PARAMETRIZATION OF THE VIBRONIC CONTRIBUTIONS TO THE b_4^0 SPIN-HAMILTONIAN PARAMETERS FOR ${}^8S_{7/2}$ GROUND STATE IONS IN FLUOROPEROVSKITES

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Parametrization of phonon induced contributions to the experimentally determined temperature dependence of the b_4^0 spin-Hamiltonian parameter for Gd³⁺ doped RbCaF₃, CsCaF₃, RbCdF₃ and TlCdF₃ single crystals is discussed. Three physically different parametrization schemes are considered, i.e. that of Einstein, Debye and Huang. It is found that the model of Huang, which predicts that the phonon induced contributions should be proportional to the Debye-Waller factor, describes best the experimental data. The method allowing determination of the Debye temperature from EPR data is also suggested.

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1. Introduction

The origin of the experimentally determined temperature variations of the spin-Hamiltonian parameters for the S-ground state ions in different diamagnetic lattices has been the subject of many investigations for a long time. As far as the ${}^{8}S_{7/2}$ ground state ions are concerned, it seemed, until recently, that at least two facts had been established experimentally for these ions doping fluorides:

 (i) the temperature dependence of the second-order spin-Hamiltonian parameters is mainly caused by the dynamic orbit-lattice effects (e.g. [1-6]) with the contributions due to the thermal expansion of a crystal lattice being insignificant, (ii) the temperature dependence of the fourth-order spin-Hamiltonian parameters is mainly caused by thermal expansion effects with phonon contributions being at most 30% of the total thermal effect (e.g. [7-9]).

However, we have recently shown [10], comparing the EPR data derived from temperature and hydrostatic pressure measurements, that for the case of Gd^{3+} ions doping fluoroperovskite single crystals the temperature dependence of b_4^0 is predominantly caused by the spin-phonon interactions which were estimated to contribute of about 70% of the total dependence observed.

Dynamic contributions attract also the attention of many theoreticians. Purely microscopic models of the phenomenon seem to yield insignificant contributions probably due to the fact that rather oversimplified approach to the crystal field theory for the S-ground state ions is still used (e.g. [11, 12]). On the other hand, semi-empirical models predict quite significant contributions and were successfully used to interpret EPR data of the S ground-state ions in different lattices [13, 14]. In the above context the problem of adequate parametrization of experimental data for the case considered in this paper is quite important, because, apart from the fact that such parametrization supplies new useful data which can be confronted with theoretical implications, one also gets a deeper qualitative insight into the origin of the spin-phonon interactions caused by the dynamic Van Vleck orbit-lattice coupling.

In our previous paper [10] we have shown, considering the particular case of the RbCdF₃:Gd³⁺ system, that the experimental results on vibronic contributions to the b_4^0 parameter can be well parametrized using the model of Debye with one adjustable parameter (i.e. the Debye temperature) and the coupling constants describing zero-point vibration contributions calculated from the models of Bates and Szymczak [13–15]. The objective of this paper is to extend this analysis to other fluoroperovskites and to verify the effectiveness of yet two other parametrization schemes, namely, that of Einstein and Huang [11].

2. The procedure of extracting the vibronic contributions from temperature and hydrostatic pressure measurements

The temperature induced changes in the b_4^0 parameter are caused by the thermal expansion of the crystal lattice and lattice vibrations. In order to separate these two contributions one can use the relation given by Walsh et al. [16]:

$$\left(\frac{\partial b_4^0}{\partial T}\right)_V = \left(\frac{\partial b_4^0}{\partial T}\right)_p - \left(\frac{\beta}{K}\right) \left(\frac{\partial b_4^0}{\partial p}\right)_T \tag{1}$$

where β is the volume thermal expansion coefficient and K is the volume compressibility coefficient.

In the temperature range investigated by us (210 to 570 K) the temperature dependence of b_4^0 is linear (see Fig. 1), therefore it can be described by a parameter $\alpha = \partial b_4^0 / \partial T$ (the slope of the straight line). The value of α contains, obviously, both contributions mentioned above. Because the percentage δ of the vibrational part has already been established [10], the vibrational part can be easily separated from the total temperature changes $\alpha_V = \delta \cdot \alpha$.

3. Models for parametrization of vibronic contributions

We shall test three parametrization schemes, namely, the Einstein, Debye and Huang parametrizations. In the Einstein approximation one assumes that the main contribution is due to the optical phonons with large values of the wave vectors, i.e. one uses the well-known Einstein relation with the optical phonon frequency $\omega_{\rm E}$ at the Brillouin zone boundary

$$b_4^0(T) = b_4^{0(E)}(RL) + K^{(4)} \coth(\hbar\omega_E/2kT),$$
 (2)

where $b_4^{0(E)}$ (RL) is the temperature independent contribution to the value of the b_4^0 called the "rigid lattice" one and $K^{(4)}$ is the zero-point vibration contribution.

In the Debye approximation an assumption is made that a paramagnetic ion is coupled to the whole phonon spectrum of the crystal thus the corresponding formula describing the vibrational effects is

$$b_4^0(T) = b_4^{0(D)}(RL) + K^{(4)}\left[1 + 8\left(\frac{T}{\Theta_D}\right)^4 \int_0^{\Theta_D/T} (e^x - 1)^{-1} x^3 dx\right].$$
 (3)

These two models are widely known and therefore need not additional discussion.

In his analysis of the Van Vleck orbit-lattice interactions for the S-ground state ions Huang [11] noticed that when the experiment is performed above the liquid nitrogen temperature the phonons with large wave vectors are well excited and at the same time the phonon density of states is also high. He came to the conclusion that in these circumstances the temperature dependent part for the spin-phonon interactions should be proportional to the Debye-Waller factor. We may assume that the parametrization of the experimental results can be also performed according to the following formula:

$$b_4^0(T) = b_4^{0(\mathrm{H})}(\mathrm{RL}) + K^{(4)} \left[1 + 4 \left(\frac{T}{\Theta_{\mathrm{D}}} \right)^2 \int_0^{\Theta_{\mathrm{D}}/T} (\mathrm{e}^x - 1)^{-1} x \mathrm{d}x \right].$$
(4)

In both Eqs. (3) and (4) Θ_D is the Debye temperature.

As seen from the form of Eqs. (2) to (4) three independent parameters, namely, the values of b_4^0 (RL), K and ω_E or Θ_D are to be inferred from experimental data.

It clearly implies, from the above discussion, that one is not able to claim a priori which parametrization model is more effective in the description of experimental data unless one confronts the particular model with the experiment.

4. The results of parametrization

The experimental results obtained by us are shown in Fig. 1. Linear dependence of the b_4^0 vs. T was observed for all investigated systems. It implies therefore that one is unable to determine unequivocally the set of three independent parameters as mentioned above. Therefore, following the method described in [10] we calculated the coupling constants $K^{(4)}$ from the model of Bates and Szymczak [13–15] and thus only the $b_4^0(\text{RL})$ and $\omega_{\rm E}$ or $\Theta_{\rm D}$ were allowed to be variable parameters.



Fig. 1. The temperature dependence of the b_4^0 spin-Hamiltonian parameter for all four investigated fluoroperovskite crystals doped with Gd³⁺. The straight lines are the best fit to the data.

The values of $K^{(4)}$ for "breathing" Γ_1 and rotational Γ_4 modes were calculated according to the following formula adopted from those given by Bates and Szymczak [13, 14]:

$$K_{\Gamma_1}^{(4)} = \frac{45\hbar}{128\pi^3\rho} G_{\Gamma_{1g}}^{(4)} \left(A_{11} + 4A_{44} - 2A_{12}\right) \omega_{\rm D}^4,\tag{5}$$

$$K_{\Gamma_4}^{(4)} = \frac{-5}{128\pi^3\rho} b_4^0 \left(A_{44} - A_{12}\right) \omega_{\rm D}^4,\tag{6}$$

where ρ is the crystal density, A_{ij} are the components of the elastic anisotropy tensor, $G_{\Gamma_{1g}}^{(4)}$ is the Γ_1 component of the magnetoelastic tensor and ω_D is the Debye temperature.

The results of our calculations of the coupling constants for Γ_1 and Γ_4 modes with the total coupling constants $K^{(4)}$ defined to be the sum of K_{Γ_1} and K_{Γ_4} are listed in Table I.

The best fit procedure to Eqs. (2) to (4) gave us the fitting parameters listed in Table II. The standard deviation of the fitting procedure is listed in Table III.

The knowledge of these parameters makes it possible to separate the vibrational and dilatational contributions to the temperature dependence of the b_4^0

parameter. As an example, this separation is illustrated in Fig. 2 for the $RbCdF_3$ crystal according to the three discussed models.

TABLE I The coupling constants $K_{\Gamma_1}^{(4)}$, $K_{\Gamma_4}^{(4)}$ and $K^{(4)}$ for Gd^{3+} in fluoroperovskites expressed in J·s⁴.

Sample	$K_{\Gamma_1}^{(4)} imes 10^{82}$	$K_{\Gamma_4}^{(4)} imes 10^{83}$	$K^{(4)} \times 10^{82}$
$RbCaF_3$	1.43	4.42	1.87
$CsCaF_3$	2.51	5.55	3.07
RbCdF3	1.16	3.17	1.48
TlCdF ₃	3.30	7.55	4.06

TABLE II The values of the fitting parameters calculated from the Einstein, Debye and Huang models.

Model	Einstein		Debye		Huang	
	$\omega_{\rm E} \times 10^{13}$	$b_4^0(\mathrm{RL}) \times 10^4$	$\Theta_{ extsf{D}}$	$b_4^0(\mathrm{RL}) \times 10^4$	$\Theta_{ m D}$	$b_4^0(\mathrm{RL}) imes 10^4$
Sample	[s ⁻¹]	$[cm^{-1}]$	[K]	$[cm^{-1}]$	[K]	[cm ⁻¹]
$RbCaF_3$	5.45	0.344	369	0.154	319	0.063
$CsCaF_3$	4.48	0.168	308	0.080	268	0.033
RbCdF₃	6.12	0.482	412	0.212	355	0.085
TlCdF ₃	4.13	0.191	282	0.090	245	0.036

TABLE IIITABLE IIIThe standard deviation of the fitting to Eqs. (2) to (4).

Model	Einstein	Debye	Huang			
\mathbf{Sample}						
$RbCaF_3$	2.923×10^{-5}	1.385×10^{-5}	6.123×10^{-6}			
$CsCaF_3$	1.086×10^{-5}	5.294×10^{-6}	1.991×10^{-6}			
RbCdF ₃	5.251×10^{-5}	2.478×10^{-5}	1.047×10^{-5}			
TlCdF ₃	2.216×10^{-5}	1.061×10^{-5}	4.683×10^{-6}			



Fig. 2. Separation of the vibrational and the dilatational contributions from the total temperature dependence of the b_4^0 parameter for RbCdF₃:Gd³⁺. The remaining dilatational part, which was obtained by subtraction of the vibrational one, depends on the used model for the vibrational change and this last is calculated according to: $(-\nabla - \nabla -)$ the Huang model; $(\cdot \cdot \Delta \cdot \cdot \Delta \cdot \cdot)$ the Debye model; $(-\cdot \bullet \cdot - \cdot \bullet \cdot -)$ the Einstein model.

5. Conclusions

- 1. The vibronic contributions to the values of the b_4^0 spin-Hamiltonian parameter measured at different temperatures can be parametrized using either the models of Einstein, Debye or Huang. However, the model of Huang seems to be most effective, because it yields the smallest standard deviation of the fitting.
- 2. The usage of the spin-phonon constants K resulting from the model of Bates and Szymczak gives reasonable values for both Einstein frequencies and Debye temperatures for all investigated systems. The determined Debye temperatures depend on the model used for the parametrization. Systematically lower values are obtained for the Huang model ($\Theta_D(H)$) than for the Debye model ($\Theta_D(D)$). The ratio of $\Theta_D(D)/\Theta_D(H)$ is almost the same for all investigated crystals (≈ 1.155) and this is what one expects if only the linear part of the series expansion of Eq. (3) and (4) is to be taken into account.

3. Although the method described in this paper does not allow to find which Debye temperature determined is more realistic (as far as we know it has not yet been established for the system studied here using other independent methods), it indicates, as we believe, some approximate limits of its variation. For comparison, Burriel et al. [17] measured the Debye temperature for KZnF₃ equal to 403 K from the phonon spectra and 395 ± 5 K from the heat capacity measurements. Unfortunately, the Gd³⁺ ions, owing to their larger ionic radii, cannot be substituted into the Zn²⁺ ion sites, which prevents us from valuable comparison of results.

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