SPIN–PHONON CONTRIBUTIONS
TO THE b_2^0 PARAMETER FOR Gd^{3+}
IN RbCdF$_3$ SINGLE CRYSTALS*

N. Guskos

Physics Department, Solid State Section, University of Athens
104 Solonos Str., Athens, 106 80, Greece

J. Kuriata and T. Rewaj

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

Temperature dependence of the b_2^0 spin-hamiltonian parameter for Gd^{3+} in RbCdF$_3$ single crystals is described. The dependence is interpreted in terms of the $4f^7$ electrons coupling to the whole phonon spectrum of the crystal. The presented data give also an insight into the dynamics of charge compensators causing a tetragonal distortion of the crystal field.

PACS numbers: 76.30.Kg

1. Introduction

$^8S_{7/2}$ ground state ions ($4f^7$ electronic configuration) constituting impurity ions in different diamagnetic lattices have been, for many years, studied mainly because of many challenging questions connected with microscopic explanation of the physical origin of their zero-field splitting (ZFS) phenomena.

Many experimental works on these ions were carried out for the system in which they enter a simple cubic eight-coordinated lattice type MF$_2$ (where M = Cd, Ca, Sr, Ba, and Pb) (e.g. [1–5] and the references given therein). In cubic systems Gd^{3+} ions replacing M^{2+} ones are subjected to the action of both the cubic crystal field and that set up by some requirements imposed by charge compensation effects. The nature of these effects in MF$_2$ is fairly well understood [5] and the dynamics of the creation and annihilation of charge compensators is described

---

elsewhere (e.g. [6]). However, relatively less is known about the charge compensation effects appearing in yet another case when a three-valent rare-earth ion can replace a two-valent one, namely, in the case of the so-called fluoroperovskite-type single crystals AMF_3 (where $A = Rb$, Cs, Tl and $M = Ca$, Cd). In the situation discussed in this paper Gd^{3+} replaces Cd^{2+} which is in the centre of an octahedron formed by six $^{19}F^-$ ions. One of the models allowing for the charge compensation is presented in Fig. 1. The charge compensation centre is an O^{2-} ion occupying
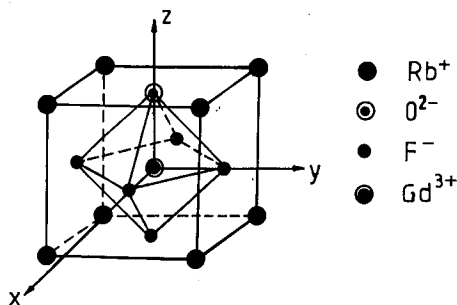

Fig. 1. A model for charge compensation in $RbCdF_3:Gd^{3+}$.

one of six fluorine positions. This type of the charge compensation mechanism was determined on the base of the value of the b_2^0 parameter measured at room temperature. In the EPR spectrum the component of the crystal field induced by the charge compensator reveals itself in the appearance of additional lines (to those already resulting from the crystal field of octahedral symmetry) forming the so-called tetragonal EPR spectrum of Gd^{3+}.

It is the objective of this paper to describe the temperature induced changes in the ZFS of Gd^{3+} impurity in $RbCdF_3$ for the effect of the tetragonal component of the crystal field set up by such charge compensators as indicated in Fig. 1. We shall also try to identify the origin of these changes and discuss them in terms of the existing theories.

2. Experimental

$RbCdF_3:Gd^{3+}$ single crystals were grown in graphite crucibles by the modified Bridgman method developed in the Kazan State University. The compounds used in the crystal growth procedure were CdF_2 and RbF (equimolar mixture) and Gd^{3+} ions were introduced through the addition of gadolinium oxide. The nominal concentration of Gd^{3+} ions in the obtained samples was about 0.1% mol.

EPR measurements were carried out using a standard X-band spectrometer type Varian-4 working with a steady magnetic field modulation of 100 kHz. The magnetic field was scaled using usual NMR proton technique. The measurements were carried out in the temperature range from 160 K up to 530 K. The temperature was controlled using a thermocouple with the precision not worse than 0.5 K.

3. Results and discussion

The EPR spectrum of Gd^{3+} in $RbCdF_3$ recorded at different temperatures and with the magnetic field orientation $\boldsymbol{B} \parallel [100]$ is shown in Fig. 2. The lines
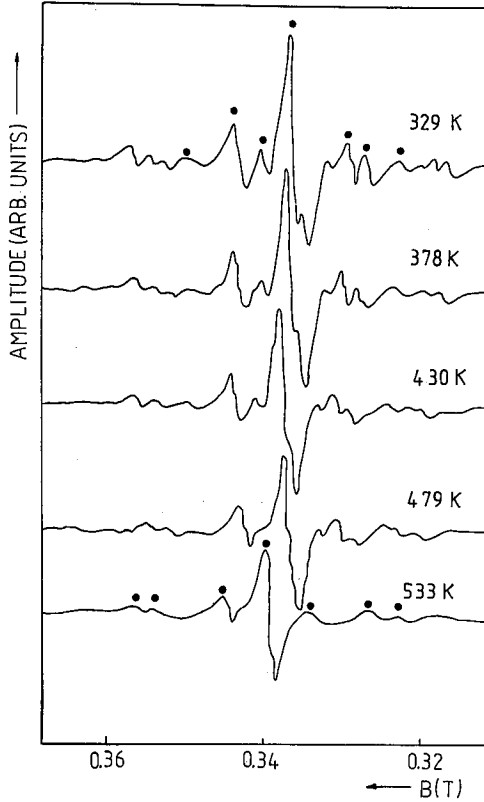

Fig. 2. Temperature dependence of the EPR spectrum of $RbCdF_3$:Gd^{3+} ($\boldsymbol{B} \parallel [100]$).

forming the cubic spectrum are indicated by the circles and the rest of the lines are due to the distortion of the cubic field by local charge compensators.

The spectrum of Gd^{3+} in arbitrary symmetry (neglecting hyperfine and superfine interactions) can be described by the following spin Hamiltonian:

$$\mathcal{H} = \mu_B S\hat{g}B + \sum_{n,m} b_n^m O_n^m. \tag{1}$$

Here b_n^m are phenomenologically determined spin-hamiltonian parameters. O_n^m are the Stevens equivalent operators and the rest of the symbols have their usual meaning. The first term in (1) represents the Zeeman energy and the second one the effect of ZFS. For the particular case discussed in this paper the observed spectrum can be described by the Hamiltonian of the following form:

$$\mathcal{H}_{ZFS} = \frac{1}{3}b_2^0 O_2^0 + \frac{1}{60}\left(b_4^0 O_4^0 + b_4^4 O_4^4\right) + \frac{1}{1260}\left(b_6^0 O_6^0 + b_6^4 O_6^4\right). \tag{2}$$

Here the quantization axis was chosen to be aligned parallel to the axis of tetragonal distortion.

The values of the spin-hamiltonian parameters b_n^m appearing in (2) determined at room temperature were the same (within the experimental error) as those reported by Arakawa [7] and therefore need not be repeated here.

The temperature dependence of the b_2^0 spin-hamiltonian parameter is presented in Fig. 3. It is quite natural to assume that the temperature dependence of
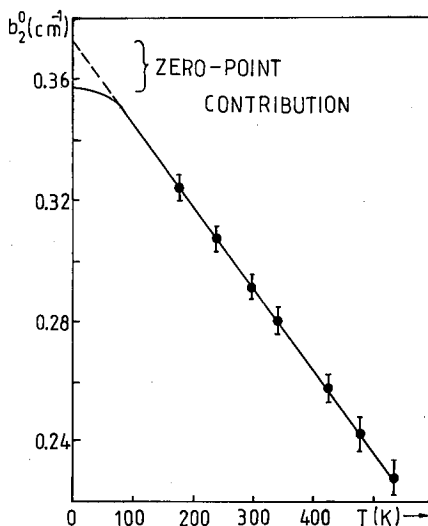

Fig. 3. Temperature dependence of the b_2^0 parameter for RbCdF$_3$:Gd^{3+}. The continuous line represents the best fit to Eq. (4).

the spin-hamiltonian parameters is essentially caused by two effects: the effect of thermal expansion and that due to some means of a coupling which exists between the magnetic $4f^7$ electrons and lattice vibrations. This coupling should be quite indirect (due to rather obvious fact that the $^8S_{7/2}$ ground state feels the action of the crystal field only through higher excited states modified by spin–phonon interactions). The above two effects may be analyzed on the ground of a natural relation given by Walsh et al. [8]:

$$\left(\frac{\partial b_n^m}{\partial T}\right)_{\mathrm{P}} = \left(\frac{\partial b_n^m}{\partial R_{\mathrm{L}}}\right)_{\mathrm{P}} \left(\frac{\partial R_{\mathrm{L}}}{\partial T}\right)_{\mathrm{P}} + \left(\frac{\partial b_n^m}{\partial T}\right)_{\mathrm{R}}. \tag{3}$$

Here, the first term on the right hand side represents an explicit thermal expansion effect whereas the second one describes an implicit phonon one. It is rather impossible to separate these two terms unless one has at his disposal the data derived from hydrostatic or uniaxial stress experiments (see the discussion in [9]). Since we do not have any information about the behaviour of the tetragonal spectrum under a controlled deformation introduced by an external stress, we have to recourse to two experimental facts. Firstly, Rewaj et al. [10] have recently shown that the temperature dependence of the b_4^0 spin-hamiltonian parameter is in about

70% determined by the effect of spin–phonon interactions. Secondly, during our previous studies carried out for the $^8S_{7/2}$ ground state ions in MF_2 [11–14] we systematically found that the temperature induced changes in the values of the second-order spin–lattice coefficients (including this one related to the tetragonal distortion) are predominantly caused by the spin–phonon interaction leaving the effect of thermal expansion quite unimportant. Furthermore, we also found that the temperature dependence of the second-order spin–lattice parameters can be equally well-parametrized either in terms of the localized mode model of Einstein or in terms of the Debye model which assumes that a paramagnetic ion is coupled to the whole phonon spectrum of the crystal.

This latter approach results from the fact that although in the acoustic mode the ions vibrate "in phase" nonetheless some phonons (with the density of states being not negligible) can, at the same time, be specified by the wave vector q, the length of which may be sufficient to produce quite large displacements of a paramagnetic ion with respect to its ligands. Since the parametrization in the Debye model is, in some respect, more informative than that in the Einstein model we have chosen to adopt the former to describe our experimental data. Since the b_2^0 parameter can be related to the internal energy of the system we are thus entitled to parametrize it in terms of the well-known function

$$b_2^0(T) = b_2^0(\mathrm{RL}) + K \left[1 + 8 \left(\frac{T}{\Theta_\mathrm{D}} \right)^4 \int_0^{\Theta_\mathrm{D}/T} (e^x - 1)^{-1} x^3 \mathrm{d}x \right], \qquad (4)$$

where $b_2^0(\mathrm{RL})$ is the "rigid-lattice" value of b_2^0, K is the coupling constant describing the contribution arising from zero-field vibrations of the lattice and Θ_D is the "Debye temperature". The quotation mark is used here, because this temperature is treated here to result only from the assumed model of parametrization and can have nothing to do with the usual meaning of the term. It is due to the fact that EPR deals with local interactions between a paramagnetic ion and its surrounding whereas the "true" Debye temperature, as well-known, is defined for a continuous bulk medium.

The best fit procedure of our experimental results to Eq. (4) gave us the following parameters describing the observed effect:

$$b_2^0(\mathrm{RL}) = 0.373(8) \text{ cm}^{-1}, \quad K = -0.0258(8) \text{ cm}^{-1}, \quad \Theta_\mathrm{D} = 253 \pm 3 \text{ K}. \quad (5)$$

The effectiveness of the procedure is illustrated in Fig. 3.

We can thus come to the conclusion that the contribution of the zero-point vibrations of the lattice amounts to 15%. It is noteworthy that this value is comparable to that found for the second-order spin–lattice coefficients for MF_2 single crystals doped with $^8S_{7/2}$ ground state ions [11–14].

Obviously, the description of the phenomenon given above is the phenomenological one and the question arises about the physical origin of the observed contributions resulting from lattice dynamics. There are many possible mechanisms leading to the phonon induced contributions to the spin Hamiltonian parameters of $^8S_{7/2}$ ground state ions. A number of them, implying from rotational invariance of the spin Hamiltonian, have been discussed by Bates and Szymczak [15, 16]. Recently, a new model predicting some phonon contributions arising from the inclusion of the relativistic character of the $4f^7$ electron wave functions has been

proposed [17]. Although strict calculations of the contributions given by this model are now not possible to carry out, for the particular case considered in this paper, nevertheless some general features of the model indicate, like it was found in [18], that these contributions are too small to account for the observed temperature dependence of the second-order spin-hamiltonian parameters.

It is quite clear that the disparity between theoretical and experimental results must result from the fact that the model proposed in [17] derives the orbit–lattice parameters from the point-charge model for the crystal field which assumes that the $4f^7$ electron wave function is totally centred on the magnetic ion. However, as shown experimentally for the discussed case [19, 20], the $4f^7$ wave function is in fact admixed to the $2p$ and $2s$ orbitals of $^{19}F^-$ and in this admixture a great role is played by the outer electronic shells of Gd^{3+}. We thus postulate that the strong temperature dependence of the b_2^0 spin-hamiltonian parameter reported in this paper is due to the enhancing role of overlap and covalency effects.

Finally, it is wirth pointing out that Fig. 2 illustrates qualitatively the dynamics of the vanishing of the tetragonal spectrum with the temperature increase. As seen from the figure, up to about 530 K one observes both the lines resulting from the cubic and tetragonal crystal field components. Starting from about 533 K up we observed practically only the cubic spectrum. The most possible mechanism for such a behaviour of the EPR spectrum may be related to the fact that with the temperature increase the mobility of the charge compensator is also increased which leads to:

(i) the effective increase in the distance between the paramagnetic ion and a charge compensator,

(ii) the averaging of the tetragonal distortion over all possible axes of the fluorine octahedral due to rapid rotational motion of the compensator.

We wish to thank Dr. J. Typek from the Technical University of Szczecin for his help in computer processing of experimental data.

References

[1] J. Kuriata, N. Guskos, T. Rewaj, *Acta Phys. Pol. A* **62**, 199 (1982).

[2] J. Kuriata, N. Guskos, T. Rewaj, J. Szumowski, K. Falkowski, *Phys. Status Solidi B* **74**, 683 (1976).

[3] J. Kuriata, W. Pastusiak, *Acta Phys. Pol.* **A66**, 627 (1984).

[4] J. Kuriata, W. Pastusiak, *Acta Phys. Pol.* **A64**, 441 (1983).

[5] W. Hayes, *Crystals with Fluorine Structure*, Clarendon Press, Oxford 1974.

[6] T. Rewaj, *Fiz. Tverd. Tela* **10**, 1272 (1968).

[7] M. Arakawa, *J. Phys. Soc. Jpn.* **47**, 523 (1979).

[8] M.W. Walsh, J. Jeener, N. Blombergen, *Phys. Rev.* **139**, A1339 (1965).

[9] T. Rewaj, in: *Proc. RAMIS-85 Conf.*, UAM, Poznań 1985, p. 201.

[10] T. Rewaj, M. Krupski, J.Y. Buzaré, in: *25th Congr. AMPERE, Magnetic Resonance and Related Phenomena*, Ed. M. Mehring, J.U. von Schütz, H.C. Wolf, Springer-Verlag, Stuttgart 1990, p. 42.

[11] J. Kuriata, N. Guskos, T. Rewaj, *Phys. Status Solidi B* **83**, K79 (1977).

[12] J. Kuriata, N. Guskos, T. Rewaj, *Phys. Status Solidi B* **106**, 607 (1981).

[13] J. Kuriata, J.M. Baker, T. Rewaj, N. Guskos, *Phys. Status Solidi B* **120**, K135 (1983).

[14] J. Kuriata, N. Guskos, W. Pastusiak, *Phys. Status Solidi B* **133**, K133 (1986).

[15] C.A. Bates, H. Szymczak, *Phys. Status Solidi B* **74**, 225 (1976).

[16] C.A. Bates, H. Szymczak, *Z. Phys. B* **28**, 67 (1977).

[17] W. Pastusiak, J. Kuriata, *Phys. Status Solidi B* **135**, K69 (1986).

[18] W. Pastusiak, J. Kuriata, in: *Proc. 24th Congr. AMPERE, Magnetic Resonance and Related Phenomena,* Ed. J. Stankowski, N. Piślewski, S. Idziak, UAM, Poznań 1988, p. B54.

[19] J.Y. Buzare, M. Fayet-Bonnet, J.C. Fayet, *J. Phys. C, Solid State Phys.* **14**, 67 (1981).

[20] J.Y. Buzare, M. Fayet-Bonnet, J.C. Fayet, *J. Phys. C, Solid State Phys.* **13**, 857 (1980).