

The Nature of Energy States in Solids

Using the methods of quantum mechanics and group theory Van Vleck,¹ Penney and Schlapp² and Amelia Frank³ have developed a theory for the behavior of energy levels of an atom when subjected to the electric fields of other atoms in a crystalline solid. They have treated in detail the hydrated sulphates of neodymium, praseodymium and samarium.

They applied their theory to the experimental results of Gorter and de Haas⁴ on the magnetic susceptibility of Pr and Nd salts and were able to reproduce the experimental curves from 14°K to room temperatures. While the agreement here was very good, unfortunately, a number of other discrepancies made their appearance. Thus the potential field constant D in the equation $V = D(x^4 + y^4 + z^4)$, which one would expect to be very similar for the various rare earths due to their similar chemical and crystallographic properties, is about four times as large for neodymium as for praseodymium. Further, while one would expect Er and Nd to behave somewhat similarly since they have the same spectroscopic term only inverted, the actual susceptibility data are not alike, for the $1/\chi$, T diagram for Er gives almost a straight line while for Nd it is distinctly curved. It should be mentioned, however, that the experimental work of Gorter and de Haas is not in agreement with two room temperature points determined by Zernicke and James,⁵ and Cabrara.⁶ Finally, the agreement with samarium is extremely poor. Spedding and Bear⁷ have also found experimentally at least five low lying levels while the maximum number permitted by theory is two in a cubic field and three in a combined cubic and rhombic field.

In view of these discrepancies I have thought it advisable to study the energy levels of the rare earths spectroscopically. In collaboration with Dr. Nutting and Mr. Hamlin, I have found that the lowest state of neodymium is split into at least three levels with a separation of 76 and 260 cm^{-1} from the lowest state. Theory as applied to the work of Gorter and de Haas demands about 0, 243 and 834. Our work is in definite disagreement with these results. However, if the experimental work of the above authors is disregarded the relative separations are the same as predicted by theory. With our separations most of the discrepancies disappear. The magnetic susceptibilities as calculated from these levels give a $1/\chi$, T diagram which is almost a straight line in good agreement with the experimental work on erbium. Further the calculated susceptibility agrees within experimental error with the room temperature values of Zernicke and James, and Cabrara. Finally the field constant D , being only one-third as big as before is in good agreement with that of praseodymium. The discrepancy in the case of samarium seems to be real and bears out the author's contention that there must be an additional electronic level lying near the basic one in that case.

In exactly the same way that Penney and Schlapp treated neodymium and praseodymium, I have treated

erbium and dysprosium using the field constants as determined by Nd after correcting them for the additional screening according to Slater's method and found the basic state of Er^{+++} would be split into five levels separated by 19 cm^{-1} , 38 cm^{-1} , 83 cm^{-1} and 87 cm^{-1} from the basic state.

Nutting and Meehan have advised me by letter that they have observed levels at 0, 19, 41 and 85 cm^{-1} . This agreement is remarkable when one realizes that there are no arbitrary constants involved so that the relative splitting cannot be altered. As there is a slight leeway in the value of the screening constants used, the over-all spreading could be varied slightly and has been chosen to give the best fit. The value used, however, is well within the experimental error of determining screening constants by any other method.

The levels calculated for Dy while of the right order of magnitude were not in good agreement with the experiment, but this is not surprising for the basic state of Dy is the same as that for Sm, except that it is inverted, and if an extra level exists there one would expect it to be present in Dy also and while it would probably be farther away it would still perturb the splitting of the basic state.

The excellent agreement in the case of Nd and Er seems to indicate that Penney and Schlapp's assumption of a cubic field is justified. While the magnetic susceptibility would not be very sensitive to the existence of a rhombic term in the potential energy equation, the splitting of the levels would be extremely sensitive. From our data the rhombic term could not be more than 2 percent of the cubic term as there is absolutely no evidence of the rhombic splitting in our photographs.

From the above results it can be seen that a study of the absorption spectra offers a powerful tool for determining the position, symmetry and distance of the atoms in the first row about the ion being studied. It, therefore, complements x-ray studies in that this method is most powerful in the region where the x-ray measurements are least reliable. It also should give considerable information about the potential and electric fields which exist about an ion in a crystal or in solution.

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¹ Van Vleck, *The Theory of Electric and Magnetic Susceptibility* (Oxford Press).

² Penney and Schlapp, *Phys. Rev.* **41**, 194 (1932).

³ Amelia Frank, *Phys. Rev.* **48**, 765 (1935).

⁴ Gorter and de Haas, *Leiden Comm.* 218b.

⁵ Zernicke and James, *J. Am. Chem. Soc.* **48**, 2827 (1926).

⁶ Cabrara, *Comptes rendus* **180**, 669 (1925).

⁷ Spedding and Bear, *Phys. Rev.* **46**, 975 (1934).