

DYNAMIC ORBIT-LATTICE INTERACTIONS FOR $\text{PbF}_2:\text{Gd}^{3+}$ SINGLE CRYSTALS*

J. KURIATA, T. REWAJ

Institute of Physics, Technical University of Szczecin, Al. Piastów 17, 70-310 Szczecin,
Poland

AND N. GUSKOS

Department of Physics, University of Athens, Solonos Str. 104, 10677 Athens, Greece

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Temperature dependence of the second-order spin-lattice coefficients for $\text{PbF}_2:\text{Gd}^{3+}$ is reported. It is shown that the thermal expansion of the crystal lattice contributes only in about 14% to the observed dependence and the rest should be ascribed to a dynamic coupling between the $4f^7$ electrons and lattice vibrations. The results are parametrized in both the Einstein and the Debye models and it is shown that the phenomenological parameters obtained from such parametrization can be made to coincide in both models if a specific value of the Einstein frequency ω_E is properly chosen. Both models of parametrization show that the Γ_{3g} vibrating mode couples to the $4f^7$ electrons much weaker than the Γ_{5g} one.

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1. Introduction

The problem of the determination of the role played by dynamic orbit-lattice interaction for S -ground state ions embedded in a crystalline environment has gained much interest because it can essentially contribute to a better understanding of the zero-field splitting and relaxation phenomena (e.g. [1, 2]). It has now become quite apparent that a theory principally based on the simple and rather naive point-charge approach to the orbit-lattice interactions predicts insignificant contributions resulting from a lattice dynamics to the zero-field splitting of the

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S-ground state ions [3–5] compared to some estimations derived from the experiment (e.g. [5–14]). Therefore, it is commonly felt that an approach based on the molecular orbital method, so that one could include covalency and overlap effects, should rather be used in order to solve the problem adequately. However, such an approach which obviously has to combine the knowledge of an explicit form of molecular orbitals built for the complex under discussion with the way in which these orbitals couple with lattice vibrations is certainly extremely difficult to carry out and, as far as we know, has not yet been carried out for rare-earth complexes (although some quite promising calculations were done for the *S*-ground state iron in complexes [2, 15]). In this situation the results of systematic experimental studies become very valuable because they can allow for at least a phenomenological description of the dynamic coupling between the $4f^7$ electrons and lattice vibrations.

It should be pointed out, however, that the analysis of the experimental data is also very much complicated by the fact that the "static" effects of the temperature induced changes of the spin-Hamiltonian parameters, due to thermal expansion of the crystal, are very difficult to separate from the effects originating from lattice vibrations. According to Walsh et al. [16] the temperature dependence of a spin-Hamiltonian parameter b can be represented as:

$$\left(\frac{\partial b}{\partial T}\right)_P = \left(\frac{\partial b}{\partial T}\right)_{R_L} + \left(\frac{\partial b}{\partial R_L}\right)_T \left(\frac{\partial R_L}{\partial T}\right)_P. \quad (1)$$

Here, the second term on the right side of the equation represents the contribution resulting from thermal expansion, whereas the first term represents the contribution from lattice vibrations. The contributions of these two terms can be estimated by comparing the measured temperature dependence of a spin-Hamiltonian parameter with the data derived from hydrostatic [17] or uniaxial [18] EPR stress experiments. This latter method has been used in [19] for the case of the b_4^0 spin-Hamiltonian parameter where it was found that the contribution due to the effect of thermal expansion is $88.2 \pm 77.8\%$ of the total temperature dependence observed. Obviously, in view of the large experimental error, such an estimation is highly uncertain. Serious difficulties, appearing during the interpretation of the b_4^0 spin-Hamiltonian for $\text{PbF}_2:\text{Gd}^{3+}$ and resulting from the lack of the exact knowledge of the role played by vibronic effects, have recently been discussed in [20].

The objective of this paper is to discuss the temperature dependence of the rank-2 spin-Hamiltonian parameters corresponding to the crystal field terms of Γ_{3g} and Γ_{5g} symmetry induced in the local environment of Gd^{3+} in PbF_2 by the application of an external uniaxial stress. Such studies are interesting not only in the context discussed above but also in view of the fact that PbF_2 possesses many physical properties, more or less related with its lattice dynamics, which distinguish it from other MF_2 crystals ($M = \text{Cd}, \text{Ca}, \text{Sr}, \text{Ba}$). These properties are: the existence of two phases (α -phase orthorhombic D_{2h}^{16} and β -phase cubic O_h^5 , the latter being metastable below 583 K [21]), abnormally low melting point [21], low value of the Debye temperature Θ_D [22] and superionicity [23]. With the help of *S*-ground state ions introduced into the PbF_2 lattice, this latter property is frequently studied by investigation of temperature induced changes in the

spin-Hamiltonian parameters [24–25]. In the case of such studies the prior determination of the limitations imposed on these changes by thermal expansion and lattice vibrations is, certainly, of paramount importance.

2. Experimental

PbF_2 single crystal doped with Gd^{3+} was supplied to us by Dr J.M. Baker from the Clarendon Laboratory, University of Oxford. For the uniaxial stress experiment the crystal was first subjected to the X-ray orientation procedure and then precision cutting was done so that the stress could be applied along the [110] direction and the observation of the stress induced EPR line shifts could be carried out with the orientation of the steady magnetic field parallel to [100], [110] and [111] directions. The sample had a form of a parallelepiped with the dimensions of $1 \times 1 \times 40 \text{ mm}^3$. The maximal stress applied did not exceed $3 \times 10^7 \text{ Pa}$ and measurements were carried out in the temperature range from 130 to 600 K using a standard X-band EPR spectrometer with the 100 kHz modulation of the steady magnetic field. The stress induced shifts of the EPR lines were controlled using a digital proton NMR magnetometer type MJR-110.

3. Results and discussion

The EPR spectrum of $PbF_2:Gd^{3+}$ observed for the undeformed sample could be described, for the whole temperature range, by the conventional spin-Hamiltonian for a cubic local symmetry of Gd^{3+} :

$$\mathcal{H} = \frac{b_4^0}{60} (O_4^0 + 5O_4^4) + \frac{b_6^0}{1260} (O_6^0 - 21O_6^4) \quad (2)$$

with the values of the spin-Hamiltonian parameters b_n^m being consistent with those reported in [26].

During the experiment we did not notice a necessity to complete (2) with any additional term, apart from that introduced by the perturbation caused by the uniaxial stress and given below, over the whole range of temperatures and stresses. This means that during the experiment the cubic local symmetry around Gd^{3+} was maintained and no structural phase transitions of the type reported, for example, by Klement and Cohen [27] were detected. The observed cubic symmetry means also that the mechanism of the compensation of an excessive charge of Gd^{3+} , which replaces Pb^{2+} in the lattice, is predominantly of the remote type [28]. However, the analysis of the superhyperfine structure observed at 77 K indicated that the EPR line corresponding to $-3/2 \longleftrightarrow -1/2$ electronic transition may consist of a superposition of two lines: one coming from cubic and one from low-symmetry sites [29].

The effect of the applied stress was, according to the method given by Calvo et al. [18], described by a perturbation of the following form:

$$\mathcal{H}_{S-L} = \sum_{n,i,\alpha} G_{\Gamma_i}^{(n)} O_{i,\alpha}^{(n)} \mathcal{E}_{i,\alpha}. \quad (3)$$

Here, $G_{\Gamma_{1g}}^{(n)}$ are constants called the spin-lattice coefficients, describing the coupling of the $4f^7$ electrons to stress induced crystal field terms transforming according to Γ_{ig} irreducible representations of the cubic group O_h . The remaining symbols appearing in (3) have their usual meaning.

As follows from (3) (to the first order of perturbation calculations), the shifts of the EPR lines for two conjugate electronic transitions (i.e. $\pm M_S \longleftrightarrow \pm M_S + 1$) should be identical, as far as their absolute values are taken into account, and zero for the $-1/2 \longleftrightarrow +1/2$ transition. Only slight discrepancies between absolute values of the shifts were measured for the conjugate transitions, what together with a shift observed for the $-1/2 \longleftrightarrow +1/2$ electronic transition, incline us to ascribe them rather to the effect of a stress induced change in the g -value, a phenomenon first reported for the $^8S_{7/2}$ ground state ions in [30], than to the effect due to a possible presence of low-symmetry centres.

Due to a large experimental error, reaching about 80%, we were unable to measure the temperature dependence of the rank-4 spin-lattice coefficients. The averaged values of these parameters are as follows: $G_{\Gamma_{1g}}^{(4)} = 3.6 \times 10^{-4} \text{ cm}^{-1}$, $G_{\Gamma_{3g}}^{(4)} = -1.6 \times 10^{-4} \text{ cm}^{-1}$ and $G_{\Gamma_{5g}}^{(4)} = 1.7 \times 10^{-4} \text{ cm}^{-1}$. However, as reported previously for other MF_2 single crystals doped with Gd^{3+} and Eu^{2+} [6, 7, 10-13], substantial temperature-induced changes are found for both second-order spin-lattice coefficients $G_{\Gamma_{3g}}^{(2)}$ and $G_{\Gamma_{5g}}^{(2)}$. For the case investigated here, these changes are shown in Fig. 1 and Fig. 2.

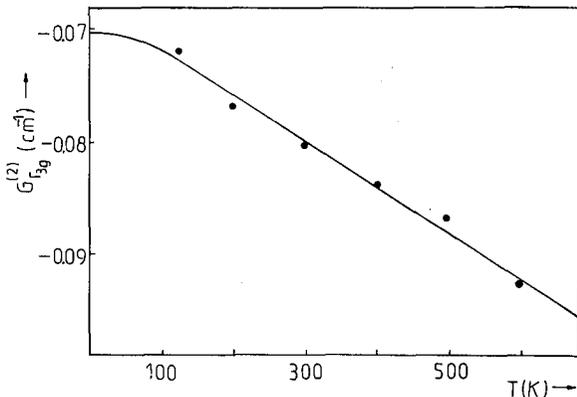


Fig. 1. The temperature dependence of the $G_{\Gamma_{3g}}^{(2)}$ spin-lattice coefficient for $\text{PbF}_2:\text{Gd}^{3+}$. The continuous line represents the best fit plot to eq. (7).

In order to determine the contribution introduced by the effect of thermal expansion of the crystal we shall first calculate the value of the power exponent describing the dependence of $G_{\Gamma_{3g}}^{(2)}$ on the metal-ligand distance R_L appearing in the following relation: $G_{\Gamma_{3g}}^{(2)} \propto R_L^{-t_2}$. We extrapolate (linearly) the results presented

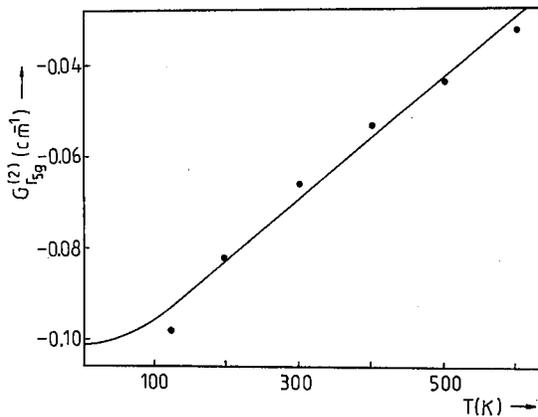


Fig. 2. The temperature dependence of the $G_{F_{3g}}^{(2)}$ spin-lattice coefficient for $\text{PbF}_2:\text{Gd}^{3+}$. The continuous line represents the best fit plot to eq. (7).

in Fig. 1 and Fig. 2 to $T = 0\text{ K}$ to obtain values of $G_{F_{3g}}^{(2)}(\text{RL})$ and $G_{F_{3g}}^{(2)}(\text{RL})$ (i.e. the values corresponding to the "rigid" lattice) and then we apply the relation given in [31]:

$$t_2 = 1 - 2G_{F_{3g}}^{(2)}(\text{RL})/G_{F_{3g}}^{(2)}(\text{RL}). \quad (4)$$

Inserting our values of $G_{F_{3g}}^{(2)}(\text{RL})$ we obtain $t_2 = -1.88$. The low and negative value of t_2 found for $\text{PbF}_2:\text{Gd}^{3+}$ is consistent with the data obtained for other systems [12, 32-33]. The effect of thermal expansion can be estimated, neglecting higher order terms in α , from:

$$\frac{1}{G_{F_{3g}}^{(2)}} \frac{\partial G_{F_{3g}}^{(2)}}{\partial T} \approx t_2 \alpha, \quad (5)$$

where α is the thermal expansion coefficient.

For pure PbF_2 single crystals $\alpha = 29 \times 10^{-6} \text{ K}^{-1}$ [22] and thus eq. (5) assumes the value of $5.45 \times 10^{-5} \text{ K}^{-1}$. However, the value of α around the impurity Gd^{3+} ion can be different from the value for the pure lattice. As far as we know, no experimental data have been given so far for the value of the local thermal expansion coefficient and therefore we have to recourse to the Grüneisen equation relating thermal expansibility with compressibility through:

$$\alpha = \frac{\gamma C_p}{3VB_s}, \quad (6)$$

where γ is the Grüneisen constant, C_p is the lattice heat capacity at constant pressure, V is the mole volume and B_s is the adiabatic bulk modulus. For PbF_2 the above parameters have been determined by Roberts and White [22] and are as follows: $\gamma = 2.33$, $C_p = 24.5 \text{ J (mole)}^{-1} \text{ K}^{-1}$, $V = 10.5 \text{ cm}^3$ and $B_s = 62.5 \text{ GPa}$.

The values corresponding to 300 K are analyzed here in order to avoid the problem of underestimation of the contribution introduced by thermal expansion. Local values of the compressibility modulus for a few first coordination shells of $^{19}\text{F}^-$ in $\text{PbF}_2:\text{Gd}^{3+}$ normalized to the values corresponding to the pure lattice have been calculated by Fainstein [34] using the method described in [35]. For the nearest eight $^{19}\text{F}^-$ neighbours the result is 0.718088 what gives, according to (6), the value of α_{loc} equals $40.1 \times 10^{-6} \text{ K}^{-1}$, assuming that neither γ , C_p or V changes substantially after doping. The increase of the thermal expansion coefficient to the value given above would thus rise the contribution resulting from thermal expansion expressed by (5) to the value of $7.5 \times 10^{-5} \text{ K}^{-1}$.

However, as can be seen from Fig. 1 the measured value of (5) equals $5.5 \times 10^{-4} \text{ K}^{-1}$. Therefore, the effect of the thermal expansion of the crystal may be responsible in about 14% for the observed temperature dependence of $G_{R_{ig}}^{(2)}$. Such a small contribution lies approximately within the limits of the error connected with the experimental determination of the spin-lattice coefficients. As can be found from the data given by Catlow et al. [36], also the temperature dependence of the elastic constants will yield negligible contributions to the observed temperature relation of $G_{R_{ig}}^{(2)}$. Therefore, in the following treatment we shall assume that the relationships presented in Fig. 1 and Fig. 2 represent predominantly the effect arising from the coupling of the $4f^7$ electrons with lattice vibrations. Such effect should be proportional to the square of the thermal average of the vibration amplitude over different modes of the GdF_2 complex or, in other words, to the mean internal energy of the lattice. Following the fact that in the optic mode the vibrations occur in antiphase, so that the relative displacement of the paramagnetic ion and its ligands is great, the Einstein model for lattice vibrations is generally used to parametrize the experimental data. This model leads then to the following temperature dependence of $G_{R_{ig}}^{(2)}$ [6]:

$$G_{R_{ig}}^{(2)}(T) = G_{R_{ig}}^{(2)}(\text{RL}) + K_{R_{ig}}^{(2)} \text{ctgh}(\hbar\omega_E/2k_B T), \quad (7)$$

where ω_E is the Einstein frequency and $K_{R_{ig}}^{(2)}$ is the coupling parameter describing the magnitude of the spin-phonon interaction or the contribution resulting from zero-point vibrations of the complex. At high temperatures (7) assumes the form:

$$G_{R_{ig}}^{(2)}(T) = G_{R_{ig}}^{(2)}(\text{RL}) + \frac{2k_B}{\hbar\omega_E} K_{R_{ig}}^{(2)}(T) \quad (8)$$

from which it implies that within the experimental conditions, as described in this paper, only the values of $G_{R_{ig}}^{(2)}(\text{RL})$ and $K_{R_{ig}}^{(2)}/\omega_E$ can be determined unequivocally. These parameters are listed in Table I which also includes, for comparison purposes, the existing data for other $\text{MF}_2:\text{Gd}^{3+}$ systems.

TABLE I

The values of $G_{\Gamma_{ig}}^{(2)}$ (RL) and $K_{\Gamma_{ig}}^{(2)}$ for $\text{MF}_2:\text{Gd}^{3+}$ obtained from the parametrization in the Einstein model.

	$G_{\Gamma_{3g}}^{(2)}$ (RL) (cm^{-1})	$10^{16}K_{\Gamma_{3g}}^{(2)}/\omega_E$ (cm^{-1}s)	$G_{\Gamma_{5g}}^{(2)}$ (RL) (cm^{-1})	$10^{16}K_{\Gamma_{5g}}^{(2)}/\omega_E$ (cm^{-1}s)	Source
PbF_2	-0.068(5)	-1.5(2)	-0.098(6)	5.6(6)	this paper
CaF_2	-0.200(1)	-3.50(2)	-0.129(3)	4.35(5)	[7]
CdF_2	-0.197(1)	-5.80(1)	-0.097(1)	5.10(2)	[7]

As seen from Table I the results for $G_{\Gamma_{3g}}^{(2)}$ (RL) and $K_{\Gamma_{3g}}^{(2)}/\omega_E$ are consistent with those for other $\text{MF}_2:\text{Gd}^{3+}$ systems but the results for $G_{\Gamma_{5g}}^{(2)}$ (RL) and $K_{\Gamma_{5g}}^{(2)}$ differ significantly. Taking into account the values of the elastic constants $c_{11} - c_{12}$ needed to describe the strain of the Γ_{3g} symmetry one can notice that they are about 3 times smaller for PbF_2 than for CaF_2 whereas that for the Γ_{5g} symmetry differ much less [36]. Thus, the low absolute value of the $G_{\Gamma_{3g}}^{(2)}$ (RL) could result from exceptionally low values of the corresponding $c_{11} - c_{12}$ elastic constants. The low absolute value of the $K_{\Gamma_{3g}}^{(2)}/\omega_E$ would, however, indicate that the vibrating mode Γ_{3g} couples relatively weakly with the $4f^7$ electrons of Gd^{3+} in PbF_2 . It may be suggested, that this disparity between the coupling with the Γ_{3g} and Γ_{5g} modes, which must be related rather to the properties of the crystalline state of PbF_2 and not to the electronic structure of the paramagnetic ion in MF_2 , may somehow contribute to the existence of two structurally different phases of PbF_2 .

The successful parametrization of the experimental data in the Einstein model does not, however, exclude a possibility that the data may be parametrized in the Debye model. It is conceivable that the acoustic phonons for which the density of states is large can, at the same time, be described by wavevectors q of sufficiently large magnitude to produce relative displacements of the paramagnetic ion and its ligands to reflect itself in measurable by EPR contributions caused by the interactions occurring via the orbit-lattice coupling. In the Debye model the functional dependence of the spin-lattice coefficients on temperature would assume the form:

$$G_{\Gamma_{ig}}^{(2)}(T) = G_{\Gamma_{ig}}^{(2)}(\text{RL}) + K_{\Gamma_{ig}}^{(2)} \left[1 + 8 \left(\frac{T}{\Theta_D} \right)^4 \int_0^{\Theta_D/T} \frac{x^3 dx}{\exp(x) - 1} \right]. \quad (9)$$

TABLE II

The values of $G_{\Gamma_{ig}}^{(2)}$ (RL) and $K_{\Gamma_{ig}}^{(2)}$ for $\text{PbF}_2:\text{Gd}^{3+}$ obtained from the parametrization in the Debye model (the standard deviation of the fitting did not exceed 0.004).

$G_{\Gamma_{3g}}^{(2)}$ (RL) (cm^{-1})	$10^3 K_{\Gamma_{3g}}^{(2)}$ (cm^{-1})	$G_{\Gamma_{5g}}^{(2)}$ (RL) (cm^{-1})	$10^3 K_{\Gamma_{5g}}^{(2)}$ (RL) (cm^{-1})
-0.067	-3.6	-0.113	12.3

The parametrization carried out in this scheme leads then to the values listed in Table II and the plot of (7) is presented in Fig. 1 and Fig. 2 by the continuous line. In the fitting we used the Debye temperature for PbF_2 , $\Theta_D = 230 \text{ K}$ [22]. As seen from Tables I and II the "rigid" lattice values of $G_{F_i g}^{(2)}$ are (within the experimental error) the same. It may be noticed that the values of the coupling parameters $K_{F_i g}^{(2)}$ can be made to coincide in both models of parametrization if ω_E is chosen to be about $2.5 \times 10^{13} \text{ s}^{-1}$. This value seems to be a reasonable estimation of the "averaged" frequency of the optic mode for the investigated systems. Thus, we come to the conclusion that within the experimental uncertainty of the method one can not unequivocally state which model for the coupling of the $4f^7$ electrons with lattice vibrations, i.e. the localized Einstein one or the coupling with the whole phonon spectrum of the crystal (the Debye one), is responsible for the measured temperature dependence of the spin-lattice coefficients. The same conclusion was reported by Bill [37] who studied the temperature dependence of the axial crystal field splitting parameter b_2^0 for Gd^{3+} in PbFCl and Na_2S . However, if the $4f^7$ spins were coupled to the whole phonon spectrum, as strongly suggested by the results of a careful analysis carried out, both theoretically and experimentally by Bates and Szymczak [8, 9] then, of course, one could use (7) to determine the Debye temperature of a system based on the data on the temperature dependence of the spin-lattice coefficients.

As mentioned in the introduction, rather little is known about the microscopic origin of the dynamic effects of the orbit-lattice interactions for rare-earth ions. Baker [38] suggested a simple and natural approach in which he showed that the contribution of the lattice dynamics to the zero-field splitting parameters should be proportional to $\langle u^2 \rangle V_{OL}^2 / R_L^2$, where $\langle u^2 \rangle$ is the mean square displacement of atoms and V_{OL} is the mean orbit-lattice interaction energy. In the point-charge model the values of V_{OL} for different $\text{MF}_2:\text{Gd}^{3+}$ single crystals were evaluated in [39]. The mean square displacement may be calculated from the well known formula (e.g. [40]):

$$\langle u^2 \rangle = \frac{h}{2\mu\omega_E} \text{ctgh} \frac{\hbar\omega}{2k_B T}, \quad (10)$$

where μ is the reduced mass. Metal-ligand distances R_L for various $\text{MF}_2:\text{Gd}^{3+}$ systems are given in [38]. Taking into account all these data it is easy to show that the relative contribution of the dynamic orbit-lattice interactions to the spin-lattice coefficients for $\text{PbF}_2:\text{Gd}^{3+}$ compared to the other $\text{MF}_2:\text{Gd}^{3+}$ systems cannot be explained in the approach of Baker, although it was shown previously [12] that this model leads to satisfactory results when applied to analogous studies for the $\text{MF}_2\text{Eu}^{2+}$ systems. It has been reported recently that the model under discussion explains very effectively the temperature dependence of the spin-Hamiltonian parameters for $\text{Li Y}_{1-x}\text{Yb}_x\text{F}_4:\text{Gd}^{3+}$ [14]. All this would support the above conclusion that the different behaviour of the $\text{PbF}_2:\text{Gd}^{3+}$ system should be connected with its specific crystalline properties which distinguish this system from other fluorites doped with Gd^{3+} .

The analysis of a more advanced theoretical model presented recently in [41], which includes relativistic two-phonon orbit-lattice contributions, leads to the con-

clusion that if the orbit-lattice parameters are calculated in the point-charge approximation then insignificant dynamic contributions are obtained (in the sense that they are far too small to be detected experimentally) both for the $G_{F_{3g}}^{(2)}$ and $G_{F_{5g}}^{(2)}$ coefficients. However, the relative signs of the $K_{F_{1g}}^{(2)}$ coupling constants are correctly predicted, what suggested that the small contributions resulting from the model may be rather connected with the inadequacy of the point-charge approximation used in the estimation of the values for the second-order two-phonon orbit-lattice coupling parameters than with the physical idea of the relativistic approach to the effect of lattice dynamics upon the energetical structure of the $4f^7$ ($^8S_{7/2}$) ions, especially in view of the fact that the contribution of the relativistic effects to the "static" values of the spin-lattice coefficients is now unquestionable [42-44].

In conclusion, we hope that the new data presented in this paper would stimulate further theoretical effort to solve adequately the problems linked with the microscopic interpretation of the role played by a dynamic crystal field for $^8S_{7/2}$ ground state ions.

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References

- [1] R. Orbach, H.J. Stapleton, *Electron Paramagnetic Resonance*, ed. S. Geschwind, Plenum Press, New York, London 1972, Chapt. 2.
- [2] K.H. Shrivastava, *Phys. Rep.* **20**, 137 (1975).
- [3] C.Y. Huang, *Phys. Rev.* **159**, 683 (1967).
- [4] W. Pastusiak, J. Kuriata, *Phys. Status Solidi B* **135**, K69 (1986).
- [5] W. Pastusiak, J. Kuriata. *Abstr. XXIV-th Congr. AMPERE on Magnetic Resonance and Related Phenomena*, eds. J. Stankowski, N. Piślewski, S. Idziak, Adam Mickiewicz University Press, Poznań 1988, p. B54.
- [6] S.B. Oseroff, R. Calvo, *Phys. Rev. B* **5**, 2474 (1972).
- [7] S.B. Oseroff, *Phys. Lett. A* **41**, 387 (1972).
- [8] C.A. Bates, H. Szymczak, *Phys. Status Solidi B* **74**, 225 (1976).
- [9] C.A. Bates, H. Szymczak, *Z. Phys. B* **28**, 67 (1977).
- [10] J. Kuriata, N. Guskos, T. Rewaj. *Phys. Status Solidi B* **83**, K79 (1977).
- [11] J. Kuriata, N. Guskos, T. Rewaj, *Phys. Status Solidi B* **106**, 607 (1981).
- [12] J. Kuriata, J.M. Baker, T. Rewaj, N. Guskos, *Phys. Status Solidi B* **120**, K135 (1983).
- [13] J. Kuriata, N. Guskos, W. Pastusiak, *Phys. Status Solidi B* **133**, K133 (1986).

- [14] L.E. Misiak, S.K. Misra, *Phys. Rev. B* **38**, 8673 (1988).
- [15] K.H. Shrivastava, *J. Phys. C* **2**, 777 (1969).
- [16] W.M. Walsh, J. Jeener, N. Bloembergen, *Phys. Rev. A* **139**, 1338 (1965).
- [17] W.R. Hurren, H.M. Nelson, E.G. Larsen, J.H. Gardner, *Phys. Rev.* **185**, 624 (1969).
- [18] R. Calvo, R.A. Isaacson, S. Sroubek, *Phys. Rev.* **117**, 484 (1969).
- [19] T. Rewaj, *Proc. RAMIS-85 Conf.*, Adam Mickiewicz University Press, Poznań 1985, p. 201.
- [20] T. Christidis, *Abstr. XXIV-th Congr. AMPERE on Magnetic Resonance and Related Phenomena*, ed. J. Stankowski, N. Piślewski, I. Idziak, Adam Mickiewicz, University Press, Poznań 1988, p. B25.
- [21] M.A. Bredig, *Colloques Internationaux C.N.R.S. N° 205-Etude des transformations cristallines a haute temperature*, 183 (1971).
- [22] R.B. Raberts, G.K. White, *J. Phys. C* **19**, 7167 (1986).
- [23] V.M. Carr, A.V. Chadwick, R. Saghatian, *J. Phys. C* **11**, L637 (1978).
- [24] C. Evora, V. Jaccarino, *Phys. Rev. Lett.* **39**, 1554 (1977).
- [25] J. Shinar, V. Jaccarino, *Phys. Rev. B* **27**, 4034 (1983).
- [26] J.M. Baker, R.L. Wood, *J. Phys. C* **12**, 4033 (1979).
- [27] W. Klement Jr, L.H. Cohen, *J. Electrochem. Soc.* **126**, 1403 (1979).
- [28] W. Hayes, *Crystals with the fluorite structure*, Clarendon Press, Oxford 1974, p. 345.
- [29] J. Kuriata, T. Rewaj, N. Guskos, *Acta Phys. Pol.* **A75**, 427 (1989).
- [30] D. Zadunayski de Basch, G.E. Barberis, R. Calvo, *Solid State Commun.* **18**, 1439 (1974).
- [31] G.E. Stedman, D.J. Newman, *J. Phys. C* **7**, 2347 (1974); corrigenda: *J. Phys. C* **8**, 1070 (1975).
- [32] J. Kuriata, N. Guskos, T. Rewaj, J. Szumowski, K. Falkowski, *Phys. Status Solidi B* **74**, 683 (1976).
- [33] F. Prissok, G. Lehmann, *J. Phys. Condens. Matter.* **1**, 5481 (1989).
- [34] F. Fainstein, *Tables of calculated equilibrium distances and local compressibilities for all divalent rare earth ions in fluorites*, (private information).
- [35] F. Fainstein, M. Tovar, C. Ramos, *Phys. Rev. B* **29**, 3039 (1982).
- [36] C.R.A. Catlow, J.D. Comins, F.A. Germano, R.T. Harley, W. Hayes, *J. Phys. C* **11**, 3197 (1978).
- [37] H. Bill, *Phys. Status Solidi B* **89**, K49 (1978).
- [38] J.M. Baker, *J. Phys. C* **12**, 4039 (1979).
- [39] J. Kuriata, W. Pastusiak, *Acta Phys. Pol.* **A66**, 627 (1984).
- [40] R.P. Feynman, *Statistical Mechanics*, W.A. Benjamin Inc., Reading (Mass.) 1972, Chapt. 2.
- [41] W. Pastusiak, *Acta Phys. Pol.* **A73**, 39 (1988).
- [42] J. Kuriata, N. Guskos, T. Rewaj, *Acta Phys. Pol.* **A62**, 199 (1982).

- [43] J. Kuriata, W. Pastusiak, *Acta Phys. Pol.* A64, 441 (1983).
- [44] W. Pastusiak, J. Kuriata, *Phys. Status Solidi B* 111, K147 (1982).