

Further Relationships Between Absorption Spectra of Rare Earth Solids and Crystal Structure

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Citation: [The Journal of Chemical Physics](#) **5**, 160 (1937); doi: 10.1063/1.1749996

View online: <http://dx.doi.org/10.1063/1.1749996>

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Further Relationships Between Absorption Spectra of Rare Earth Solids and Crystal Structure

The atoms in a solid are so close together that they exert powerful electric fields upon one another and thus cause a Stark splitting of the energy states of the atoms. The nature of the splittings will, of course, depend on the states involved, the symmetry of the surrounding atoms in the solid and on the nature and distances of the surrounding atoms. This problem has been treated theoretically by a number of investigators notably Bethe and Van Vleck. Penney and Schlapp¹ have treated the specific case of the splitting of the basic state of Nd^{+++} in a cubic field. They evaluated the constants in their equations so as to give the best fit with the experimental work of Gorter and de Haas² on the magnetic susceptibility of $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. We were not able to locate the levels where they were predicted by that work. We did, however, find levels with the same relative separations, but with only about one-third the over-all separation. Evaluating the constants in Penney and Schlapp's equations from our levels, we calculated the magnetic susceptibility of the salt at various temperatures and obtained results in excellent agreement with the experimental results of Zernicke and James, S. Meyer, Selwood and others but not in agreement with Gorter and de Haas or Jackson.³ Further, using the constants as determined for Nd^{+++} I calculated the levels for Er^{+++} and found excellent agreement with the levels determined spectroscopically by Nutting and Meehan.⁴

While any rhombic term in the potential equation should be easily detected experimentally since it causes splitting of a number of the levels, no such splitting was observed and we were forced to conclude that no rhombic field existed greater than two percent of the cubic field. The Nd^{+++} and Er^{+++} investigated are in monoclinic crystals. While one might expect that the octahedron of oxygens about the rare earth ion would give a field predominantly cubic, it seems astonishing that a rhombic term should not arise from the remaining atoms in the crystal. We are extending our investigation to include as many salts as possible. In view of the interesting results which we are obtaining it seems advisable to report some of them at this time.

The hydrated sulphates of the rare earths crystallize in a homologous series of the form $\text{R}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and are completely isomorphic with each other. In these salts, which are monoclinic, the rare earth ion is presumably surrounded by an octahedron of oxygen atoms, four of which are part of water molecules and two of which belong to the sulphate. Dr. Howe and I have photographed the absorption spectrum of $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ at various temperatures and found that the basic state is split into four levels in agreement with theory. Mr. Keller and I have also photographed $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ containing a small amount of $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ as an impurity. The basic state of Nd^{+++}

is split exactly the same as in the pure $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. The excited states are also split the same but are shifted to the violet by three or four wave numbers.

The chlorides of the rare earths form a homologous series of the form $\text{RCl}_3 \cdot 6\text{H}_2\text{O}$. The crystals are also monoclinic and presumably have the six oxygens of the water molecules grouped around the rare earth ion in the form of an octahedron. One would, therefore, expect that the splitting of the states in the chloride and the sulphate would be the same. This was found to be true in the case of Gd salts.⁵ One might expect it to be true in the case of Nd^{+++} , but if one examines the homologous series of the chlorides one finds that it ends at Nd^{+++} and that Pr^{+++} , Ce^{+++} and La^{+++} form chlorides containing $7\text{H}_2\text{O}$. The seventh water apparently enters a hole in the lattice brought about by the increasing size of the rare earth ion. In $\text{Nd}_2\text{Cl}_3 \cdot 6\text{H}_2\text{O}$ this hole is almost certainly present but is not large enough to contain a water molecule. It will, however, permit the octahedron to expand into it slightly, and therefore, the crystal fields about the rare earth ion will be slightly weaker than expected and the over-all splitting of the basic state in the chloride will be less than in the sulphate.

Mr. Hamlin and I have photographed the spectrum of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ and have found levels at 0, 62 and probably at 215 as compared to 0, 77 and 260 cm^{-1} , in the sulphate. We found no evidence of a rhombic field as the 62 cm^{-1} level was not split. Mr. Keller and I have photographed the absorption spectra of $\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$ containing Nd^{+++} as an impurity. Here the water occupies the hole in the lattice and we would expect the fields to be stronger. We found that the 77 cm^{-1} level was now shifted to 104 cm^{-1} .⁶ The excited levels of these salts behave in a much more complicated manner and cannot be accounted for on the simple theories. There are too many lines in the multiplets so that some of them have to be of oscillational or vibrational origin. They are strongly evident in the case of Pr and are progressively less evident as the atomic weight is increased. Beyond Gd only a few, if any, can be of that type. We are extending these investigations to salts of Ho, Tm and Er and hope to have more results available shortly.

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¹ Phys. Rev. 41, 194 (1932).

² Leiden Commu. 278b.

³ The experimental results on the magnetic susceptibility of $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ are not satisfactory in that they do not agree among themselves. The low values obtained by Gorter and de Haas, and Jackson, which we do not check, also give an excellent fit with theory so that their relative values must be nearly correct. Perhaps the absolute values are in error. In any case more experimental work on this salt would be welcome.

⁴ Phys. Rev. 50, 574 (1936).

⁵ J. Chem. Phys. 5, 33 (1937).

⁶ Drs. Meehan and Nutting have informed me privately that they also found that the lines of the other rare earths are markedly shifted when crystallized with $\text{Ce}_2(\text{SO}_4)_3$ salts which belong to a different crystal type.