A Comparative Study of Crystal Field Calculations for Tm^{++}: CaF_2 and Tm^{++}: SrF_2 Using the Covalent and Ionic Models with Different Exchange Potentials*

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Recebido em 9 de Agosto de 1973

The crystal field parameters b_4 and b_6 were calculated and compared with the experimental values for Tm^{++}: CaF_2 and Tm^{++}: SrF_2. Calculations were performed using the ionic and covalent models. Use has been made of Slater's and Gaspar-Kohn-Sham's exchange potentials in order to obtain radial wave functions for Tm^{++} and F^-. Caiculations showed that the present uncertainties in the values of the radial wave functions imply that both models are merely qualitative.

Os parâmetros b_4 e b_6 do campo cristalino foram calculados e comparados com os valores experimentais para o, Tm^{++}: CaF_2 e para o Tm^{++}: SrF_2. Os cálculos foram efetuados usando os modelos iônico e covalente. Usaram-se os potenciais de troca de Slater e de Gaspar-Kohn-Sham para obter as funções de onda radiais para o Tm^{++} e para o F^-. Os cálculos mostraram que as atuais incertezas nos valores das funções de onda radiais implicam em que ambos modelos sejam meramente qualitativos.

In studying several rare-earths ions, in different crystalline matrices, discrepancies were found between the experimental values of the energy levels and those calculated by the ionic model. A number of authors[1-5] attribute such discrepancies to covalent effects. On the other hand, papers by one of us[6,7] show that the uncertainty on the knowledge of the radial wave functions leads to large uncertainties in the calculated values of (r').

The purpose of the present paper is to investigate the influence of the radial wave functions on the crystal field parameters, when calculated using either the ionic or the covalent models.

For cubic symmetries the crystal field can be written[S] as

$$V_c = 22\sqrt{\pi}\, b_4 [Y_4^0 + \sqrt{5/14}\,(Y_4^4 + Y_4^{-4})] -$$
$$- 66/5\,\sqrt{13\pi}\, b_6 [Y_6^0 - \sqrt{7/2}\,(Y_6^4 + Y_6^{-4})].$$

The parameters b_4 and b_6 were calculated for $Tm^{++}:CaF_2$ and $Tm^{++}:SrF_2$. The radial wave functions were generated by the computational program of Herman and Skillman[9], using the modified potential. The Slater's[10] and Gaspar-Kohn-Sham's[11,12] exchange potentials have been used to obtain the $4f$ radial wave functions of the Tm^{++} ion and that of Slater for the 2s and $2p$ orbitals of the F^- ion.

In the calculation using the ionic model, use was made of the values of (r^4) and (r^6) computed by one of us[7], and the lattice sums computed by Vetri and Bassani[13].

When calculating these parameters by means of the covalent model only the s, $p\sigma$ and $p\pi$ bounds between the $4f$ orbitals of the Tm^{++} ion and the 2s and $2p$ orbitals of the first neighbours F^- ions have been considered.

The Wolfsberg-Helmholz[14] approximation was adopted in order to eliminate the non-diagonal terms of the secular equation. The diagonal terms used were those estimated by Axe and Burns[3].

The calculated and experimental values of the b_4 and b_6 parameters are compareci in Table I.

Matrix	Param.	Experimental	Ionic Model		Covalent Model	
			Slater's Exchange	Gaspar-Kohn Sham's Exch.	Slater's Exchange	Gaspar-Kohn-Sham's Exchange
CaF$_2$	b_4	46*	13	23	14	51
	b_6	5.1	0.65	2.0	2.7	10
SrF$_2$	b_4	40**	9.3	16	8.2	33
	b_6	4.2	0.42	1.3	1.6	6.8

Table 1 - Values of b_4 and b_6 (cm^{-1}). [*Reference 8; ** Reference 4]

This table shows that their values depend largely on the assumed form of the wave functions, for both models. The Gaspar-Kohn-Sham's exchange leads to good results for the covalent model, but it should be noticed that had use been made of this exchange for the F^- ion, quite different results would be obtained.

Some comments are pertinent at this point:

1. It is possible to explain the experimental energy levels of some rare-earth ions, in certain matrices, by means of the ionic model using appro-priate wave functions[6,13];

2. It is apparent from our results that this is also the case using the covalent model;

3. The wave-functions are strongly dependent on the technique used for their calculation such as adopting modified or non-modified potentials in the Herman-Skillman's method.

Therefore, one may conclude that both the ionic model and the covalent model exhibit a large dependence on'the used wave functions and one cannot decide based only on these grounds which is the more applicable. Both lead to results that are merely qualitative.

The covalent model could lead to better results if one uses a more complete set of wave functions including the excited levels. This, however, would result in a considerable increase in computational time. It seems evident that a more potent method is required in order to get reliable results in acceptable computational times.

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