

ION COMPRESSION AND THE COLOUR OF RUBY

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THE spectra of many transition-metal compounds have been interpreted successfully by means of crystal-field (ligand-field) theory. The hydrates have received more attention than any other class of compound, and the band assignments for their spectra are fairly complete¹. If the spectra of transition-metal ions dissolved in glasses or in other oxide materials² are compared with those of the hydrated ions, the correspondence between them is found to be very close, provided that the metal ion is octahedrally co-ordinated in the host lattice. For trivalent ions in glasses the only observed differences are small shifts of the absorption bands to longer wavelengths, corresponding to a decrease of 5–15 per cent in Δ , the fundamental crystal-field splitting of the d -orbitals. In the case of the chromium ion (Cr^{3+}), the hydrate has band maxima at 17,400 cm^{-1} and 24,700 cm^{-1} , corresponding to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transitions, respectively¹. In glasses these maxima are displaced to 15,400 cm^{-1} and 22,200 cm^{-1} . The green colour of hydrated chromic salts, chromic oxide and chromic ion in most oxide lattices is due to these two bands, particularly to the one with its maximum near 16,000 cm^{-1} .

The optical properties of the ruby, which consists of a small quantity of Cr_2O_3 dissolved in an Al_2O_3 matrix, have been regarded as anomalous. One would expect that solutions of chromium ions in the corundum lattice of Al_2O_3 would be green, and in fact solutions containing a large quantity of Cr_2O_3 dissolved in $\alpha\text{-Al}_2\text{O}_3$ or any quantity of Cr_2O_3 dissolved in $\beta\text{-Al}_2\text{O}_3$ are green in colour. But rubies are red. Furthermore, red solutions of Cr_2O_3 become green on heating but revert to their original colour on cooling³. Explanations of these facts based on the presence of an oxidation state of chromium other than three have been excluded by magnetic and other studies. The suggestion that the change from red to green observed as the concentration of Cr_2O_3 is increased is connected with the antiferromagnetic exchange coupling which undoubtedly occurs in Cr_2O_3 is excluded by the reversion of green solutions to red on cooling.

The simplest remaining possibilities are that the chromium ions are not octahedrally co-ordinated or that although they are octahedrally co-ordinated they are subjected to an anomalously large crystal field. We shall show that an interpretation based on the second of these hypotheses can be justified by intuitive arguments and is consistent with all the available experimental evidence. The first hypothesis is without any support, since the corundum structure which involves octahedral co-ordination of the metal ions is adopted both by $\alpha\text{-Al}_2\text{O}_3$ and by Cr_2O_3 .

The red colour of ruby is due to an absorption band the maximum⁴ of which is at about 19,000 cm^{-1} . Thus, according to our interpretation, the crystal-field parameter Δ in ruby has increased by 20 per cent relative to that in other oxide materials. In the

electrostatic theory, Δ is proportional to R^{-5} where R is the metal-anion distance, so that a reduction of 20 per cent in Δ corresponds to a reduction of the metal-oxygen distance by 4 per cent. Taking the radius of the chromium ion as 0.65 Å. and that of the oxygen ion as 1.40 Å., we find a normal Cr-O distance of 2.05 Å., so that a shortening of the Cr-O distance by 0.08 Å. would be sufficient to account for the observed difference in colour. While we do not believe that the crystal-field theory can give accurate absolute values for Δ in terms of molecular dimensions, we nevertheless believe the above estimate to be of the right order of magnitude.

The radius of the aluminium ion (Al^{3+}) is 0.50 Å., that is, substantially smaller than the radius of the chromium ion (Cr^{3+}). It therefore seems certain that if aluminium ions were replaced by chromium ions in a solid lattice without changing the positions of the neighbouring anions an enormous repulsion energy would result. In practice, this would be decreased by the relaxation of the host lattice. The final position of the anions, however, would not correspond to the normal ionic radius of the impurity ion but to some intermediate radius between that of the host and the impurity. The above very rough calculation suggests that in ruby this radius is about 0.57 Å., which by chance is just the mean of the ionic radii of aluminium and chromium.

Thilo and co-workers⁵ have shown that at room temperature $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solutions containing up to 8 atom-per cent Cr_2O_3 are red in colour, but that solutions containing a greater amount become progressively more green. They also showed that there is little change in the lattice parameters of Al_2O_3 until 8 atom-per cent of Cr_2O_3 has been added and that then the lattice parameters increase linearly until those for pure Cr_2O_3 are reached. This strongly supports our interpretation in terms of 'compression' of the chromium ion.

It was also noted that the temperature at which the transition from red to green occurred decreased with the concentration of chromium ions. This, presumably, is because the relaxation of the lattice takes place more easily when a larger amount of chromium ions is present.

It has been reported⁶ that certain $\text{Cr}^{3+}\text{-Al}^{3+}$ spinels are also red when the chromium ion concentration is sufficiently low, but green otherwise. The same mechanism is presumably at work in these cases as in ruby. It seems possible that the colour of chromium ions in oxide matrices may provide a general method for determining the 'pressure' to which the ion is subjected. Certainly a red colour is obtained in the 'hard' corundum and spinel lattices and a green one in the 'softer' glasses.

¹ Jorgensen, C. K., Proceedings, Tenth Solvay Conference in Chemistry, Brussels (1956). Orgel, L. E., *J. Chem. Phys.*, **23**, 1004 (1955).

² Weyl, W. A., "Coloured Glasses", Society of Glass Technology Monograph (1951).

³ Thilo, E., Jander, J., Seeman, H., and Sauer, R., *Naturwissenschaften*, **37**, 399 (1950).

⁴ Henning, F., and Heuse, W., *Z. Physik*, **20**, 132 (1923).