molecule has an angular or pyramidal structure. The deviation from co-linearity or co-planarity probably increases with increasing Δ. A few examples of the kind of structures we may expect according to this rule may be given.

Co-linear: CO_2, ON_2, CS_2, $(NN_2)^-$, $(HF_2)^-$
Angular (polar): OH_2, SO_2, OO_2? (ozone), SH_2, NO_2, $(NO_2)^-$
Co-planar: $(BO_3)^{-3}$, $(CO_3)^{-2}$, $(NO_3)^-$, SO_3, BH_3, BF_3
Pyramidal (polar): $(PO_3)^{-3}$, $(SO_3)^{-2}$, $(ClO_3)^-$, $(AsO_3)^{-3}$, $(SeO_3)^{-2}$, $(BrO_3)^-$, $(OH_3)^+$, NH_3, PH_3, AsH_3, PF_3, PCl_3 and so on.

In no case is there observed a contradiction to the rule, so it may be used with some confidence for predictions. For a more complete information about my work on the groups I can refer to my paper which is to be published shortly.

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Interpretation of the Spectra of Rare Earth Crystals

From the work of J. Becquerel, Brunetti, Ephraim, Freed and Spedding, and others, it is known that the absorption spectra of rare earth crystals consist of narrow bands which become resolved into sharp lines as the temperature of the crystals is lowered. The lines tend to gather into multiplets, and arise from energy levels which resemble in their behavior the energy levels of atoms subjected to electric and magnetic fields much more than they resemble the levels of molecules. For example, the positions of the lines are but very little influenced by the negative ions present, and such influence amounts only to the expected slight shifting caused by the different electric fields set up by the various ions in the lattice. Furthermore, the lines do not fade out as the temperature is lowered, but are still strong at the temperature of liquid helium. Again, the lines are polarized, as would be the case if the levels were split apart by electric fields.

In a paper which is to be published soon in this journal, Dr. Freed and I have presented a partial energy-level diagram for Gd^{+++} self-consistent within the accuracy we were able to attain (1 cm^{-1} for position, 4 cm^{-1} for resolution), derived from eight sets of data. The data were:[1,2,3] Absorption spectra of $GdCl_3 \cdot 6H_2O$ at ordinary temperatures, and at that of liquid nitrogen and of liquid hydrogen. Gd^{+++} even at room temperatures gives sharp spectra, but as the temperature is lowered the lines shift somewhat owing to changes in the effective electric fields caused by the ingathering of the crystal lattice;[4,5] Absorption spectra of $GdBr_3 \cdot 6H_2O$ at room and liquid nitrogen temperatures;[6,7] Transverse Zeeman effect on the *a* and *b* axis of monoclinic

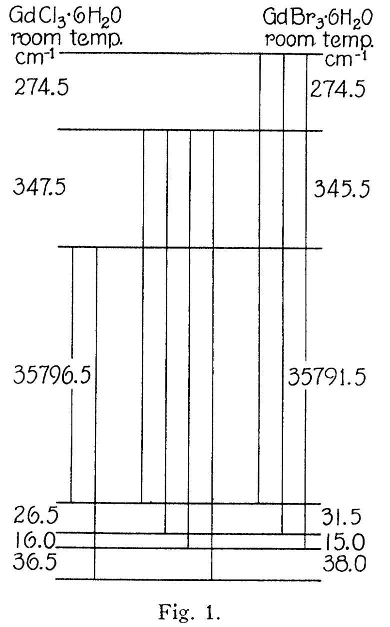

Fig. 1.

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[1] F. Hund, Linien Spektren, Julius Springer, Berlin.

[2] Woltjer and Kammerlingh Onnes, Leiden Comm. No. 167 C.

[3] Giauque, J. Am. Chem. Soc. **49,** 1870 (1929).

[4] (a) H. A. Kramers, Proc. Amst. Acad. **32,** 1176 (1929); **33,** 9 (1930). (b) H. A. Kramers et J. Becquerel, Proc. Amst. Acad. **32,** 1190 (1929). (c) J. Becquerel, W. J. de Haas, et H. A. Kramers, Proc. Amst. Acad. **32,** 1206 (1929). (d) H. A. Kramers, Proc. Amst. Acad. **32,** 1196 (1929) and private conversation.

[5] Freed and Spedding (a) Nature **123,** 525 (1929); (b) Phys. Rev. **34,** 945 (1929); (c) J. Am. Chem. Soc. **52,** 3747 (1930); (d) Phys. Rev. **35,** 1408 (1930).

$GdCl_3 \cdot 6H_2O$;[5] Longitudinal Zeeman effect on the c axis of $GdCl_3 \cdot 6H_2O$. The diagram, shown in Fig. 1, is not consistent with other methods of reasoning. For instance, in his brilliant work on complex spectra, by making use of Russell-Saunders coupling and the Pauli exclusion principle, Hund calculates the basic levels of the rare earth ions. He then calculates the magnetic susceptibilities of the gaseous ions and his values agree remarkably well with those obtained experimentally from the solids themselves. For Gd^{+++} he obtains an ^8S term, which is single, as are all S terms. Wolljer and Kamerlingh Onnes[2] have measured the magnetic susceptibility of $Gd_2(SO_4)_3 \cdot 8H_2O$ from 1.3°K to room temperature, and Giauque[3] shows that their results are in perfect accord with the assumption of an ^8S basic level.

Kramers and J. Becquerel,[4] from their work on the paramagnetic rotation of polarized light in xenotime, conclude that the rotation is due to the presence of Gd^{+++} ions in the mineral, and that the Gd^{+++} is in the ^8S state, which is split into several components in the crystal field. Even in the anhydrous crystals with which they were dealing the splitting is not expected to amount to more than a few cm^{-1}. Certainly in the hydrated salts which were used by Giauque and by Freed and me the effect must be much less, less even than our resolving power.

The diagram as it is presented requires either metastable levels of high energy or wide splitting in the lower level, both forbidden by the arguments set down above. However, if the electron distributions in the rare earth elements are examined, it becomes apparent how these conflicting notions may be brought into agreement. According to the Bohr-Stoner scheme, the distribution of electrons in Gd^{+++} ion is as follows:

$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$	$4p$	$4d$	$4f$	$5s$	$5p$
2	2	6	2	6	10	2	6	10	7	2	6

In previous papers Dr. Freed and I point out that the optically and magnetically active $4f$ electrons give rise in solids to atomic rather than molecular spectra since the complete $5s$ and $5p$ shells partially shield the $4f$ electrons and tend to prevent close coupling between them and neighboring ions and water molecules. There are two ways in which one of the $4f$ electrons may be excited. Firstly, it may remain under this screening influence of the $5s$ and $5p$ shells. To do this, however, n and l of the electron can not change since the exclusion principle forbids any other values. Therefore the only possible excitation comes about through one of the spins reversing itself, thus giving rise to sextet terms. A jump of this sort rarely occurs in atomic spectra and, moreover, it is to be expected that the energy involved would be large. Secondly, the electron may jump outside the strong protection of the $5s$ and $5p$ shells and occupy the $5d$, $5f$, and $5g$ or higher shells, but most probably the $5d$ shell. In this event, Russell-Saunders coupling would presumably be effective for each part of the atom, but owing to the same screening activity on the part of the $5s$ and $5p$ levels it would be much weaker between the halves and would result in $j-j$ coupling. In this instance a $^7F_0$ term would be formed inside and would join with the $^2D_{3/2}$ term outside to give the combined term, $[^7F_0{}^2D_{3/2}]3/2$. Of course, other types of coupling are possible, especially if the splitting of the terms caused by the electric fields of the crystals is large as compared with the $j-j$ coupling. At least there would be a strongly coupled part inside joined by a relatively weak bond to the excited electron outside.

If this is true it would be expected that the intervals, $^7F_0 - {}^7F_1$, $^7F_1 - {}^7F_2$, and so on would occur in the spectra. Although as a first approximation they would be equal for terms of the type, $[^7F_2{}^2D_{3/2}]7/2\,[^7F_2{}^2D_{3/2}]9/2$, there would nevertheless be some differences, greater or less depending on the difference in energy of the terms coupling with them. Also, splitting of the levels, $[^7F_2{}^2D_{3/2}]7/2\,[^7F_2{}^2D_{3/2}]5/2$, owing to the electric fields in the crystal, should be nearly alike, but under high dispersion differences should become apparent. This is precisely what is found to be the case. I am just now repeating the work cited above, using a spectrograph with a dispersion of 2A per mm and have found small differences, amounting to about 1 cm^{-1}, between splitting arising from different groups.

Evidences of coupling of the sort suggested should also be found in the gaseous spectra of the rare earths, so that very different terms from those predicted on the basis of Russell-Saunders coupling would be obtained. The spectra would be closely analogous to x-ray spectra with the exception that the energy values of the optical levels are of such an order of magnitude that their interaction with the x-ray levels can no longer be ignored.

It may be well to mention a few of the more striking facts noted when the spectra are photographed with an instrument of high dispersion. Ordinarily, perhaps half the lines are doublets of about 1 cm^{-1} separation, but if the crystals are under strain many more lines resolve and the separation becomes greater. This splitting may be attributed to the action of the electric fields in the crystal on the basic level. Professor Kramers[4d] has suggested that the ^8S level should dissolve into four slightly separated levels. These, with the rules of selection which are applicable, should give separations of the sort observed. Just as was anticipated, the spectrum of a triclinic crystal photographed by Mr. G. C. Nutting and me shows the dissolution into pairs to be much more pronounced, with several of the lines which apparently were single in the monoclinic $GdCl_3 \cdot 6H_2O$ resolved clearly into doublets. In a magnetic field the double lines split into several components, usually five or more, and in most instances it seems that still more components would appear under higher dispersion. As a usual thing the lines tend to separate into two groups of components which, under low dispersion, show as doublets of the sort reported by J. Becquerel, and Freed and Spedding.

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High Velocity Vapor Jets at Cathodes of Vacuum Arcs

From measurements of the force of recoil on the cathode of an arc drawn in a high vacuum, and from measurements of the amount of cathode material which was lost, Tanberg[1] has calculated the mean velocity of the material leaving the cathode to be the extraordinarily high one of over 10^6 cm per sec. K. T. Compton[2] has proposed a theory of the development of high molecular velocities, but explains that, "... this criticism does not alter Mr. Tanberg's basic conclusion regarding a high speed neutral vapor stream. It merely suggests an electrical mechanism for the acquiring of these speeds instead of assuming a terrifically high temperature at the cathode."

Close scrutiny of Dr. Compton's suggestion that high velocity neutral molecules leave the cathode as a result of the existence of an accommodation coefficient for the positive ions neutralized at the cathode, indicates, however, that the velocity of these molecules cannot be nearly as great as the velocity obtained by Tanberg. The maximum velocity of the neutralized ions cannot be expected to be much greater than that corresponding to the cathode drop, whereas Tanberg observed velocities of an order corresponding to 70 volts. Hence, if the reaction of the neutralized positive ions is to account for the force upon the cathode observed by Tanberg, the stream of neutralized positive ions leaving the cathode with part of their original energy must be of much greater density than the high velocity stream calculated by Tanberg. In fact, Compton, by assuming that all the positive ions participate in the reaction, calculates that the average energy of the neutralized ions need be less than 0.4 volt to give the force measured by Tanberg.

The high speed stream of Tanberg must still be assumed to leave the cathode *region*, even though the mechanism proposed by Compton may possibly account for the way in which force is communicated to the cathode itself. Because of the high vacuum, the only material leaving the cathode region is substantially only the material lost from the cathode, which Tanberg weighed. The force on the cathode must equal the momentum of the material leaving the cathode *region*, regardless of whether this material acquires its velocity at the cathode surface or elsewhere in the region.

The argument for the necessary existence of Tanberg's high speed stream seems to be valid unless there is a high density of gas in the vessel in which the experiment is carried out. In such a case, the lower speed neutralized positive ions of Dr. Compton could communicate their momentum to many gas molecules, without any of them acquiring a high velocity. But a high gas pressure in the tube during the period of arcing does not seem likely. To obtain a high density of copper vapor throughout the vessel would require almost complete reflection of copper atoms at the walls of the vessel, a condition which does not seem very probable for heavy metal atoms. If such complete reflection did occur, one would expect to have a uniform deposit of copper on all parts

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[1] Tanberg, Phys. Rev. **35**, 1080 (1930).

[2] K. T. Compton, Phys. Rev. **36**, 706 (1930).