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Authors

McLaughlin, Raich D.
Conway, John G.

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Shifts in spectral lines of Pr^{3+} which result from changing the cation-anion distance have been studied. This was done by recording the spectra of a few per cent Pr^{3+} which had been incorporated into the anhydrous trichlorides of Ce, Nd, Sm, Gd, and the anhydrous tribromides of La and Ce. In addition, data for Pr^{3+} in $\text{Gd}(\text{EtSO}_4)_3 \cdot 9\text{H}_2\text{O}$ were compared with existing data on Pr^{3+} in $\text{Ce}(\text{EtSO}_4)_3 \cdot 9\text{H}_2\text{O}$.¹ In all of these systems Pr^{3+} has the same point symmetry. The results are displayed in Table 1 and Fig. 1. In this figure the positions of the states are plotted along the ordinate. The radii of the rare earth ion of the host lattice are plotted along the abscissa.² It is felt that the radius of the host rare earth ion represents a measure of the cation-anion distance of the incorporated Pr^{3+} ion. That is, it is assumed that the Pr^{3+} ion causes negligible distortions of the host crystal lattice.

Two types of shifts occur. The main shift results from the change in position of the center of gravity of the crystal-field states. A minor shift of crystal-field states with respect to each other is also observed. This latter shift will be discussed later.

The main shift is consistent with the theory described by Jørgensen,³ and inconsistent with suggestions made by Wong and Richman.⁴ Jørgensen ascribes this effect to a decrease in coulombic interaction between the f electrons on the same atom. This decrease is caused by an expansion of the

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Fig. 1. Positions of states as a function of ionic radii of rare earth ions of the host crystals.

wave functions which results from interactions between the rare earth cation and neighboring anions. A smaller cation-anion distance leads to a greater cation-anion interaction, which in turn results in a decrease in the energies between the levels because of the smaller coulombic interaction. This is probably the main cause of the red shift of spectral lines observed upon lowering the temperature or increasing the pressure. The linear dependence of level position upon atomic radii demonstrated by the trichloride system is noteworthy. This indicates that atomic radii as determined by x-ray diffraction depend linearly on the reciprocal of the average distance between shielded f electrons. Like Jørgensen, we find that the bromide ion expands the rare earth wave function more effectively than the chloride ion. The lack of shift in the ethylsulfates indicates that the Pr^{3+} cation-anion distance is little affected by the rare earth ion of the host. This is reasonable since this crystal is more dilute with respect to rare earth ions that are the trichlorides or the tribromides.

The shifting of crystal field states is evidenced by the lack of parallelism in lines drawn through points which represent the position of states originating from the same J value. This is most evident in states that represent the crystal-field splitting of 1D_2 . The relative position of these states is described to first order in terms of the crystal-field parameters $A_2^0 \langle r^2 \rangle$ and $A_4^0 \langle r^4 \rangle$.⁵ The experimental results for trichlorides and tribromides may be explained in two ways: $A_2^0 \langle r^2 \rangle$ and $A_4^0 \langle r^4 \rangle$ become larger as the cation-anion distance decreases or these quantities are constant but second order effects are important. The pronounced shift of states in the ethylsulfates must arise from crystal-field distortions. This is suggested since, as was discussed earlier, there is evidence for little change in cation-anion distance in this system.

Discussions with D. H. Templeton and R. B. Judd were helpful in the attempt to explain the observed effects.

Table I

Positions of crystal-field states of Pr^{3+} in various host crystals

$2S + 1$ L_J	μ	LaCl_3^a	CeCl_3	NdCl_3	SmCl_3	GdCl_3
$3P_2$	± 2	22 247.2	22 232	22 211	22 191	22 172
	± 1	22 227.7	22 210	22 191	22 172	22 154
	0	22 206.9	22 191	(22 172)	(22 149)	22 138
$3P_1$	0	21 096.2	21 082			21 027
	± 1	21 065.9	21 051			20 999
$3P_0$	0	20 474.7	20 460	20 439	20 421	20 407
$1P_2$	± 1	16 779.5	16 772			16 750
	± 2	16 731.2	16 722			16 685
	0	16 630.5				16 567
$3H_4$	3	33.8	31	32	28	25

Table I (Continued)

$2S + 1L_J$	μ	LaBr ₃ ^b	CeBr ₃	Ce(E t SO ₄) ₃ · 9H ₂ O ^c	Gd(E t SO ₄) ₃ · 9H ₂ O
$3P_2$	±2	22 148	22 128	22 440.5	22 438
	±1	22 133	22 105	22 447.6	22 448
	0	22 112	22 085	22 424.8	22 414
$3P_1$	0	20 996	20 977	21 289.6	21 294
	±1	20 966	20 944	21 276.1	21 276
$3P_0$	0	20 373	20 350	20 687.0	20 688
$1D_2$	±1	16 717	16 707	16 955	16 964
	±2	16 670	16 655	16 857.7	16 860
	0	16 572	16 549	16 709.3	16 695
$3H_4$	3	17	9	11.9	13

^a G. H. Dieke and R. Sarup, J. Chem. Phys. 29, 741 (1958).

^b These values differ slightly from those of E. Y. Wong and I. Richman.
See reference 4.

^c See reference 1.

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