PHYSICAL REVIEW
LETTERS

VOLUME 14 | 3 MAY 1965 | NUMBER 18

ENERGY LEVELS OF Pr^{3+} IN THE VAPOR STATE

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(Received 16 February 1965)

An analysis of the emission spectrum of triply ionized praseodymium in the vapor state has resulted in the determination of all the energy levels of the ground $4f^2$ configuration, except for the $^1S_0$ level. This is the first case where levels of the $4f^n$-type ($n > 1$) configurations of triply ionized rare earths have been found in the free ion. Previously, energy-level data for these configurations have been deduced from absorption and fluorescence spectra of crystals containing rare earths as impurities. These new data provide the first opportunity for a direct experimental determination of the effect of the crystal field on the free ion energy levels of the rare earths.

The spectrum was obtained with a sliding spark discharge[2] operating at 50-A peak current. It was photographed from 800 to 2100 Å in the first order of a 35-ft Eagle vacuum spectrograph at a reciprocal dispersion of 0.78 Å/mm.

The energy levels of the $4f^2$ configuration derived from these data are given in column 1 of Table I. From the fit of the lines to the final energy-level scheme we estimate that the accuracy of these levels is ±0.2 cm^{-1}. We derived the electrostatic and spin-orbit parameters given in Table II by means of a least-squares fit of the energy formulas to the experimental levels. The rms deviation of the levels from their calculated positions is 125 cm^{-1}. The significance of deriving five electrostatic parameters from only six observed terms by least squares may be questionable.

Table I. Experimental levels of the $4f^2$ configuration of Pr^{3+} in the vapor state compared with those obtained from Pr^{3+} in $LaCl_3$ (see reference 3). The crystal levels are the barycenters of the Stark components adjusted to bring the $^3H_4$ level to zero.

	E (vapor state) (cm^{-1})	E (crystal) (cm^{-1})	difference (cm^{-1})
$^3H_4$	0	0	0
$^3H_5$	2152.2	2117.4	34.8
$^3H_6$	4389.1	4306.3	82.8
$^3F_2$	4996.7	4846.6	150.1
$^3F_3$	6415.4	6232.3	183.1
$^3F_4$	6854.9	6681.7	173.2
$^1G_4$	9921.4	9697.6	223.8
$^1D_2$	17 334.5	16 639.3	695.2
$^3P_0$	21 390.1	20 383.4	1006.7
$^3P_1$	22 007.6	20 984.9	1022.7
$^1I_6$	22 211.6	21 324.5	887.1
$^3P_2$	23 160.9	22 139.1	1021.8

Table II. Interaction parameters of the $4f^2$ configuration (in cm^{-1}), with rms errors.

$E^0 = 6384 \pm 82$
$E^1 = 4972 \pm 59$
$E^2 = 22.6 \pm 0.4$
$E^3 = 484 \pm 3$
$\zeta_f = 741 \pm 23$
$\alpha = 19 \pm 4$

However, the resulting values are practically unchanged from those obtained from the $4f^26s$ configuration[2] of Pr^{2+}, and are therefore considered to be reasonable. The $^1S_0$ level is the only level of $4f^2$ not found experimentally. Its calculated position is at about 51 400 cm^{-1}.

In column 2 of Table I the corresponding levels of Pr^{3+} in the LaCl_3 crystal[3] are given. These are the centers of gravity of the groups of Stark components arising from the levels. For those components which have not been found experimentally, the calculated positions given in reference 3 were used. The comparison in column 3 indicates that the spacing of the terms is compressed in the crystal while the spin-orbit splitting of the terms is approximately equal. This is consistent with the nephelauxetic effect,[4] in which the interelectronic repulsion energy of the $4f$ electrons is decreased because of the penetration of the Pr^{3+} ion by the electrons of the ligands. Since this effect should be much greater for the outer part of the $4f$ wave function, it can be expected to play an important role in determining the E^k parameters, whereas ζ_f, which is determined by the inner part of the wave function, is relatively unaffected.

We are grateful to B. G. Wybourne for his valuable comments concerning the relation of the crystal levels to the free ion levels, and to N. Spector for his assistance in the calculation of the interaction parameters. We wish to acknowledge the help of V. Kaufman in making the exposures of the Pr spark.

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