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## Temperature and hydrostatic pressure dependences of the $b_4^0$ spin-Hamiltonian parameter for $Gd^{3+}$ in fluoroperovskite single crystals

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**Abstract.** Both the temperature and the pressure dependences of the  $b_4^0$  spin-Hamiltonian parameter for  $RbCaF_3$ ,  $CsCaF_3$ ,  $RbCdF_3$  and  $TlCdF_3$  doped with  $Gd^{3+}$  have been reported. On the assumption that  $b_4^0$  depends on the metal–ligand distance according to a law  $b_4^0 \sim r^k$  the following values of  $k$  were obtained:  $-20.9$ ,  $-27.1$ ,  $-24.9$  and  $-29.3$ , respectively. It was found that the temperature dependence of  $b_4^0$  is predominantly caused by spin–phonon interactions which were estimated to contribute about 68% to the total dependence observed. The effectiveness of some theoretical models predicting the role of vibronic contributions is also discussed.

### 1. Introduction

The adequate explanation of the physical nature of the zero-field splitting (ZFS) phenomenon for rare-earth S ground-state ions still constitutes a challenging problem for both experimentalists and theoreticians. In spite of the fact that a large amount of experimental data is available, even the establishment of reliable empirical laws describing ZFS is often frustrated, as pointed out for instance by Baker (1979), by unknown data on local distortions and contributions resulting from the zero-point vibrations of a crystal lattice.

Although rank-two spin-Hamiltonian parameters seem to be, at least qualitatively, understood within the framework of present theories (Kuriata and Pastusiak 1984), the rank-four parameters are much more difficult to analyse because their interpretation requires recourse to a higher order of perturbation calculation. In this context, systematic experimental investigations combining both temperature- and hydrostatic-pressure-induced changes in the fine-structure splitting parameters are particularly valuable.

Rare-earth ions subjected to the action of a cubic crystal field are described by the following spin-Hamiltonian (Baker *et al* 1958):

$$\mathcal{H}_{\text{cub}} = \frac{1}{60}b_4^0(O_4^0 + 5O_4^4) + \frac{1}{1260}b_6^0(O_6^0 - 21O_6^4). \quad (1)$$

The absolute value of the  $b_6^0$ -parameter is usually much smaller than that of  $b_4^0$  and therefore we shall further assume that the fine-structure splitting of the ground state is sufficiently well described by only  $b_4^0$ .

The dependence of the  $b_4^0$ -value on the metal–ligand distance has been the subject of many papers. Perhaps most representative data have been gathered so far for  $\text{Eu}^{2+}$  and  $\text{Gd}^{3+}$  in  $\text{MF}_2$  single crystals with  $\text{M} \equiv \text{Cd}, \text{Ca}, \text{Sr}, \text{Ba}$  and  $\text{Pb}$  (see, e.g., Rewaj and Krupski (1978, 1980) and Rewaj (1985)). The analysis carried out in the above papers indicated that temperature-induced changes in the  $b_4^0$ -value are predominantly due to the effect of thermal expansion of the  $\text{MF}_2$  crystal lattice and that the power exponent in the law describing the  $b_4^0$ -dependence on the metal–ligand distance assumes the value of about  $-10$ .

The present paper is devoted to similar studies extended to fluoroperovskite single crystals doped with  $\text{Gd}^{3+}$ . The local symmetry of  $\text{Gd}^{3+}$  in fluoroperovskites (when remote charge compensation mechanisms prevail) differs from that for fluorides in that the fluorine coordination number is sixfold octahedral in the present case. Thus, at first glance, all differences between the EPR parameters determined for these two systems should somehow be related to different coordination numbers.

## 2. Experimental details

Single crystals of  $\text{RbCaF}_3$ ,  $\text{CsCaF}_3$ ,  $\text{RbCdF}_3$  and  $\text{TlCdF}_3$  doped with  $\text{Gd}^{3+}$  were grown by the Bridgman–Stockbarger technique in the Equipe de Physique de l'Etat Condensé, Le Mans.

EPR measurements were carried out using a standard X-band spectrometer working with a 100 kHz modulation of the steady magnetic field. The temperature of a sample was changed using a gas flow technique with an accuracy of  $\pm 0.5$  K.

Hydrostatic pressure measurements, up to 550 MPa, were made using a device described in detail by Stankowski *et al* (1976). All pressure measurements were carried out at a constant temperature  $T = 290$  K.

## 3. Results

The temperature dependences of the absolute value of the  $b_4^0$  spin-Hamiltonian parameters are shown in figure 1, whereas the hydrostatic pressure dependences are shown in figure 2. As seen from the figures, both dependences proved to be linear in the measured temperature and pressure regions.

The temperature-induced changes in  $b_4^0$  for  $\text{RbCaF}_3$ ,  $\text{CsCaF}_3$  and  $\text{RbCdF}_3$  are consistent with those reported previously by Buzaré *et al* (1980), Arakawa *et al* (1982) and Rewaj *et al* (1990, 1991). The data for  $\text{Gd}^{3+}$  in  $\text{RbCdF}_3$  and  $\text{TlCdF}_3$  are presented here for the first time. Because we could not find any EPR data for  $\text{TlCdF}_3:\text{Gd}^{3+}$  in the literature, we list as follows the results obtained for  $T = 298$  K at atmospheric pressure:  $b_4^0 = -(3.49 \pm 0.02) \times 10^{-4} \text{ cm}^{-1}$ ;  $b_6^0 = (0.72 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}$  and  $g = 1.9888 \pm 0.0001$ .

The dependence of  $b_4^0$  upon the metal–ligand distance  $r$  can be calculated using the thermal expansion and compressibility coefficients (Rousseau *et al* 1975, Ridou 1978, Ridou *et al* 1984) and assuming that both coefficients (bulk values) do not differ too much from the local values. The plots of  $\log b_4^0$  versus  $\log r$  for different

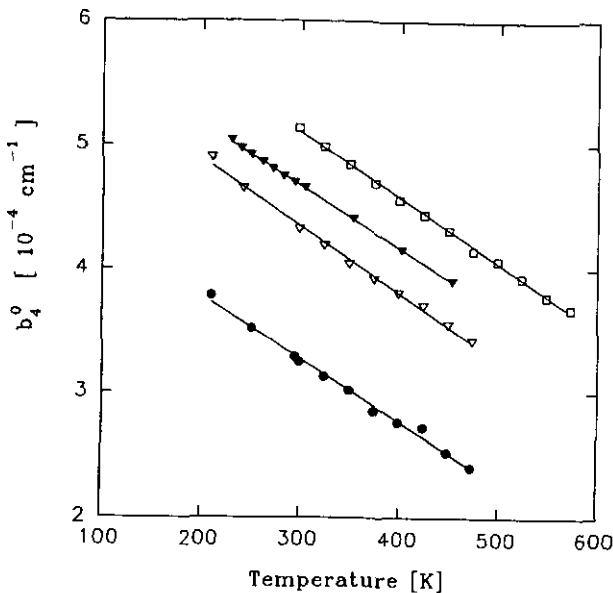


Figure 1. Temperature dependence of the  $b_4^0$  spin-Hamiltonian parameter for fluoroperovskite crystals doped with  $Gd^{3+}$ :  $\square$ , CsCaF<sub>3</sub>;  $\blacktriangledown$ , RbCaF<sub>3</sub>;  $\nabla$ , RbCdF<sub>3</sub>;  $\bullet$ , TlCdF<sub>3</sub>.

systems are presented in figure 3. Obviously, during the construction of these plots we assumed tentatively that the observed changes in  $b_4^0$  were caused only by the change in the metal-ligand distances induced by temperature or stress according to a law  $b_4^0 \sim r^k$ .

The above assumption leads to different values of  $k$  depending on whether they are determined on the basis of temperature or pressure data. These values, denoted respectively by  $k_T$  and  $k_P$ , are listed in table 1. For all systems investigated here, the absolute value of  $k_T$  is much larger than that of  $k_P$ . This strongly suggests that the effect of thermal expansion cannot exclusively be used to interpret our data on the temperature dependence of the  $b_4^0$  spin-Hamiltonian parameter and that the effect of lattice vibrations has to be taken into account. In order to separate the contributions resulting from these two effects, one can use the relation given by Walsh *et al* (1965). According to this relation the contribution to the  $b_4^0(T)$  resulting from lattice vibrations is

$$(\partial b_4^0 / \partial T)_V = (\partial b_4^0 / \partial T)_P - (\beta / K)(\partial b_4^0 / \partial P)_T \tag{2}$$

where  $\beta$  is the volume thermal expansion coefficient and  $K$  is the volume compressibility coefficient.

Again it may be argued that the analysis based on this relation is of little value because of the lack of knowledge of the local values for  $\beta$  and  $K$ . However, Ivanenko and Malkin (1970) suggested that the relative change in  $\beta$  (i.e.  $\beta_{loc} / \beta_{bulk}$ ) is the same as that in  $K$  and thus the ratio of  $\beta / K$  would be unchanged for doped crystals.

Using equation (2) we estimated the contributions to  $b_4(T)$  resulting only from the effect of thermal expansion, and on the basis of these data we again determined

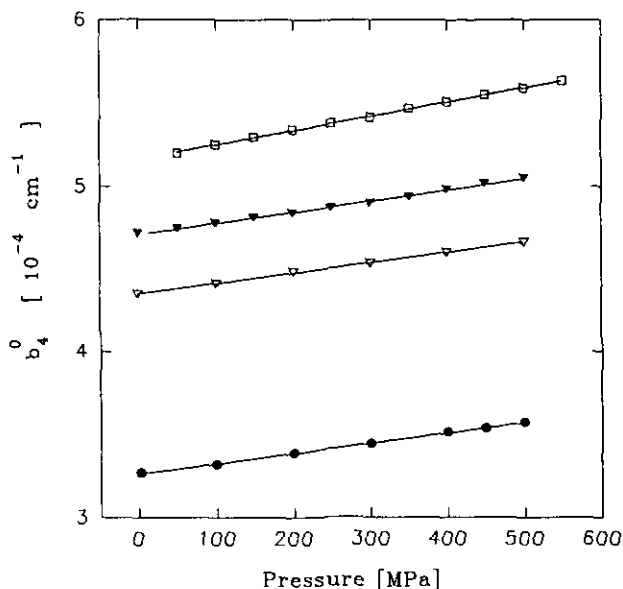


Figure 2. Hydrostatic pressure dependence of the  $b_4^0$  spin-Hamiltonian parameter for fluoroperovskite crystals doped with  $Gd^{3+}$ :  $\square$ , CsCaF<sub>3</sub>;  $\blacktriangledown$ , RbCaF<sub>3</sub>;  $\nabla$ , RbCdF<sub>3</sub>;  $\bullet$ , TlCdF<sub>3</sub>.

the power-law exponents  $k$  corresponding to these contributions. All the results of our measurements and estimations are listed in table 1. In order to compare these data with those known for other crystals, we listed in table 2 the logarithmic derivatives, expressing relative changes in  $b_4^0$  according to a method proposed by Müller and Berlinger (1986).

Comparing the results listed in these tables with the corresponding data obtained previously for the  $MF_2:Gd^{3+}$  system, one can easily notice three facts.

(i) The absolute values of the power-law exponents  $k$  describing the radial dependence of the  $b_4^0$  spin-Hamiltonian parameter through a dependence of  $b_4^0 \sim r^k$  type are larger for fluoroperovskites than for fluorides by a factor ranging from 2 to 3.

(ii) The effect resulting from vibronic interactions is much more pronounced for fluoroperovskites (it amounts to about 68% and seems to be rather independent of the host lattice) than for fluorides for which the effect of thermal expansion is dominant.

(iii) The values of  $[\partial(\ln b_4^0)/\partial T]_P$  for perovskite crystals doped with  $Gd^{3+}$  are very similar and seem to be independent of the coordination number.

#### 4. Discussion

The most striking feature of our results is the fact that the  $k$ -values are so high. The reason underlying this observation is not known to us but it is worth noting that

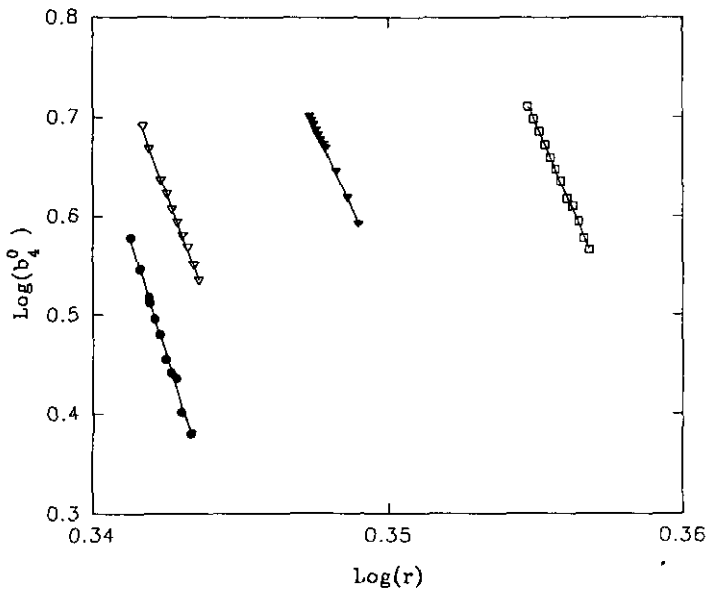


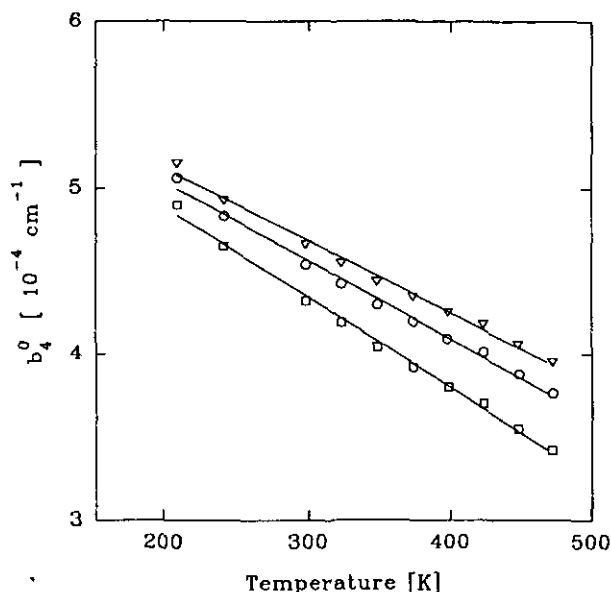
Figure 3. Plots of  $\log b_4^0$  versus  $\log r$ :  $\square$ , CsCaF<sub>3</sub>;  $\blacktriangledown$ , RbCaF<sub>3</sub>;  $\nabla$ , RbCdF<sub>3</sub>;  $\bullet$ , TiCdF<sub>3</sub> (from the temperature dependence of  $b_4^0$ ).

high values of  $k$  were also recently determined for  $Gd^{3+}$  in  $NH_4Ce(SO_4)_2 \cdot 4H_2O$  and  $NH_4Sm(SO_4)_2 \cdot 4H_2O$  single crystals by Misra and Li (1992). They were able to explain this result on the basis of the application of the superposition model of Newman assuming that apart from a radial distortion of the crystal lattice around the paramagnetic ion there exists also a small angular distortion. In the light of this observation the high values of  $k$  determined in this paper could be, at least partially, interpreted assuming that in our case both types of distortion are temperature dependent.

The second problem needing closer examination is the role played by spin-phonon interactions. Microscopic theories dealing with these interactions for rare-earth complexes are now being studied (see, e.g., Pastusiak and Kuriata (1992)) and in their present form cannot be directly applied to discuss our results. We shall use therefore the semiempirical model of Bates and Szymczak (1975, 1976, 1977) which was proven to interpret adequately the EPR temperature data on  $^8S_{7/2}$  ground-state ions in  $MF_2$ . The model under discussion predicts two significant contributions to the spin-Hamiltonian parameters:

- (i) the contribution resulting from lattice anharmonicity;
- (ii) the contribution derived from the fact that the orbit-lattice Hamiltonian should be invariant under rotational transformations.

The application of both models requires knowledge of basic thermodynamic parameters describing the properties of the investigated crystals and their elastic anisotropy. Below we shall discuss, as an example, the results of detailed calculations for the particular case of the  $RbCdF_3:Gd^{3+}$  system.



**Figure 4.** The effect of the spin-phonon contributions to  $b_4^0(T)$  for  $\text{RbCdF}_3:\text{Gd}^{3+}$  resulting from the two mechanisms considered in the paper for  $\Theta_D = 253$  K:  $\square$ , experimental results;  $\circ$ , experimental results with the inclusion of the correction from lattice anharmonicity;  $\nabla$ , as above and including additionally rotational modes.

The components of the  $A_{ij}$ -tensor describing the elastic anisotropy of cubic crystals can be calculated from the values of the elastic constants according to equation (12) of Bates and Szymczak (1975). These equations have to be corrected, probably because they contained errors, by a factor including the crystal density. Using these corrected equations we obtained the values of the  $A_{ij}$ -tensor components given in table 3.

The spin-phonon contributions to the  $b_4^0$  spin-Hamiltonian parameter resulting from models (i) and (ii) are given by Bates and Szymczak (1976, 1977) as

$$\delta b_4^0(\text{anh.}) = \frac{45h}{128\pi^3\rho} G(A_{11} + 4A_{44} - 2A_{12}) \left[ \omega_D^4 + 8 \left( \frac{kT}{h} \right)^4 \int_0^{\Theta_D/T} \frac{x^3 dx}{\exp x - 1} \right] \quad (3)$$

$$\delta b_4^0(\text{rot.}) = \frac{-5}{256\pi^3\rho} b_4^0(A_{44} - A_{12}) \left[ \omega_D^4 + 8 \left( \frac{kT}{h} \right)^4 \int_0^{\Theta_D/T} \frac{x^3 dx}{\exp x - 1} \right]. \quad (4)$$

Here  $\rho$  is the crystal density,  $G$  is the  $\Gamma_{1g}$  component of the magnetoelastic tensor, and  $\Theta_D$  and  $\omega_D$  are the Debye temperature and frequency, respectively.

In our calculations we used  $\rho = 3.586 \times 10^3 \text{ kg m}^{-3}$  and the value of  $G = (0.62 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}$  found directly from our pressure measurements.

As seen from the above equations, the contributions introduced by both models will substantially depend on the value of the Debye temperature. Unfortunately, as far as we know, this has not yet been determined for the systems investigated here.

Table 1. The values of the experimental parameters derived from temperature and hydrostatic measurements for different fluoroperovskites doped with  $Gd^{3+}$ .

Sample	$(\partial b_4^0 / \partial T)_P$ ( $10^{-6} \text{ cm}^{-1} \text{ K}^{-1}$ )	$(\partial b_4^0 / \partial P)_T$ ( $10^{-6} \text{ cm}^{-1} \text{ MPa}^{-1}$ )	$\beta = (1/V)(\partial V / \partial T)$ ( $10^{-6} \text{ K}^{-1}$ )	$K = (1/V)(\partial V / \partial P)$ ( $10^{-6} \text{ MPa}^{-1}$ )	$(\partial b_4^0 / \partial T)_V$ ( $10^{-6} \text{ cm}^{-1} \text{ K}^{-1}$ )
RbCaF <sub>3</sub> :Gd <sup>3+</sup>	-50.4 ± 0.3	6.7 ± 0.1	50.4	-19.8	-33.4
CsCaF <sub>3</sub> :Gd <sup>3+</sup>	-53.3 ± 0.8	8.6 ± 0.1	53.0	-19.7	-33.3
RbCdF <sub>3</sub> :Gd <sup>3+</sup>	-54.7 ± 1.3	6.3 ± 0.1	50.4	-16.9	-36.0
TlCdF <sub>3</sub> :Gd <sup>3+</sup>	-50.8 ± 1.4	6.2 ± 0.2	50.4	-17.2	-32.7
Vibrational					
Sample	contribution to $(\partial b_4^0 / \partial T)_P$ (%)		$k_T = \partial(\log b_4^0) / \partial(\log \tau)$ from $b_4^0(T)$	$k_P = \partial(\log b_4^0) / \partial(\log \tau)$ from $b_4^0(P)$	K for dilatational part only
RbCaF <sub>3</sub> :Gd <sup>3+</sup>	66.3		-66.9 ± 1.1	-20.1 ± 0.6	-20.9
CsCaF <sub>3</sub> :Gd <sup>3+</sup>	56.6		-68.8 ± 2.0	-20.5 ± 0.1	-27.1
RbCdF <sub>3</sub> :Gd <sup>3+</sup>	65.9		-95.8 ± 1.1	-24.7 ± 0.5	-24.9
TlCdF <sub>3</sub> :Gd <sup>3+</sup>	64.3		-81.8 ± 1.5	-31.3 ± 0.5	-29.3



Table 2. The data on  $b_4^0$  logarithmic derivatives and vibronic contributions for different systems doped with S-state ions.

Sample	Coordination number	$b_4^0(T \approx 300 \text{ K})$ ( $10^{-4} \text{ cm}^{-1}$ )	$[\partial(\ln b_4^0)/\partial T]_P$ ( $10^{-4} \text{ K}^{-1}$ )	$(\beta/K)[\partial(\ln b_4^0)/\partial P]_T$ ( $10^{-4} \text{ K}^{-1}$ )	$[\partial(\ln b_4^0)/\partial T]_V$ ( $10^{-4} \text{ K}^{-1}$ )	Vibration contribution to $[\partial(\ln b_4^0)/\partial T]_P$ (%)	References and remarks
RbCaF <sub>3</sub> :Gd <sup>3+</sup>	6	-4.65	-11.3	-3.5	-7.8	69.2	This paper
CsCaF <sub>3</sub> :Gd <sup>3+</sup>	6	-5.14	-12.2	-4.3	-7.9	65.0	This paper
RbCdF <sub>3</sub> :Gd <sup>3+</sup>	6	-4.32	-13.3	-4.1	-9.1	68.8	This paper
TlCdF <sub>3</sub> :Gd <sup>3+</sup>	6	-3.25	-16.8	-5.3	-11.5	68.4	This paper
CsCdF <sub>3</sub> :Gd <sup>3+</sup>	6	-4.82	-13.0	—	—	—	Arakawa et al (1982); $\Delta T = 487$ - 300 K only
KZnF <sub>3</sub> :Gd <sup>3+</sup>	12	-8.59	-11.2	—	—	—	Arakawa et al (1979); $\Delta T = 487$ - 300 K only
SrTiO <sub>3</sub> :Gd <sup>3+</sup>	6	-5.70	-11.2	-1.7	-9.5	85.2	Rimai et al (1964)
SrTiO <sub>3</sub> :Fe <sup>3+</sup>	6	-96.60	-5.4	-3.3	-2.1	39.0	Rimai et al (1964); $b_4^0(P)$
CdF <sub>2</sub> :Gd <sup>3+</sup>	8	-48.22	-4.5	-2.6	-1.9	42.5	Rewaj (1969); $b_4^0(T)$ Rewaj and Krupski (1978)

**Table 3.** The values of the  $A_{ij}$ -tensor components for  $RbCdF_3$ .

Crystal	$A_{11}$ ( $10^{-18} \text{ s}^5 \text{ m}^{-5}$ )	$A_{12}$ ( $10^{-18} \text{ s}^5 \text{ m}^{-5}$ )	$A_{44}$ ( $10^{-18} \text{ s}^5 \text{ m}^{-5}$ )
RbCdF <sub>3</sub>	24.0	-15.0	57.1

Therefore, in this situation we can only carry out rather crude estimations within some limits of  $\Theta_D$  indicated so far in the literature.

During our previous parametrization of the spin-phonon interactions for  $RbCdF_3:Gd^{3+}$  carried out for the  $b_2^0$  spin-Hamiltonian parameter (Guskos *et al* 1992) we found that the temperature dependence of this parameter was best described in terms of the Debye model with  $\Theta_D = 253$  K. Using this value of the Debye temperature we estimated the role of the spin-phonon interactions resulting from both the above-listed mechanisms and the result is illustrated in figure 4. From the slopes of the lines presented in figure 4, one can find that the spin-phonon interactions can account for about 20% of the vibronic contributions derived experimentally using the method of Walsh *et al*.

However, Burriel *et al* (1987) determined the Debye temperature for  $KZnF_3$  equal to 403 K from the phonon spectra calculations and  $395 \pm 5$  K from the heat capacity measurements. They claimed also that the temperature thus determined should be rather representative for all cubic perovskites. In this context, the Debye temperature used by us while plotting figure 4 would be too small. Therefore, in our next calculations of the spin-phonon contributions we let  $\Theta_D$  be a variable parameter and came to the conclusion that for  $\Theta_D = 370$  K the whole vibronic contribution found experimentally can be explained within the framework given by the theory of Bates and Szymczak.

The Debye temperature determined in this way seems to be quite realistic and therefore we hope that the results presented will encourage other researchers working in the field of EPR to pay more attention to including dynamic interactions during the interpretation of the spin-Hamiltonian parameters measured at high temperatures.

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