements).

Because of the fairly complicated state of affairs, the analysis has to proceed in several steps as the empirical material becomes more complete. For all these problems the Zeeman effect will give very important data which cannot be obtained in any other way.

4. LINE WIDTH AND SATELLITE STRUCTURE

At 4°K the lines of all neodymium salts are considerably sharper than at 77°K, and this increased sharpness is needed for the resolution of the Zeeman components. This is clearly shown in Fig. 3 which gives traces of the S group of $(La+Nd)Cl_3$ with and without field. The figure shows that at liquid nitrogen temperature there would be no chance whatsoever of resolving the Zeeman pattern which, however, is clearly shown on the lowest trace at 4°K.

Even at the lowest temperatures not all lines are equally sharp. Some salts have all their lines less sharp than those of other salts. This may be explained by the fact that the crystal structure is less perfect in such salts. Another reason for less sharp lines is the following. The fact that we do have sharp lines in the rare earth salts depends on the fact that there is negligible interaction between neighboring ions. This is equivalent to saying that the wave functions of the $4f$ orbits of neighboring neodymium ions do not overlap. Whether this is true or not obviously depends on the spacing of these ions and we may expect less sharp lines for

simple salts where the distance between neighboring Nd-ions is relatively small than for the more complex salts. It is true for instance that the lines in $\text{Nd}_2\text{Zn}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ are considerably sharper than for the simple nitrate $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. In the former there are 1.5 Zn atoms, six NO_3 complexes, and 12 H_2O molecules for each Nd ion, whereas there are only three NO_3 complexes and six H_2O molecules for the simple nitrate. Dilution with another ion sometimes sharpens the lines because it increases the average distance between Nd ions. This is the case for the dilution by La in the chloride. In other cases dilution broadens the lines. This happens for dilution by La in the sulfate or dilution by Pr in the chloride. In this case, the Nd ions probably do not fit perfectly into the lattice of the other substance, and this produces a distorted lattice with less sharp lines. Both causes for line broadening probably play a role in some of our salts. The whole matter deserves further experimental investigation.

There is, however, also a great difference in sharpness between the different lines of the same crystal.¹¹ Figure 4 which gives the A group for five salts shows this clearly. The line A_4 in the bromate or A_2 and A_3 in the ethylsulfate are clearly broader than the other lines of the same salt.

At the present time, definite evidence is lacking on which an explanation for the difference in sharpness could be based.

Some lines show a close fine structure which has also been observed for other rare earth salts and has been studied particularly for europium¹² and praseodymium compounds.¹³ It is particularly evident in the bromate (see Fig. 5), where many lines are split into three sharp components with nearly equal intensities. The splitting varies from line to line. The maximum distance between the outer components is 8 cm^{-1} for the resonance line R_1 . It is less than half of this for all other observed lines.

There are several possible reasons for this kind of fine structure, which will be called satellite structure in order to distinguish it from true fine structure.¹⁴ Imperfections in the crystal structure can give rise to shifts, but one would then expect a general broadening rather than a splitting into sharp components. Another possibility would be that there are several crystal domains with slightly different structures in a macroscopic crystal. The fact that the satellite structure

seems to be the same for different individual crystals speaks against this possibility. If different neodymium ions have slightly different surroundings, that means if the crystal symmetry is lower than one would expect from the x-ray analysis, multiple lines can arise. This explanation would be in accord with the observed fact,¹³ that this type of satellite structure changes if the rare earth ion is diluted by another ion, for instance by La^{+++} . It is also in agreement with the observation on europium bromate.¹² We have observed that there is no magnetic interaction between the satellite structure components. The Zeeman effect components show all the same satellite structure as the field free line.¹⁵ (Fig. 8.)

Another possibility for satellite structure would be interaction between neighboring neodymium ions. Sharp components can, however, only result when the interaction is restricted to the immediate neighbors. The whole problem of the satellite structure of the rare earth absorption lines can be settled only after further experimental work.

5. THE ZEEMAN EFFECT

When the crystal is placed in a magnetic field, in general each line of a neodymium salt is split into four components. This is equivalent to saying that both the upper and lower level are split into two components, a result which must be expected for all noncubic crystals. No exceptions have been encountered from this rule for any Nd^{+++} line, which means that we have not found any transition to the expected 4S level or that the 4S level has been modified by interactions so as to split into two levels even in the absence of a magnetic field.

From the splitting of the lines, the splitting of the levels can be deduced unambiguously when one takes into account that the splitting of the ground level must be common to all lines. The splitting of each level can then be expressed in terms of the normal splitting ($eH/4\pi mc$). We designate these splittings by s_1 and s_2 if the chief axis of the crystal is parallel or perpendicular to the magnetic field, respectively.¹⁶

There are cases where $s=0$ for the upper level and thus the line consists only of two components.

While all lines have in common that they split into four components, they differ in the magnitude of the splitting and the polarization as well as in how the pattern changes if the crystal is rotated in the magnetic field. This means that not only do the different lines of the same salt show different Zeeman effects but also analogous lines in different salts are quite different in this respect. This emphasizes that the magnetic behavior of the Nd-ion is greatly modified by the crystal

¹¹ In this paper we are only concerned with pure electronic transitions. In neodymium and other rare earth salts, there occur also lines which are due to the superposition of electronic transitions with molecular and crystal vibrations. Such lines are in general much more diffuse. They are considerably weaker than the pure electronic lines in these salts.

¹² K. H. Hellwege and H. G. Kahle, *Z. Physik* **129**, 85 (1951).

¹³ A. M. Hellwege and K. H. Hellwege, *Z. Physik* **135**, 615 (1953).

¹⁴ In the literature this structure is generally called "hyperfine structure," which term should be rejected, because it suggests that nuclear effects play a role. We call such structure satellite structure no matter if there is one main line accompanied by weaker components or whether all components have comparable intensities.

¹⁵ See in this connection also H. E. D. Scovil and K. W. H. Stevens, *Proc. Phys. Soc. (London)* **A65**, 954 (1952).

¹⁶ In most papers on magnetic resonance, these splittings are called g values. This is confusing, as the splitting in general is not equal to the Landé g factor. For such cases, where the magnetic quantum number M has a meaning, we have $s=2Mg$.

TABLE II. Magnetic splitting of the ground level and Stark splitting a of the first excited state, ${}^4F_{3/2}$. The symbols have the following meaning: s_1 (s_2), magnetic splitting in Bohr units for chief axis parallel (perpendicular) to field; n_1 and n_2 , number of different lines from which the values were obtained; a , natural splitting of the first excited state ${}^4F_{3/2}$. If there is a plus sign, the $M=3/2$ lies above the $H=1/2$ level. For a minus sign, the opposite situation prevails. When no sign is given, the assignment of M values is unknown (or has no meaning).

	s_1	n_1	s_2	n_2	a
$\text{Nd}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	0.420	6	2.629	17	-31.17
second level	3.38	2	0	2	
$\text{Nd}_2\text{Zn}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	0.450	5	2.659	9	-31.54
$\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$	2.32	2	2.34	2	37.45
$\text{Nd}(\text{C}_2\text{H}_3\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	3.50	7	2.061	8	+19.21
$(\text{La}+\text{Nd})\text{Cl}_3 \cdot 7\text{H}_2\text{O}$	2.446	13	2.885	12	39.16
$\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$	0.58	8	1.28	9	73.68
$(\text{Pr}+\text{Nd})\text{Cl}_3$	1.791	^a	3.975	^a	29.63
$\text{Hd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	1.74	4	2.07	2	84.71
$(\text{La}+\text{Nd})_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	0.69	2	1.34	2	54.89
$\text{Nd}(\text{C}_2\text{H}_3\text{O}_2) \cdot \text{H}_2\text{O}$	2.76	5	2.29	5	33.86

^a These values were obtained by means of magnetic resonance measurements by J. H. Anderson and C. A. Hutchison [Phys. Rev. 97, 76 (1955)]. Through the cooperation of Professor Hutchison we were able to examine the absorption spectrum of one of their crystals, and there is faint but distinct absorption due to neodymium impurities. The value of the ${}^4F_{3/2}$ splittings was obtained from our plate. The magnetic splittings are those reported by Anderson and Hutchison as those of the praseodymium ion. The evidence now strongly indicates that this was probably due to the neodymium impurity. The praseodymium lines were relatively broad and this would explain the absence of distinct radio-frequency resonance peaks.

field, and in turn indicates that from the Zeeman effect data valuable quantitative information concerning the forces within the crystal can be obtained.

In Table II, the magnetic splitting of the ground state of all nine investigated salts are given. The ground-state data can be obtained with great reliability as they are present in each line and, even if most lines of a particular salt are relatively diffuse, enough sharp lines can usually be found to obtain the ground state splitting with satisfactory accuracy. In general, the agreement between the individual values derived from each line is within a few times 0.01 cm^{-1} unless the line is diffuse or poor otherwise. Such lines have been excluded from the average. Probably the greatest single source of errors in the present measurements is the uncertainty in the orientation of the crystal axis.

The splitting of the upper states are listed in Table III. In general, each splitting here is derived only from one line which furnishes two values. Only those lines are listed which are sharp enough to give full resolution of the pattern. It is likely that future investigations with more carefully chosen crystals may give splittings of additional lines.

The lines in each group are numbered according to decreasing wavelengths, for instance, A_1 , A_2 , A_3 , etc. The lines with the same symbol in different salts do not, however, necessarily correspond to the same transition.

It would be very important to obtain the magnetic splittings of all five Stark components of the ground electronic state, but at 4°K of course only the lowest of these is occupied. At the higher temperatures where the other components appear, the lines are usually too

broad to show a clear Zeeman pattern. There are a few favorable cases where at liquid nitrogen temperatures there are some lines sharp enough so that one can obtain the splitting of the second Stark component. In Table II and Fig. 7 this is given for $\text{Nd}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$. Experiments are under way to make measurements at temperatures between 4°K and 77°K which would be most favorable for this level.

For an isolated line, the Zeeman pattern is always symmetrical in position (but not intensity) with respect to the field-free line. (See Fig. 8.) If, on the other hand, the magnetic splitting of the upper state is of the same order as the distance between neighboring levels, we have a phenomenon analogous to the Paschen-Back¹⁷ effect. There are numerous examples of such effects in the spectra here described. In no case, however, is the magnetic splitting large compared to the total Stark splitting of a state. If this were the case, the Zeeman effect would be essentially that of the free ion. The

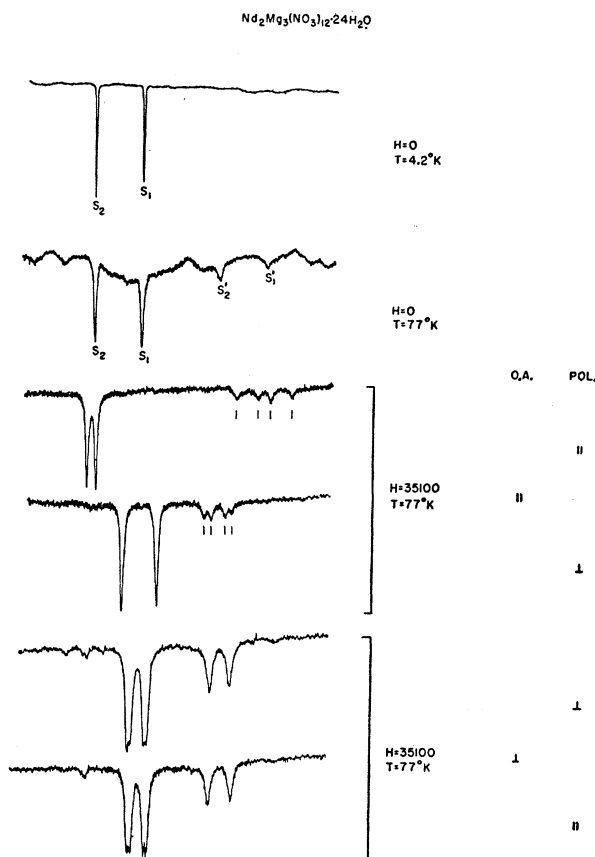


FIG. 7. Transitions from the lowest (S_1 , S_2) and second Stark level (S_1' , S_2') of the ground state to the same upper states, for magnesium neodymium nitrate.

¹⁷ The Paschen-Back effect as observed in the spectra of free atoms occurs when the magnetic splitting is of the same order as or larger than the distance between the components of a multiplet (same L and S , different J). In the crystal spectra, we are dealing in general with two or more neighboring Stark components (same J , different " M ").

TABLE III. Magnetic splitting of the excited states.

	Nd ₂ Mg ₃ (NO ₃) ₁₂		Nd ₂ Zn(NO ₃) ₁₂		Nd(BrO ₃) ₃		Nd(C ₂ H ₅ SO ₄) ₃		(Nd+La)Cl ₃	
	<i>S</i> ₁	<i>S</i> ₂	<i>S</i> ₁	<i>S</i> ₂	<i>S</i> ₁	<i>S</i> ₂	<i>S</i> ₁	<i>S</i> ₂	<i>S</i> ₁	<i>S</i> ₂
<i>R</i> ₁	0.99	0	0.98	0			0.525	0.815	0.63	0.51
<i>R</i> ₂	0.27	0.71		0.81				0	0.80	1.18
<i>S</i> ₁	5.38	0.27	5.40	0.27	1.18	3.61			1.44	1.53
<i>S</i> ₁ '	(5.44)									
<i>S</i> ₂	1.15	3.44	1.21	3.45					2.46	2.03
<i>S</i> ₂ '	(1.09)	(3.15)								
<i>S</i> ₃	3.55	0.67							1.05	0.95
<i>S</i> ₄	2.77	0							0.32	3.94
<i>S</i> ₅									0.84	0
<i>A</i> ₁	^a	0.95		1.00						
<i>A</i> ₂	^b	^b	^b	^b			^b		4.34	
<i>A</i> ₃	^b	^b	^b	^b	^b	^b	^b			
<i>A</i> ₄	2.59	0			^b	^b		2.76	2.39	2.64
<i>A</i> ₅	3.21	1.28	3.20	1.35			4.64 ^c	0.95	2.40	5.19
<i>A</i> ₆	0.60	2.59		2.61						
<i>C</i> ₃	3.98	3.51	3.92	3.56						
<i>D</i> ₁	0.42	0		0			1.32 ^c	0.21	0	0.86
<i>D</i> ₂	1.41	0			1.32	0			0.88	0.48
<i>D</i> ₃	0.91	0								
<i>D</i> ₄	2.12	1.68								
<i>E</i> ₁	1.82	0.80		0.86					1.83	1.75
<i>E</i> ₂	2.19	0		0					1.67	1.51
<i>E</i> ₃		0.88								
<i>E</i> ₄		0.61								
<i>I</i> ₁							0.74	0.71		
<i>I</i> ₂							1.19	3.28		
<i>K</i> ₁							1.07	2.04		
	NdCl ₃ ·6H ₂ O		Nd(C ₂ H ₃ O ₂) ₃ ·H ₂ O		Nd ₂ (SO ₄) ₃ ·8H ₂ O		(Nd+La) ₂ (SO ₄) ₃ ·9H ₂ O			
	<i>S</i> ₁	<i>S</i> ₂	<i>S</i> ₁	<i>S</i> ₂	<i>S</i> ₁	<i>S</i> ₂	<i>S</i> ₁	<i>S</i> ₂		
<i>R</i> ₁	0.28	0.51	0.35	1.12						
<i>S</i> ₁	0.81	2.66								
<i>B</i> ₁	0.95	3.73								
<i>B</i> ₂	0.77	2.48								
<i>B</i> ₃		3.26								
<i>C</i> ₁					4.47	3.37				
<i>C</i> ₂					2.59	3.06				
<i>D</i> ₁	1.41	3.28								
<i>D</i> ₂	1.15	2.40								
<i>D</i> ₃	1.37	2.74								
<i>E</i> ₁	0.90	2.09			2.39					
<i>E</i> ₂					4.78					
<i>E</i> ₃							2.35		3.01	
<i>F</i> ₁			2.84	8.27					2.32	
<i>G</i> ₁			0.47	6.52						
<i>G</i> ₂			2.68	4.38						
<i>G</i> ₃			2.72	3.73						

^a Pattern unresolved.^b Line was too diffuse for resolution of the components.^c These values should be increased by 9% because the crystal axis was not parallel to the field.

situation is almost always that of a pair of closely spaced Stark levels with the other levels sufficiently far away as not to interfere.

In that case, one must expect, that for small fields the magnetic splitting of each level is independent of that of the other. For larger fields, the result will be in first

approximation as if the unsplit lines were repelling each other and the magnetic splitting were superimposed on the new positions of the lines. Furthermore, the amount of the splitting will be changed. For very large fields there will be four equidistant components. The transformation of the pattern is caused by an interaction of

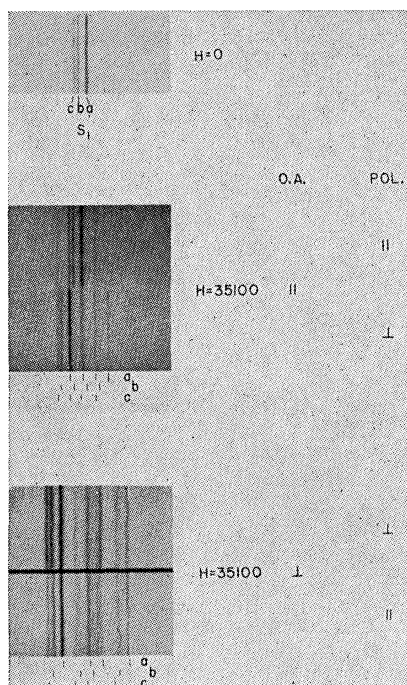


FIG. 8. Zeeman effect of a line of neodymium bromate with satellite structure. There is no interaction between the various satellite components.

the two levels caused by the magnetic field, and the completeness of the transformation depends on how the influence of the magnetic field compares with that of the crystal electric field which caused the original splitting of the level pair. Obviously the magnetic interaction depends on the direction of the magnetic field with respect to the crystal axis, so that it should be different for the parallel and perpendicular effects. (See Fig. 9.)

The observed Paschen-Back effects follow this pattern. Figure 10 gives an example. The outer parts of the diagram give the position of the levels for $H=0$, the inner parts for a field of 35 000 gauss with the magnetic field parallel (left) or perpendicular (right) to the crystal axis. The dotted lines are the centers of the magnetic pairs. The upper one is approximately as much raised as the lower one is depressed. For the parallel case, the four levels are approximately equidistant. Whether this represents the approximation for the large-field case, only an investigation with varying fields can disclose. This would also be necessary for settling other details.

6. INTERPRETATION

The Stark splitting and the shift of the levels are caused by the internal crystal field. If this field is known, the energy levels can in principle be calculated.

In the magnetic field, a level of the free ion with the total angular momentum J is split into $2J+1$ equidistant levels shifted with respect to the field free level

by

$$\Delta E = gM\beta H, \quad (1)$$

where H is the magnitude of the magnetic field, β the Bohr magneton, M the magnetic quantum number, and g the magnetic splitting factor.

If an electric field with axial symmetry is introduced, the levels of the free ion are shifted and split, but except for $M=0$ double degeneracy remains, as the levels with $+M$ and $-M$ have the same energy. The Zeeman effect is still given by (1) if the magnetic splitting is small compared to the electric splitting and H is parallel to the electric symmetry axis. The splitting is thus $s_1^0 = 2gM$ in Bohr units. The values of g may have been changed by the crystal field interactions from those of the free ion. If the magnetic field is perpendicular to the crystal axis there is no Zeeman splitting except for $M=\frac{1}{2}$ when the splitting is

$$s_2^0 = g(J + \frac{1}{2}).$$

In an actual crystal, the electric field is never axially symmetric but has a lower symmetry which is represented by one of the 32 point groups. The wave functions of the electron in the actual field can always be represented as a linear combination of the wave functions of the axially symmetric case. The symmetry of the field limits the terms that can occur in the linear combination, or in other words makes it impossible for some states to interact. The general theory of this kind of interaction and how it depends on the symmetry has been given by Bethe,¹ Hellwege,¹⁸ and others. If there

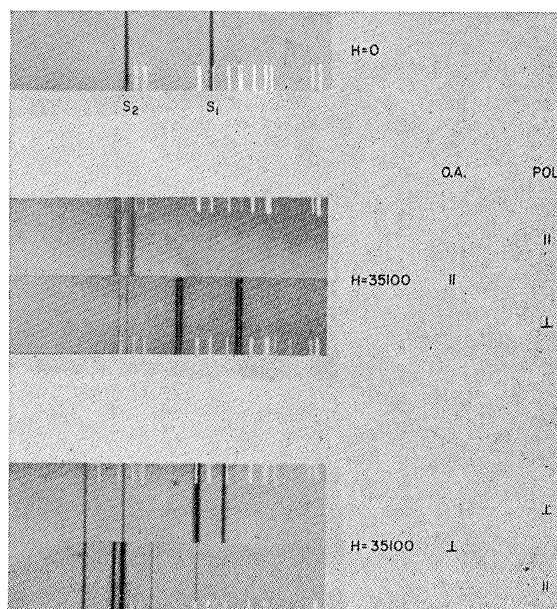


FIG. 9. Splitting of the lines S_1 and S_2 of magnesium neodymium nitrate. For the case in which the optical axis is parallel to H , the small separation is that of the ground state. The direction of polarization is referred to the crystal axis.

¹⁸ K. H. Hellwege, Ann. Physik 4, 35, 127, 136, 143, 150 (1948), etc.

is a p -fold axis, a level with a given M can only interact with those levels with $M \pm np$ where n is an integer.

If the crystal field is not large, interactions with components of the same state (same J) will be mainly responsible for the shifts. If the symmetry (p) is high and J small, it is possible that there cannot be any interactions within this state. For instance for $J = \frac{3}{2}$, we have M values $\pm \frac{1}{2}$, $\pm \frac{3}{2}$. For threefold or higher symmetry there are no two interacting levels, as there are no level pairs with the condition $M' = M \pm np$ except $\pm \frac{3}{2}$ for $p = 3$. Interaction of this pair is impossible because of the symmetry that leads to Kramers degeneracy.

In this case, there will be no difference in the Zeeman effect between the case of an axially symmetric field and the actual crystal field. When J is larger or the symmetry is lower, this is no longer the case. It is possible that even then one term in the series development will predominate so that the situation can be regarded as a small perturbation of the axially symmetric case, but this is not necessarily so. In a case like the point Group D_2 , where there are three twofold axes perpendicular to each other, it is clear that singling out one of them as the approximate axis of symmetry cannot have any physical significance.

It is not the purpose of this paper to go into the details of the quantitative interpretation of the Zeeman effects. A few of the main points will suffice.

Normal State

The normal state $^4I_{9/2}$ splits into 5 Stark components. The Zeeman effect of the lowest component has been observed for all salts, that of the second component only for $\text{Nd}_2\text{Mg}_3(\text{NO}_3)_{12}$. For trigonal or higher symmetry, the data are sufficient to obtain the angle dependence of the wave function.

For trigonal symmetry, we have three symmetry

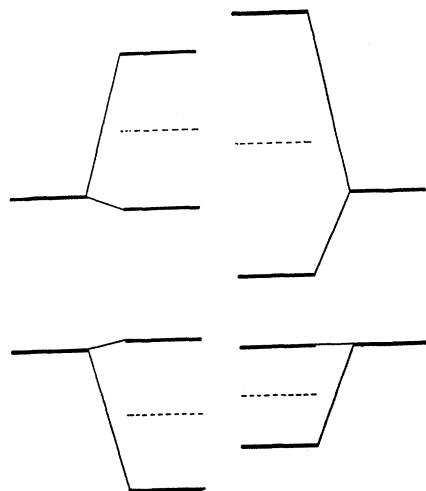


FIG. 10. Paschen-Back effect for the A_4 , A_5 pair of absorption lines in $(\text{La}+\text{Nd})\text{Cl}_3 \cdot 7\text{H}_2\text{O}$.

TABLE IV. Mixing coefficients for the lowest state of the uniaxial crystals.

	a_1^2 $M = -5/2$	a_2^2 $1/2$	a_3^2 $7/2$
$\text{Nd}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	0.839	0.117	0.033
$\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.634	0.000	0.365
$\text{Nd}(\text{C}_2\text{H}_3\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	0.350	0.029	0.621

types characterized by the symmetry quantum numbers¹⁸ μ , with $\mu = \pm \frac{1}{2}$ and $\frac{3}{2}$. The $\mu = \pm \frac{1}{2}$ levels form a degenerate pair. Those with $+\frac{3}{2}$ and $-\frac{3}{2}$, although belonging to the same symmetry type, cannot interact because of Kramers degeneracy.

For the $\mu = \frac{1}{2}$ levels we have the wave function

$$\psi = a_1\psi_{-\frac{1}{2}} + a_2\psi_{\frac{1}{2}} + a_3\psi_{7/2}.$$

The Zeeman splitting, if the trigonal axis is parallel to the field, is

$$s_1 = (-5a_1^2 + a_2^2 + 7a_3^2)g.$$

If the axis is perpendicular to the field, the splitting is

$$s_2 = (5a_2^2 + 8a_1a_3)g.$$

With the normalization condition

$$a_1^2 + a_2^2 + a_3^2 = 1,$$

and the observed splittings s_1 and s_2 , it is possible to find the mixing constants a_1 , a_2 , a_3 or at least their absolute values, if one can assume the Russell-Saunders values for the g factors. As we know that this can be only an approximation, we cannot trust the results to have a very high numerical accuracy.

Only the double nitrates, the bromate, and the ethylsulfate are uniaxial crystals, and the evidence shows that they have a trigonal axis parallel to the optic axis.

The values in Table IV for the mixing coefficients are consistent with the observed data, although there is some uncertainty in the phase. For the monoclinic and triclinic salts, the present data do not permit a calculation of the mixing coefficients.

For neodymium magnesium nitrate, where the Zeeman effect also of the second Stark component of the ground level has been observed, we have $s_1 = 3.37$ and $s_2 = 0$, which means that $\mu = \frac{3}{2}$ for this level. This assignment is also consistent with the polarization of the lines originating from this component. It is opposite to that of the lines from the lowest Stark component (Fig 7), which indicates that the second component must have different symmetry. It must therefore be a linear combination of $M = \frac{3}{2}$ and $M = 9/2$, and the mixing coefficients,

$$b_1^2 = 0.728, \quad b_2^2 = 0.272,$$

are consistent with the observed splitting.

The normal states of rare earth salts have been

TABLE V. Predicted and observed Zeeman splittings for the ${}^4F_{3/2}$ lines. The observed splittings are given in parentheses below the observed values.

	S_1	S_2
$M' = \frac{1}{2}$	$g, -0.34$ (0.27)	$2g, -0.68$ (0.71)
$M' = \frac{3}{2}$	$3g, -1.02$ (0.99)	0 (0)

repeatedly discussed in connection with paramagnetic resonance measurements.¹⁹

Excited States

The interpretation of the excited states is much less certain than that of the ground states. Of the various attempts at identification of the excited states, only those of Satten⁶ and Jørgensen¹⁰ need be considered here. Even these cannot be relied on for details, as the calculations on which they are based cannot be very accurate and therefore no entirely satisfactory picture can be obtained.

The study of the Zeeman effect gives considerable clarification, but additional study is required before a completely consistent classification is possible. The reason for this is that evidently some of the group of lines (for instance S and A) contain more than one excited state. Close-lying states may interact even without the presence of the crystal field. This has as a consequence that the resulting states cannot even approximately be described by L, S coupling notation. The crystal field provides additional possibilities for interaction. This makes it virtually impossible to make any predictions of what the Zeeman effect should be. There are however a few cases where the situation is less complex. The following remarks indicate what information can be considered reasonably reliable at the present time.

R Group

As upper state 4F_3 was suggested by Satten. This should yield two Stark components with $\mu = \frac{3}{2}$ and $\mu = \pm \frac{1}{2}$. In all cases, two lines have been observed which for many salts show satellite structure. In the sulfate this suggests that there are four instead of two lines. Unfortunately, for many salts one of the lines is so diffuse that the splitting cannot be observed. The situation is particularly favorable for $\text{Nd}_2\text{Mg}_3(\text{NO}_3)_{12}$ where both lines have resolvable splittings. For trigonal and higher symmetry, there cannot be any mixing through the crystal field for $J = \frac{3}{2}$, so that the same conditions as for axial symmetry should prevail. We have then the predicted pattern shown in Table V; the observed values for the splitting are given in parentheses

in the line below. This is consistent with $g = 0.34$, while the Russell-Saunders value for 4F_3 is 0.40. The agreement between calculated and observed values is quite satisfactory, particularly if one considers the fact that the measurements had to be made partly under very unfavorable conditions. That the g value is smaller than the Russell-Saunders value, and not larger, as one should expect from the fact that the chief interactions should be with levels of larger g , should not give too much concern as long as we have no clear picture of all possible interactions. Moreover, any misalignment of the crystal axis would produce smaller splittings.

We can therefore say that the Zeeman effects confirm 4F_3 as the upper state of the R group. For magnesium neodymium nitrate the lower Stark component of 4F_3 has $M = \frac{3}{2}$. For the ethyl sulfate, it is the upper component. For that state, $s_2 = 0$, so that the corresponding line splits only into two components, which fact can easily be recognized.

The splitting pattern for 4F_3 should be the same as expressed in Table V for the other uniaxial salts. For the bromate, the width of the lines and the presence of satellite structure make the data unreliable. For the ethyl sulfate, the situation is more favorable. The results contained in Table III for this salt are, however, not in accord with what should be expected. It is possible that the presence of satellite structure has confused the interpretation of the Zeeman pattern. Additional observations at different field strengths are needed to clear this point up.

If 4F_3 is the upper state of the R group, we must expect the transitions to 4F_3 , ${}^4F_{7/2}$, and ${}^4F_{9/2}$ with 3, 4, and 5 components approximately at the position of the S , A , and B groups. The S and A groups have at least 5 components, however (see Figs. 3 and 4). This means that either the assignment is incorrect or that other levels interfere. We are inclined to favor the latter view. Satten predicts the ${}^2H_{11/2}$ level near 4F_3 and 4S near ${}^4F_{7/2}$. These levels would interact with each other and thus lose some of their original properties. In particular, the 4S level would split even without the magnetic field into a pair of twofold degenerate levels.

The chances for interaction between different levels increase as we go to higher levels where the spacing of the levels is closer. As long as there is any remnant of the L, S coupling left, we must assume that the transitions to the quartet levels are stronger than those to the doublet levels. The identification of the C , D , E , and G groups with transitions to the 4G multiplet suggested in part by Satten seems therefore reasonable, but if this is correct there must be interferences from other levels. At present it seems premature to go into further details.

There is one further case where the Zeeman effect can give a clearcut confirmation of a proposed classification. There is a sharp isolated line (I_1) near 4280 Å. Its Zeeman effect is clear in the ethyl sulfate. The

¹⁹ See for instance J. H. Van Vleck, Ann. N. Y. Acad. Sci. 55, 928 (1952); B. Bleaney and K. W. H. Stevens, Repts. Progr. in Phys. 16, 108 (1953); K. D. Bowers and J. Owen, Repts. Progr. in Phys. 18, 304 (1955).

TABLE VI. Comparison with paramagnetic resonance data.

	Optical absorption		Paramagnetic resonance	
	s_1	s_2	s_1	s_2
$\text{Nd}_2 \cdot \text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}^a$	0.420	2.629	0.45 ± 0.05	2.72 ± 0.02
$\text{Nd}(\text{C}_2\text{H}_3\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}^b$	3.50	2.06	3.535 ± 0.001	2.072 ± 0.001

^a A. H. Cooke and H. J. Duffus, Proc. Roy. Soc. (London) **A229**, 407 (1955).

^b Bleaney, Scovil, and Trenam, Proc. Roy. Soc. (London) **A223**, 15 (1954).

splitting of the upper state is $s_1=0.74$, $s_2=0.71$, which means that within the limits of experimental errors the splitting is the same with the axis parallel or perpendicular to the field. As the line is an isolated line even in the field of lowest symmetry, there can be only one Stark component. Both facts indicate that $J=\frac{1}{2}$. The magnitude of the splitting is consistent with ${}^2P_{\frac{1}{2}}$, which would give $s_1=s_2=0.67$.

7. RELATION TO MAGNETIC PROPERTIES

The phenomena described in this paper are closely related to paramagnetic resonance phenomena, which deal directly with the transitions between the Zeeman components of the ground state of a paramagnetic ion. The splitting of the ground state is obtained in both types of experiments, and in general there is good agreement (see Table VI). The accuracy that can be obtained seems to be approximately the same for both methods, although the magnetic resonance measurements should be capable of higher intrinsic accuracy. These also can obtain the nuclear hyperfine structure of the levels which cannot be resolved in the optical absorption measurements. On the other hand, the latter can obtain also the magnetic splitting of the excited states and thus furnish considerably more extended data which can be applied to the exploration of the crystal field. It also appears that the interpretation of the optical data is often simpler as a large frequency interval is covered with many positively identifiable lines, whereas the magnetic resonance measurements deal only with a very small frequency interval on a greatly enlarged scale.

While the agreement in Table VI is in general very satisfactory, there are some discrepancies which exceed the limits of experimental errors. Possibly one explanation is that in general we are dealing with the pure salts while the magnetic resonance measurements were made with the neodymium ions highly diluted by lanthanum. The difference in the crystal field produced

by the dilution may be sufficient to account for the differences. Moreover, in some of our measurements the orientation of the crystal axis in the magnetic field could not be carried out with very high accuracy.

The relation between the magnetic splittings of the Stark components and the macroscopic magnetic properties, such as susceptibility and paramagnetic rotation, has often been discussed and need not be dealt with in detail here. All neodymium salts are highly anisotropic. If the magnetic measurements are made on powder with the individual crystals oriented at random, it is necessary to average over all orientations. If the splittings in the direction of the three principal axes are s_1 , s_2 , and s_3 , the average of the squares is given by

$$\langle s^2 \rangle_{\text{av}} = \frac{1}{3}s_1^2 + \frac{1}{3}s_2^2 + \frac{1}{3}s_3^2,$$

which for uniaxial crystals, with s_1 the splitting for the field parallel to the axis and s_2 perpendicular to it, becomes

$$\langle s^2 \rangle_{\text{av}} = \frac{1}{3}s_1^2 + \frac{2}{3}s_2^2.$$

The splitting with the field in an arbitrary direction θ, φ is determined by

$$[s(\theta, \varphi)]^2 = s_1^2 \cos^2 \theta + s_2^2 \sin^2 \theta \sin^2 \varphi + s_3^2 \sin^2 \theta \cos^2 \varphi.$$

To find the susceptibility, this s is entered into the well-known formula for the temperature-dependent part of the paramagnetic susceptibility:

$$\chi = \frac{1}{4} N s^2 \beta^2 / kT,$$

where the susceptibility in any direction is obtained by substituting $s(\theta, \varphi)$ and the average susceptibility for a powder by taking the appropriate average of s^2 . The formula is valid when the paramagnetism of an ion is due entirely to one doubly degenerate state at field strengths and temperatures away from saturation.

We are indebted to Professor F. Spedding for some very pure neodymium and to Dr. H. Meissner for the design of the Dewar vessel.

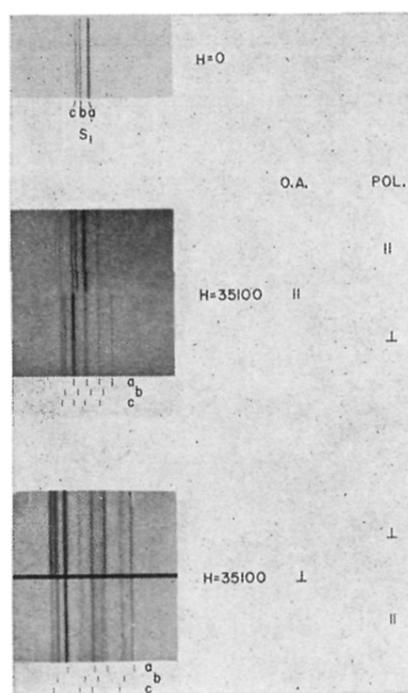


FIG. 8. Zeeman effect of a line of neodymium bromate with satellite structure. There is no interaction between the various satellite components.

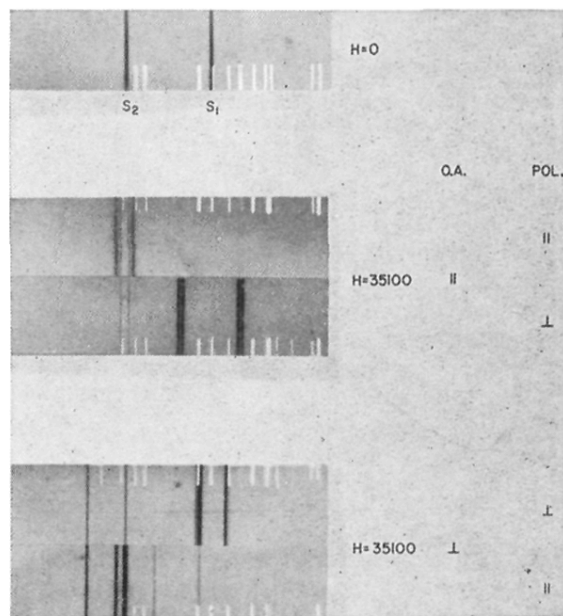


FIG. 9. Splitting of the lines S_1 and S_2 of magnesium neodymium nitrate. For the case in which the optical axis is parallel to H , the small separation is that of the ground state. The direction of polarization is referred to the crystal axis.