

MAGNETIC LINEAR BIREFRINGENCE IN RARE EARTH SYSTEMS. SECOND-ORDER APPROACH

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Out of my fondest memories of bonfires at Bachotek Schools during the hot times prior to political changes in our countries, I dedicate this paper to my good friends Petr, Ivan and Miro on the occasion of their special birthdays.

An analysis defines the improved version of the theoretical model of magnetic linear birefringence in rare earth doped materials developed and applied in several papers of Kolmakova *et al.* The approach presented here is formulated in the language of tensor operators instead of equivalent Stevens objects, and in addition the radial terms of the effective operators contributing to the polarizability tensor are all defined for the complete radial basis sets of one-electron functions. The approach is based on perturbation theory. The effective operators represent the perturbing influence of singly excited configurations $4f^{N-1}n'\ell'$ for $\ell' = d, g$ and **all** n' . The model is defined within the single configuration approximation, and it addresses especially the problem of evaluation of the radial integrals. The discussion of the tensorial form of the effective operators is completed by the numerical values of appropriate radial integrals evaluated for the ions across the lanthanide series to be used in future theoretical analysis.

Keywords: Rare earth ions; Lanthanides; Magnetic anisotropy; Polarizability tensor; Effective tensor operators; Perturbation theory; Perturbed function approach.

There is an extensive interest in development of paramagnetic liquid crystals that, to align them, require a much weaker magnetic field than in the case of diamagnetic samples. This property is especially attractive because of the wide applications of such materials. However, this property to be observed requires large magnetic anisotropy of the material. In fact the orientation of a liquid crystal in a magnetic field depends not only on the magnitude, but also on the sign of the magnetic anisotropy. It has been found¹ that the lanthanides are divided into two groups of ions that differ from each other by sign of their magnetic anisotropy. The features and behavior of a sample in a magnetic field are determined by measuring the

magnetic birefringence that is in turn used to determine the sign of magnetic anisotropy. Therefore, it is crucial for further applications of various materials, and for the modelling of specific devices, to formulate a precise theoretical model of magnetic birefringence of lanthanide doped materials, and to verify which physical mechanisms in its description are the dominant ones.

The inspiration for the research on the theoretical description of the magnetic birefringence in lanthanide doped systems was found in a series of interesting papers by Kolmakova and her collaborators²⁻⁴; the demand for a more precise model than that presented previously is reinforced by the statement in which the authors realize “*insufficient accuracy in the value of radial integrals and mean energies $\hbar\omega_0$, and neglect of contributions due to transitions to higher excited configurations $4f^{N-1}5g, \dots$, which in general cannot be disregarded*”.

The novel features of the present investigation cover the discussion of the polarizability tensor expressed in terms of effective tensor operators that act within the $4f^N$ configuration of the lanthanide ion. In addition, the problem of evaluation of the radial integrals of the second-order contributions for the complete radial basis sets of one-electron excited states of a given symmetry is solved within the perturbed function approach. The approach is illustrated by the results of numerical calculations performed for all the lanthanide ions.

EFFECTIVE OPERATORS OF SECOND ORDER

The basic formula for the polarizability tensor is very similar to the Heisenberg–Kramers expression that describes the two photon processes like electronic Raman scattering or two photon absorption⁵⁻⁹; the only difference is that the final and the initial states in the matrix elements of a product are the same. Thus the polarizability tensor is defined by a term of second-order of time dependent perturbation theory applied for the description of interactions between the matter and radiation field

$$\alpha_{\rho_1\rho_2} = \sum_{Xx} \left\{ \frac{\langle 4f^N \psi | D_{\rho_1}^{(1)} | Xx \rangle \langle Xx | D_{\rho_2}^{(1)} | 4f^N \psi \rangle}{(\hbar\omega - \Delta E_{4f^N, X})} - \frac{\langle 4f^N \psi | D_{\rho_2}^{(1)} | Xx \rangle \langle Xx | D_{\rho_1}^{(1)} | 4f^N \psi \rangle}{(\hbar\omega + \Delta E_{4f^N, X})} \right\}, \quad (1)$$

where Xx are various states of intermediate (singly excited) configurations X of opposite parity to the parity of configuration $4f^N$. In Eq. (1) the standard 3^2 components of polarizability tensor defined in Cartesian coordinates are numbered by the nine pairs of possible combinations of components ρ_1 and ρ_2 of tensor operators of electric dipole radiation

$$D_\rho^{(1)} = \sum_i r_i C_\rho^{(1)}(\vartheta_i, \varphi_i).$$

It is a common practice to describe the properties of lanthanide doped materials in the language of the Judd–Ofelt theory of one-photon $f \leftrightarrow f$ electric dipole transitions^{10,11}. This means that the theoretical model is defined within the single configuration approximation and is based on perturbation theory. Thus, adopting the assumptions and approximations of the standard Judd–Ofelt theory, one can express the polarizability tensor in terms of effective operators that act only within the $4f^N$ configuration. As a result of the so-called partial closure, the polarizability tensor has the form

$$\alpha_{\rho_1\rho_2}^{kq} = \sum_{kq} \alpha_{\rho_1\rho_2}^{kq},$$

where

$$\alpha_{\rho_1\rho_2}^{kq} = \mathcal{A}(\rho_1\rho_2; kq) X_k^\omega \langle 4f^N \psi | U_q^{(k)} | 4f^N \psi \rangle, \quad (2)$$

where $U^{(k)}$ is the unit tensor operator with rank k , and \mathcal{A} depends on the directions (components) in the following way

$$\mathcal{A}(\rho_1\rho_2; kq) = (-1)^q \begin{pmatrix} 1 & 1 & k \\ \rho_1 & \rho_2 & -q \end{pmatrix}. \quad (3)$$

The angular and radial parts of the effective operator that determines the components of the polarizability tensor have the form

$$X_k^\omega = 2 \sum_{\ell'} A_1^k(\ell') R_1(\ell') (-\epsilon_k + \epsilon_k^* \xi_{\ell'}(\omega)), \quad (4)$$

where the angular part is the standard term of Judd–Ofelt theory, and in general is defined as follows

$$A_t^k(\ell') = [k]^{1/2} \begin{Bmatrix} t & k & 1 \\ f & \ell' & f \end{Bmatrix} \langle \ell || C^{(1)} || \ell' \rangle \langle \ell' || C^{(t)} || \ell \rangle$$

and $\epsilon_k = 1$ and $\epsilon_k^* = 1$ for k even and k odd, respectively, otherwise they both vanish; ℓ' describes one-electron states of d- and g-symmetry (the even values of ℓ' are required by the selection rules for the non-vanishing reduced matrix element of the spherical tensor). $\xi_{\ell'}(\omega)$ is an approximate factor present for the asymmetric contributions to the polarizability tensor (for k odd), and it is defined as follows

$$\xi_{\ell'}(\omega) = \frac{\hbar\omega}{\epsilon_{n\ell'} - \epsilon_{4f}} \equiv \frac{\hbar\omega}{\epsilon_{5\ell'} - \epsilon_{4f}},$$

where the energy of the first excited one-electron states of ℓ' symmetry allowed by the selection rules is used. Due to this approximation of the energy denominators, it is possible to perform partial closure also for the terms with k odd, and as a consequence to derive an effective operator form of the expression.

It is seen from Eq. (3) that due to the condition for the non-vanishing $3j$ -symbol, k must be even when $\rho_1 = \rho_2 = 0$; while in a general case, due to the triangular conditions of this $3j$ -symbol, $k = 0, 1, 2$. Thus, in general, the polarizability tensor is determined in terms of effective operators by tensor operators of three possible ranks: 2 ($q = -2, -1, 0, 1, 2$), 1 ($q = -1, 0, 1$), and 0 ($q = 0$) that give the nine required components in a different representation. It should be mentioned that the expression for the polarizability in Eq. (1) differs from the basic expression for the scattering amplitude or two-photon absorption amplitude. Therefore the scalar product of electric dipole operators in Eq. (1) also gives nonzero contributions. In addition, there are symmetric terms for $k = 2$ as well as asymmetric terms for $k = 1$ (similarly as in the case of electronic Raman scattering).

As mentioned, there is an additional contribution to the polarizability tensor for $k = 0$, and it has the simple form

$$\alpha_{\rho-\rho}^{00} = (-1)^\rho \frac{2}{3\sqrt{7}} \sum_{\ell'} \langle \ell || C^{(1)} || \ell' \rangle^2 R^1(\ell').$$

The radial term in Eq. (4) is defined as a product of two radial integrals with appropriate energy denominators, namely

$$R^1(\ell') = \sum_{n'} \frac{\langle 4f | r^1 | n' \ell' \rangle \langle n' \ell' | r^1 | 4f \rangle}{(\epsilon_{4f} - \epsilon_{n' \ell'})}, \quad (5)$$

where the original energy denominators from Eq. (1) have been expressed in the terms of series of $(1 \pm x)^{-1}$ for $x = \hbar\omega / (\epsilon_{4f} - \epsilon_{n' \ell'})$, assuming that $0 < x < 1$, and limiting the expansion to the first two terms (for details of this procedure see ref.⁷). In such a way it is possible to redefine the radial term including the troublesome summation over the complete radial basis set of one-electron states of ℓ' symmetry within the definition of a new function, the so-called perturbed function¹². As a result, the radial terms of the effective operator of polarizability tensor have the form

$$R^1(\ell') = \langle \rho^1(4f \rightarrow \ell') | r^1 | 4f \rangle, \quad (6)$$

where each perturbed function $\rho^1(4f \rightarrow \ell')$ contains all the first-order corrections due to the perturbing influence of all singly excited configurations $4f^{N-1} n' \ell'$, for **all** n' , and it is defined as follows

$$\rho^t(4f \rightarrow \ell') = \sum_{n'} \frac{\langle 4f | r^t | n' \ell' \rangle}{(\epsilon_{4f} - \epsilon_{n' \ell'})} P_{n' \ell'}. \quad (7)$$

In Table I distinct contributions to the polarizability tensor are presented. In the case of asymmetric components the presence of the energy factor ξ is denoted to demonstrate that these parts of the polarizability tensor depend on the energy of the incident beam.

The terms in Table I are numbered by the values of the components of distinct electric dipole operators present in the original formula. In the case of effective polarizability, the components are distinguished by the rank of the unit tensor operator $U^{(k)}$ in Eq. (2), $\alpha_{\text{eff}} \Rightarrow \alpha_q^{(k)} = \sum_{\rho_1 \rho_2} \alpha_{\rho_1 \rho_2}^{kq} \delta(\rho_1 + \rho_2, q)$. Thus, inspection of Table I leads to the conclusion that $\alpha_q^{(2)}$ has the following components (see the solid lines in Table I)

$$\alpha_{-2}^{(2)} = \alpha_{-1-1}^{2-2}$$

$$\alpha_{-1}^{(2)} = 2\alpha_{-10}^{2-1}$$

$$\alpha_0^{(2)} = \alpha_{00}^{20} + 2\alpha_{-11}^{20}$$

$$\alpha_1^{(2)} = 2\alpha_{10}^{21}$$

$$\alpha_2^{(2)} = \alpha_{11}^{22}.$$

In the case of asymmetric terms, for $k = 1$, due to the asymmetry of the coefficient \mathcal{A} defined by Eq. (3), and because the remaining part of the effective operator is independent of ρ_1 and ρ_2 , the contributions $\alpha_q^{(1)}(\xi) = 0$ for $q = \pm 1, 0$ (see the dotted lines in Table I). In order to obtain the tensor in terms of Cartesian components, the unitary transformation has to be applied (see Appendix). The vanishing of asymmetric contributions reduces the expression for the off-diagonal components $\alpha_{x_i x_j}$ for $i \neq j$, and as expected from a general consideration rather than from symmetry properties, this leads to a symmetric matrix of polarization tensor with three out of six components being different.

The diagonal components, defined by linear combinations of $\alpha_q^{(2)}$ for $q = \pm 2, 0$, are modified by additional contributions that are due to the scalar effective operator $\alpha_0^0 = 2\alpha_{-11}^{(00)}$.

TABLE I
Second-order contributions to the polarizability tensor $\alpha_{\rho_1 \rho_2}^{kq}$

$\rho_2 \backslash \rho_1$	-1	0	1
-1	α_{-1-1}^{2-2}	$\alpha_{-10}^{1-1}(\xi)$ α_{-10}^{2-1} α_{-10}^{2-1}	α_{-11}^{00} $\alpha_{-11}^{10}(\xi)$ α_{-11}^{20}
0	$-\alpha_{-10}^{1-1}(\xi)$ α_{-10}^{2-1}	α_{00}^{20}	$\alpha_{01}^{11}(\xi)$ α_{01}^{21}
1	α_{-1-1}^{00} $-\alpha_{-11}^{10}(\xi)$ α_{-11}^{20}	$-\alpha_{01}^{11}(\xi)$ α_{01}^{21}	

NUMERICAL ILLUSTRATION

The properties of the electronic structure of lanthanide ions are represented in the expression for the polarizability tensor by the radial terms. The angular parts of each effective operator are the same for all ions across the series. Furthermore, the polarizability in each state is modulated individually by the values of diagonal matrix elements of unit tensor operators between the functions describing a particular state. It is obvious then that the accuracy of the second-order approach depends on the quality of the wavefunctions applied for the evaluation of these matrix elements (assuming that the other parts of polarizability tensor, especially the radial integrals, are evaluated exactly).

The radial integrals defined in Eq. (6) contain the perturbed function that is typical for the standard Judd–Ofelt theory of one-photon $f \leftrightarrow f$ transitions. Each of these functions describes the perturbing influence of single excited configurations in which the 4f electron is promoted to the excited states of d- or g-symmetry. It should be pointed out, that in Eq. (7) the summation over n' covers all one-electron excited states, including the continuum. Thus, the perturbed functions contain the impact due to all excitations from 4f shell to $n'd$ and $n'g$, for all n' .

The perturbed functions are the solutions of differential equations that are very similar to the hydrogen equation. These functions have very atomic-like features possessing the same number of nodes as the first excited one-electron state of a given symmetry, and they are localized closer to the origin than the first excited state (the graphical representation of the perturbed functions is discussed in ref.¹³).

The values of the radial integrals discussed here and all the other that are present in the model of Judd and Ofelt, evaluated for all lanthanide ions, are reported in ref.¹⁴; the values of integrals of the particular case that contribute to the polarizability, $R^1(d)$ and $R^1(g)$, for all lanthanides, are plotted in Fig. 1. It is seen from this figure that both curves are very smooth, and the character of changes with increasing number of 4f electrons is very similar for both types of excitations. It is seen also that there is no similarity or any correlation between the values of integrals for complementary systems that possess the same number of electrons or holes.

In order to present atomic-like properties of perturbed functions, in Fig. 2 the values of $R^1(g)$ are compared with those of radial integrals evaluated with the atomic function of Hartree–Fock model $\langle 4f|r|4f \rangle$, as an example. Obviously the values of both types of integrals are different, the physical interpretation of functions involved is different (as a matter of fact, the per-

turbed function as a linear combination of various contributions defined by Eq. (7) does not have physical interpretation), and still the behavior across the lanthanide series is so similar that the curves in Fig. 2 are almost the same, but shifted in relation to each other.

The values of the angular parts that contribute to the components of polarizability tensor are the same for all lanthanides ions, and their ratio is

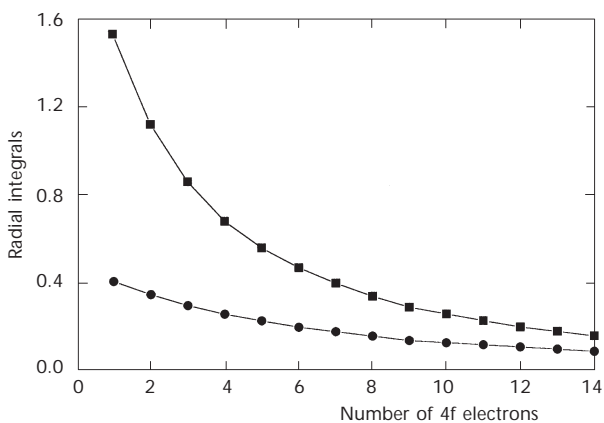


FIG. 1

Values of radial integrals $R^1(d)$ (■) and $R^1(g)$ (●) for ions across the lanthanide series

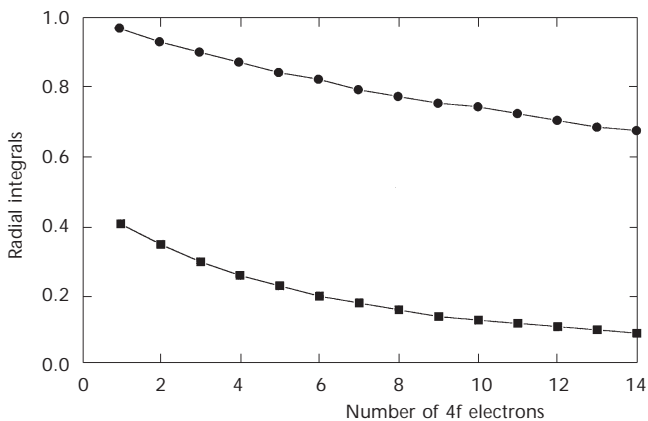


FIG. 2

Comparison of the values of $R^1(g)$ (■) with the values of $\langle 4f|r|4f \rangle$ (●) for the ions across the lanthanide series

$A_1^2(\text{d}) / A_1^2(\text{g}) = 1.8$. Since the non-zero part of polarizability tensor is associated only with the operators of rank 2, in practical calculations only X_2 from Eq. (4) has to be included. In this particular case, for k even, X_2 is independent of the energy of the incident beam ω and it has the following simple form

$$X_2 = -2(1.8\eta + 1),$$

where $\eta = R^1(\text{d})/R^1(\text{g})$, and the value of the ratio of the angular parts is used.

In Fig. 3 the values of η for all lanthanide ions are plotted. It is seen from this figure that the excitations from the 4f shell to one-electron states of d-symmetry are relatively more important than those to the g-states. The value of η decreases with increasing number of 4f electrons from 3.75 for Ce^{3+} to 1.79 for Lu^{3+} . It is apparent, however, that the excitations to the states of g-symmetry are not negligible, and have to be taken into account in any reliable numerical analysis. Finally, it should be pointed out, that the conclusions presented here are based on the results of *ab initio* calculations, since the radial integrals are evaluated in an exact way.

FINAL REMARKS

It is demonstrated here that it is a rather simple task to evaluate the second-order contributions to the polarizability tensor when the radial integrals are

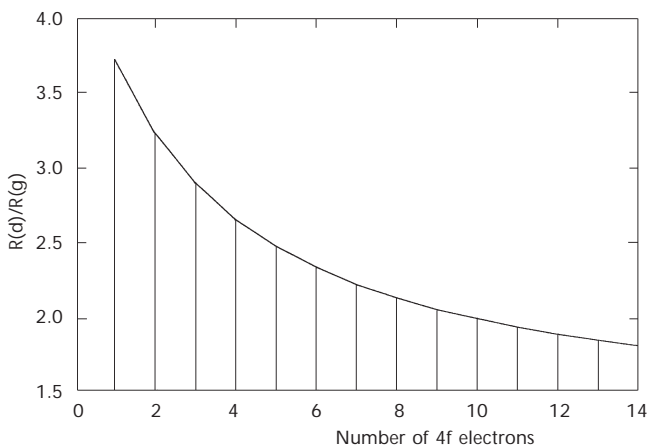


FIG. 3
Values of $\eta = R^1(\text{d})/R^1(\text{g})$ for all lanthanide ions

known. Indeed, for a given lanthanide ion, the polarizability defined in accordance with Eq. (2) has a simple form

$$\alpha_{\rho_1\rho_2}^{2q} = -2(1.8\eta + 1)\mathcal{A}(\rho_1\rho_2; 2q) \langle 4f^N\psi | U_q^{(2)} | 4f^N\psi \rangle. \quad (8)$$

The scalar part of the polarizability has the form

$$\alpha_{1-1}^{00} = \alpha_{-11}^{00} = \frac{1}{\sqrt{7}} \left(\frac{1}{\sqrt{3}} \eta - 2 \right),$$

where $\eta = R^1(d)/R^1(g) \equiv \langle \rho^1(4f \rightarrow d) | r^1 | 4f \rangle / \langle \rho^1(4f \rightarrow g) | r^1 | 4f \rangle$.

The expressions presented above are based on the free ionic system approximation, and the only impact due to the crystal field surrounding the lanthanide ion is introduced through the wave functions ψ used for the evaluation of the matrix elements of the unit tensor operator. This means that no direct influence of the crystal field upon the polarizability tensor is taken into account.

The expressions for the polarizability tensor are based on the single configuration approximation, and it does not contain the impact due to correlation effects. This means that no direct influence of the noncentral part of Coulomb interaction upon the polarizability tensor is taken into account.

The expressions above **do** include the impact caused by **all** singly excited configurations of the opposite parity to the parity of $4f^N$ configuration, and they give reliable point for further improvement of the theoretical model of very subtle properties of materials doped with lanthanides.

In the final conclusions of Kolmakova's paper² it is written: "*This finding indicates that a more detailed theoretical approach involving the splitting of excited configurations by the spin-orbit, crystal field, and electron correlation effects is needed in general*".

This quotation defines the next steps of research. Due to the sensitivity of magnetic birefringence to the influence of crystal field¹⁴, it is especially important to improve the model by third-order contributions that represent a direct perturbing influence of surroundings of the lanthanide ion.

APPENDIX

In order to simplify the numerical calculations for a particular sample for which the symmetry properties might be used, the Cartesian components

of the polarizability tensor are presented here in the terms of the contributions defined in Eq. (2):

$$\alpha_{xx} = \frac{1}{2}(\alpha_{11}^{22} + \alpha_{-1-1}^{2-2}) - \frac{1}{\sqrt{6}}(\alpha_{00}^{20} + 2\alpha_{-11}^{20} + 2\sqrt{2}\alpha_{-11}^{00})$$

$$\alpha_{yy} = \frac{1}{2}(-\alpha_{11}^{22} - \alpha_{-1-1}^{2-2}) - \frac{1}{\sqrt{6}}(\alpha_{00}^{20} + 2\alpha_{-11}^{20} + 2\sqrt{2}\alpha_{-11}^{00})$$

$$\alpha_{zz} = \frac{\sqrt{2}}{\sqrt{3}}(\alpha_{00}^{20} + 2\alpha_{-10}^{20}) - \frac{2}{\sqrt{3}}\alpha_{-11}^{00}$$

$$\alpha_{xy} = \alpha_{yx} = \frac{i}{2}(\alpha_{11}^{22} + \alpha_{-1-1}^{2-2})$$

$$\alpha_{xz} = \alpha_{zx} = (\alpha_{10}^{21} + \alpha_{-10}^{2-1})$$

$$\alpha_{yz} = \alpha_{zy} = i(-\alpha_{10}^{21} + \alpha_{-10}^{2-1}).$$

All the contributions are determined by the matrix elements of unit tensor operators $U_q^{(2)}$; only the diagonal terms are modified by α_{-11}^{00} that is independent of an electronic state.

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REFERENCES

1. Mironov V. S., Galyametdinov Y. G., Ceulemans A., Binnemans K.: *J. Chem. Phys.* **2000**, *113*, 10293.
2. Kolmakova N. P., Levitin R. Z., Popov A. I., Vedernikov N. F., Zvezdin A. K., Nekvasil V.: *Phys. Rev. B: Condens. Matter* **1990**, *41*, 6170.
3. a) Kolmakova N. P., Popov A. I.: *Physica B (Amsterdam)* **1990**, *162*, 71; b) Kolmakova N. P., Popov A. I.: *Physica B (Amsterdam)* **1992**, *179*, 19.
4. Kazei Z. A., Kolmakova N. P., Sidorenko A. A., Snegirev V. V.: *J. Exp. Theor. Phys.* **2001**, *92*, 701.
5. Smentek-Mielczarek L., Hess B. A., Jr.: *Phys. Rev. B: Condens. Matter* **1987**, *36*, 1811.

6. Smentek-Mielczarek L., Hess B. A., Jr.: *J. Chem. Phys.* **1989**, *90*, 1390.
7. a) Smentek-Mielczarek L.: *Phys. Rev.* **1989**, *40*, 2019; b) Smentek-Mielczarek L.: *Phys. Rev.* **1989**, *40*, 6499.
8. Smentek-Mielczarek L.: *J. Chem. Phys.* **1991**, *94*, 5369.
9. a) Smentek-Mielczarek L.: *Phys. Rev. B: Condens. Matter* **1992**, *46*, 14453; b) Smentek-Mielczarek L.: *Phys. Rev. B: Condens. Matter* **1992**, *46*, 14460; c) Smentek-Mielczarek L.: *Phys. Rev. B: Condens. Matter* **1992**, *46*, 14467.
10. Judd B. R.: *Phys. Rev.* **1962**, *127*, 750.
11. Ofelt G. S.: *J. Chem. Phys.* **1962**, *37*, 511.
12. Jankowski K., Smentek-Mielczarek L., Sokolowski A.: *Mol. Phys.* **1986**, *59*, 1165.
13. Smentek-Mielczarek L.: *J. Chem. Phys.* **1994**, *101*, 5363.
14. Smentek L.: *Mol. Phys.*, in press.
15. Zvezdin A. K., Popov A. I., Turkmenov K. I.: *Sov. Phys. Solids* **1986**, *28*, 974.