

with a 1 meter vacuum spectrograph. Only three combinations between $d^{10} \ ^1S_0$ and known terms are possible, *viz.*, combinations with $^3P_1^0$, $^3D_1^0$, and $^1P_1^0$ of the d^9p configuration. Only three lines with the expected frequency differences appear in the region and thus locate 1S_0 with certainty. The lines are:

Int.	λ	ν	Classification
4	1362.44	73398	$^1S_0 - d^9p \ ^3P_1^0$
7	1224.65	81655	$^1S_0 - d^9p \ ^1P_1^0$
5	1166.81	85704	$^1S_0 - d^9p \ ^3D_1^0$

The wave-lengths are believed good to somewhat better than one-tenth of an Angstrom and the separations somewhat better.

A Band Spectrum due to the Molecule N_2O_3

During a study of the absorption of light by N_2O (Abstract No. 19 Chicago Meeting of the American Physical Society, Nov. 27-28, 1931), the authors were led to an investigation of mixtures of NO and NO_2 , and have observed, in the near ultraviolet, an absorption spectrum consisting of apparently diffuse bands, due in all probability to the molecule N_2O_3 . The bands are observed in relatively large amounts of NO when small amounts of NO_2 are added, the new bands predominating over the absorption of NO_2 under these conditions. Their centers are located approximately at wave-lengths 3843, 3682, 3539, 3509, 3417, 3386, 3305, 3279. The bands do not appear to possess sharp edges nor to show any pronounced tendency to degrade

The frequency differences agree with McLennan's analysis to within 2 frequency units. The value of 1S_0 based on McLennan's term values is -15036 .

This value of the low level is further confirmed from a study of the spectrum of the low voltage arc in helium and gold vapor. In this excitation lines from the two levels $d^9S \ ^3D_1$ and 1D_2 , which are respectively 24.11 and 24.15 volts above the normal state of the gold atom and thus nearly in resonance with the He ion (24.47 volts), are very strongly excited.

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November 25, 1931.

one way or the other. The first member is exceptionally diffuse. The third member appears most intense. The bands grow weaker as they proceed to shorter wave-lengths suggesting that there may be further weaker members among the NO_2 absorption. The new bands show qualitatively the dependence to be expected upon the pressures of NO and NO_2 , and upon the temperature, decreasing noticeably with increasing temperature. A more detailed description of this spectrum will be published later.

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November 23, 1931.

A. Effect of Crystal Symmetry on the Energy Levels of Solids.

B. Experimental Evidence of Definite Orientation of Coordinated Water Molecules About Rare Earth Ions in Solution

Because of its interest to physicists, who perhaps would not see the complete paper in a chemical journal, we think that it is desirable to publish a brief summary of an article which we shall submit soon to the Journal of the American Chemical Society.

A. Photographs were taken of the absorption spectra of the Gd^{+++} ion in monoclinic crystals of $GdCl_3 \cdot 6H_2O$, $GdBr_3 \cdot 6H_2O$, $Gd_2(SO_4)_3 \cdot 8H_2O$; in hexagonal crystals of $Gd(BrO_3)_3 \cdot 9H_2O$, $Gd(C_2H_5SO_4)_3 \cdot 9H_2O$, and in a triclinic crystal, $Gd(NO_3)_3 \cdot 6H_2O$. Gadolinium IV was chosen because it is by far the most desirable ion for this type of work. It gives sharp lines at room temperature, it has the simplest spectrum of any of the rare earths, its lines and multiplets being well sepa-

rated from one another, and its basic level, $^8S_{7/2}$, is known to be single. Its chief disadvantage is that its absorption lines occur in the ultraviolet.¹

In all cases the same multiplets were observed at approximately the same frequencies, although a slight shift of the multiplets toward shorter wave-lengths was noticeable in the case of crystals of higher symmetry. The lines within the multiplets were, however, greatly affected by changes in the crystal system.

¹ Freed and Spedding, Nature **123**, 525 (1929); Phys. Rev. **34**, 945 (1929); *ibid.* **38**, 670 (1931); Spedding, Phys. Rev. **37**, 777 (1931).

From the monoclinic crystals the number and spacing of the lines was almost identical, the differences between the spectra of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ being of the same order as those between $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{GdBr}_3 \cdot 6\text{H}_2\text{O}$.² Only in two cases were distinct differences observed and both occurred in multiplets in which the lines were very closely spaced. The differences were caused by a single line of the chloride spectrum becoming two lines in the case of the sulphate. On the other hand, between the hexagonal and monoclinic crystals, there were notable differences both in the number and spacing of the lines. The over-all spread of the multiplets was less than half that shown by the monoclinic crystals, and in many cases fewer lines were observed. The spectrum of the triclinic crystal was similar to that of the monoclinic type, but its multiplets were farther spread out. Unfortunately, only two groups of lines were obtained from $\text{Gd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ owing to continuous absorption by the negative ions in the region below 3000A.

In a previous letter³ to this journal experimental evidence was presented which showed that all the lines arise from a single basic level, $^8S_{7/2}$, which is not appreciably affected by the crystal field. For this reason the position of the lines and multiplets is effectively an energy level diagram of the excited levels. The absence of sensitivity to variations in the crystal field of the mean positions of the multiplets and the great sensitivity of their component lines to this field proves that the multiplets arise from an excited electronic level which has become non-degenerate because of the electric fields of the crystal. To a first approximation, the type and magnitude of the splitting depends only on the symmetry of the crystal, and the chemical differences of the surrounding ions have only a second order effect, except for that which aids in determining the crystal form.

These facts are in good agreement with those predicted by Bethe,⁴ who, from considerations of wave mechanics and group theory has shown that degeneracy of the levels of rare earth ions, caused by the force fields of the neighboring ions in the crystal, should depend on the symmetry of the fields about the ions, and that the degeneracy should become less in fields of lower symmetry. In his calculations Bethe has made many simplifying assumptions which are not

applicable here, so that better than qualitative agreement should not be expected. While the unique structures are still unknown, careful crystallographic measurements of all our crystals have been made by Professor Adolph Pabst of this university. In general the crystals are from the class of highest symmetry of the system to which they belong. In the case of the hexagonal crystals which we have used, the symmetry about the Gd^{+++} ion appears certainly to be greater than that about the Gd^{+++} ion in the monoclinic crystals.

B. Photographs were taken of the absorption spectra of Gd^{+++} ion in solutions of $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Gd}(\text{C}_2\text{H}_3\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ of various concentrations. The positions and general spacings of the lines in all cases were very similar to those of the $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ crystals except that the lines were very much wider and the multiplets were shifted slightly toward higher frequencies. The fact that the lines of the multiplets can be clearly resolved shows that the water molecules must take definite positions about the Gd^{+++} ion in order to give a field of definite symmetry. If random distribution is assumed, there would be all types of symmetry and the multiplets would become broad, blurred bands on account of the overlapping of the various spectra. The great width of the lines does, however, show that there is considerable thermal agitation and that the water molecules vibrate about their mean positions.

A study of the number of lines in the multiplets, together with their shifts, widths, and so on, should give a great deal of information concerning the effect which temperature, concentration, additional ions, various solvents and the like have on the force fields which surround the ions in solution.

We are continuing this work and hope soon to have more detailed information concerning it.

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² Freed and Spedding, *J. Am. Chem. Soc.* **52**, 3747 (1930).

³ F. H. Spedding, *Phys. Rev.* **38**, 2080 (1931).

⁴ Bethe, *Ann. d. Physik* **3**, 133 (1929).