An Investigation on the Ionic Model of the Rare-Earth Ion Crystal Field*

MANOEL LOPES DE SIQUEIRA and
DÁLVIO E. LABORNE E VALLE
Instituto de Pesquisas Radioativas, Comissão Nacional de Energia Nuclear, Universidade Federal de Minas Gerais, C. P. 1941
Belo Horizonte MG

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Crystal field parameters are calculated using the ionic model for rare-earth ions in crystals, where there are no problems of charge compensation. The comparison between calculated and experimental values shows that the presently available knowledge of radial wave-functions is insufficient to conclude about the validity of the ionic model.

Calculam-se os parâmetros do campo cristalino, no modêlo iônico para íons de terra rara em cristais, onde não há problemas de compensação de cargas. Êstes parâmetros, quando comparados com os obtidos experimentalmente, mostram que o conhecimento dc que se dispõe atualmente das funções de ondas radiais não permite concluir sôbre a validade ou não do modêlo iônico.

1. Introduction

Due to the great interest on optical and paramagnetic resonance properties of rare-earth ions in crystals[1,2], there is today a large amount of experimental data and theoretical models and approximations.

Calculations of crystal-field splittings are carried out by using crystal potentials as perturbations on the atomic potentials. The theoretical treatment of that problem was initiated by Bethe[3]. The simple model proposed was that of point charges as the originators of the crystal field, and it was initially applied to the transition metals[4,5]. In these metals, the paramagnetic electrons which are responsible for optical and hyperfine interaction properties are the $3d^n$ electrons. Comparisons between experimental results for the iron group and the theoretical level scheme should show a good agreement. However, under careful examination, some discrepancies are apparent. This fact has lead to the use of the concept of ligand fields in which the wave-functions are the LCAO[6] for which covalence effects are not ignored.

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In some aspects, rare-earth ions are different from those of transition metals, for their configuration is $4f^n 5s^2 5p^6$. Here the spin-orbit interaction is rather stronger and the crystal field is one order of magnitude smaller than in transitions metals. Also, the orbital functions $4f^n$ are more concentrated around the ion than those of transition metals[7]. Thus, the overlap of 4f wave-functions with those of neighbouring ions and the covalent mixing should both be smaller. Some authors[8,9,10,11,12] have tried to show that deviations between experimental and theoretical values are due to covalent effects. Others suggested that they were due to the $5s^2 5p^6$ shells which shielded the crystal field and distorted the 4f orbitals, but Burns[13] has shown that this is not so. On the other hand, Freeman and Watson[14] showed that the inclusion of the interaction among the configurations obtained by changing the orbitals of the outermost electrons can produce a shielding which creates a large deviation on the crystaline energy levels. But this shielding can be nonlinear which makes questionable the parametrization scheme used in fitting experimental data.

Recently, Vetri and Bassani[15], in the study of $Sm^{2+} : SrF_2$, have explained the energy Ievels from crystal field parameters calculated by means of the ionic model. One could naturally ask whether the ionic model would explain the optical spectrum at least in first order. This is the problem we will try to analyse in this paper. We choose cases where distortion of the crystal lattice is hoped to be negligible and polarization effects small.

In the ionic model of the crystal field there are many ways to make reasonable approximations in the calculations. There are three main interactions which control the magnetic properties of a rare-earth ion in a crystal, without taking into account the mixing of configurations:

1. Electrostatic interactions (among 4f paramagnetic electrons), which couple the angular momenta of individual electrons in such a way that there results a total angular momentum L and a total intrinsic moment S.

2. Spin-orbit interactions, which couple L and **S** to give J.

3. Crystal field, which splits partially the degeneracy of $(2J + 1)$ of a given multiplet J.

In the ionic model, the most complete solution presupposes a simultaneous treatment of the interactions, which some researchers showed to be important[2,16,17,18]

Carvalho[19] has developped a computer program which enables us to perform these calculations for any f^n configuration and for any symmetry, using the technique of Racah's tensor operators[2,20]. One of the authors[21] has performed systematic calculations of Hund's level of the $4f^n$ configuration of the crystal field matrices, taking into account the mixing of irreducible representations for the same L and S but different J. Lea and co-workers[22], supplementing the work of Ebina *et al.*[23], use the pure Russell-Saunders coupling and treat the interactions separately for Hund's level and cubic symmetry. There is another approximation which consists of breaking down the $L-S$ coupling, without any mixing of irreducible representations of the crystal field with different J (Ref. 17). These last two types of approximation enable us to use Steven's equivalent operators technique[6,24].

2. Crystal Field in the Point Charge Approximation

Let us consider the model for which the crystal field acting on an ion inside a crystal is due to all ions in the lattice. In this case, we calculate the average electrostatic field in the place where the ion "should be" when it is not there[4,5]. The resulting field satisfies Laplace's equation, and the solution which gives non-vanishing matrix elements of the crystal field Hamiltonian is:

$$H_{cryst} = e \sum_{l=2}^{6} C_{lm} \langle r^l \rangle Y_{lm}(\theta, \phi)$$

where l is even, and the integration of the radial part has already been performed, since matrix elements differ only in the angular part.

The Kamiltonian of the crystal field is a scalar. Therefore, according to Bethe[3], it is a basis for the scalar representation of the point group which characterizes the symmetry of the neighbourhood around the ion. Crystal field potentials for a number of symmetries have been tabulated[6].

For cubic symmetries we have:

$$V_{cryst} = C_{40}\langle r^4\rangle(Y_{40} + (5/14)^{1/2}(Y_{44} + Y_{4-4})) + C_{60}\langle r^6\rangle(Y_{60} - (7/2)^{1/2}(Y_{64} + Y_{6-4})).$$

In the point charge model[28],

$$C_{lm} = [4\pi/(2l + 1)]\,(S_{lm}/a_0{}^{l+1})\,e$$

where S_{lm} is the lattice sum given by

$$S^{lm} = a_0{}^{l+1} \sum_{\lambda_j} (q_{\lambda_j}/r_{\lambda_j}{}^{l+1})\, Y_{lm}(\theta_{\lambda_i},\ \phi_{\lambda_j}).$$

Here, a, is the smallest distance between the rare-earth and lattice ions; q_{λ_j} is the λ_j-th ion charge placed at a distance r_{λ_j}. The lattice sum S_{lm} can be computed by Evald's method[26]. For an *NaCl*-type lattice, Wette and Nijboar[27] have evaluated S_{lm}, and found that

$$(4\pi/9)^{1/2} S_{40} = -3.5789,$$
$$(4\pi/13)^{1/2} S_{60} = -0.9895.$$

For CaF_2-type lattices, Vetri and Bassani[15] have obtained

$$(4\pi/9)^{1/2} S_{40} = \ \ 2.715,$$
$$(4\pi/13)^{1/2} S_{60} = -1.939.$$

These results differ from the ones obtained by taking into account only the nearest ions in the lattice sums[28].

The most frequently used crystal field parameters are not the C_{lm}'s but the A_{lm}'s, defined by Stevens[24]. The crystal potential is then defined by

$$V_{cryst} = \sum_{l,m} \xi_l A_{lm} \langle r^l \rangle \hat{O}_{lm}$$

where ξ_l is Stevens's α, β, γ, and $\hat{O}_{lm}$ is the operator equivalent to $Y_{lm}(\theta, \phi)$. The relationships between these parameters for a cubic field are

$$C_{40} = 8\sqrt{4\pi/9}\, A_{40},$$
$$C_{60} = 16\sqrt{\pi/13}\, A_{60}$$

Since for rare-earth ions Russell-Saunders coupling is not valid, the intermediate coupling is used[16] which requires the tensor operator technique[20]. In this case one tries to keep the same crystal field parameter A„, introducing a normalization factor, and obtains

$$V_{cryst} = \sum_{l,m} N_{lm} A_{lm} \langle r^l \rangle U^l_m$$

where U^l_m is a tensor operator equivalent to $Y_{lm}(\theta, 4)$ and N_{lm} is the normalization factor[2].

Summarizing, we can compute the crystal field parameters *A,,* with the point charge model. In order to discuss the validity of the crystal field approximation for rare-earth ions, we will use the values of *(r')* tabulated by us[25] and compare *A,, (r')* with the fitted experimental ones. However, we should choose experimental data on rare-earth ions in crystal matrices which do not distort the lattice too much. Thus, for example, we could choose divalent rare-earth ions in CaF_2-type matrices, or trivalent rare-earth ions in $LaCl_3$-type matrices. For rare-earth ions in CaF_2-type matrices, we have the following tabulated values for $e \cdot A_{lm} \cdot (r')$, in cm^{-1};

	Theoretical values		Experimental values		Reference
	$e\,A_{40}\langle r^4\rangle$	$e\,A_{60}\langle r^6\rangle$	$e\,A_{40}\langle r^4\rangle$	$e\,A_{60}\langle r^6\rangle$	
$Tm^{2+}: CaF_2$	−93	13	−181	27	(29)
$Tm^{2+}: SrF_2$	−65	8	−157	22	(30)
$Dy^{2+}: CaF_2$	−125	19	−235	31	(18)
$Dy^{2+}: SrF_2$	−87	11	−209	28	(18)
$Sm^{2+}: SrF_2$	−147	24	−109	9	(15)

Calculated values of eA_{lm} (r') for some rare-earth ions in CaF_2-type matrices (in cm^{-1})

Taking a look at this Table, one can see that the situation is confusing. The calculated and the experimental values are so much different, that the theory does not seem to even yield a first order approximation. In our opinion, a major part of the inconsistency between the experimental and calculated values comes from errors in the calculated averages *(r')*. As it has been stressed by the authors in another work[25], the averages *(r')* are much dependent on the computational techniques and the assumed exchange correlation energy. (r^6) should be specially sensitive to these small "details" in the computational method, because it depends strongly on the tails of the wave-functions. Thus, it seems that although the atomic calculations can give reliable energy eigenvalues, they are not precise enough for the calculations of the higher moments (r^4) and (r^6). Then, we are led to believe that the results given in the Table above misrepresent the possibilities of the ionic model of the crystal field. Thus one must be careful when trying to correct the ionic model and the crystal field theory to account for effects such as shielding, lattice relaxation, etc. The importance of such effects can be assessed only when better methods for the calculations of *(r')* have been devised.

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References

1. ***G.*** H. Dicke, Spectra and Energy Levels of Rare-earth Ions in Crystals (John Wiley & Sons, Inc. 1968)
2. M. J. Weber and R. W. Biering, Phys. Rev. 134, A1492 (1968).
3. H. A. Bethe, Ann. Phys. **3,** 133 (1929).
4. J. H. Van Vleck, Journ. Chem. Phys. 7, 72 (1939).
5. J. H. Van Vleck, Journ. Chem. Phys. 8, 790 (1940).
6. W. Low, Solid State Physics, edited by F. D. Seitz and Turnbull (Academic Press Inc., New York, 1960), Suppl. 2.
7. A. J. Freeman and R. E. Watson, Phys. Rev. 127, 2058 (1962)
8. C. K. Jorgensen, R. Pappalardo and H. H. Schmidtke, Journ. Chem. Phys. **39,** 1422 (1963)
9. R. Faulhaber and S. Hufner, Sol. Stat. Comm. 7, 389 (1969)
10. G. Burns, Phys. Letters (Netherlands) 25A, 15 (1967)
11. J. D. Axe and G. Burns, Phys. Rev. 152, 331 (1966)
12. R. E. Watson and A. J. Freeman, Phys. Rev. 156, 251 (1967)
13. G. Burns, Phys. Rev. 128, 2121 (1962)
14. R. E. Watson and A. J. Freeman, Phys. Rev. 133, A 1571 (1964).
15. G. Vetri and F. Bassani, Nuovo Cimento 55B 504 (1968).
16. G. B. Wybourne, Journ. Chem. Phys. 32, 639 (1965); Journ. Chem. Phys. 34, 279 (1961); Journ. Chem. Phys. 36, 230 (1962).
17. B. Dreyfus, M. Veyssie, and J. Verdone, Journ. Chem. Solids 26, 107 (1965).
18. Z. J. Kiss, Phys. Rev. 137, A 1749 (1965).
19. A. V. Carvalho, M. Sc. Thesis, ***Universidade Federal de Minas Gerais. Brasil*** (1969).
20. 3. P. Elliott, B. R. Judd, and W. A. Rucimam, Proc. Roy. Soc. (London) A240, 509 (1957).
21. M. L. Siqueira, Doctoral Thesis, ***Uniuersidade de*** São ***Paulo, Brasil*** (1968).
22. ***K.*** R. Lea, M. J. M. Leask and W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).
23. Y. Ebina and M. Tsuya, Rep. Res. Inst. Elect. Comm. Toho-Ku univ. B-12, 167-183 (1960) and B-13, 25-43 (1967).
24. K. W. H. Stevens, Proc. Phys. Soc. (London) A65, 209 (1952).
25, D. E. Laborne e Valle and M. L. Siqueira "Moments of radial function distributions for the rare-earth ions and their dependence on the calculation method to be published.
26. P. P. Ewald, Ann. Physik 64, 253 (1921).
27. F. W. De Wette and B. R. A. Nijboer, Physica 23, 309 (1957).
28. M. T. Hutching, Solid State Physics, Edited by F. Seitz and D. Turnbull (Academic Press Inc., N. York, 1965) Vol. 16
29. B. Bleaney, Proc. Roy. Soc. A277, 289 (1964)
30. J. D. Axe and G. Burns, Phys. Rev. 152, 331 (1966)