TEMPERATURE DEPENDENCE OF THE SPIN–LATTICE INTERACTION FOR Gd^{3+} IN CaF_2 AND CdF_2

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The temperature dependence of the second order spin–lattice coefficients of Gd^{3+} in CaF_2 and CdF_2 was measured. These values are compared with those obtained for Gd^{3+} in ThO_2 and CeO_2.

The measurement of spin–lattice coefficients by electron paramagnetic resonance techniques in crystals deformed by uniaxial stresses is useful to understand the behaviour of s-state ions in crystals. In cubic symmetry two spin–lattice coefficients, related to second-order spin operators in an effective spin formalism (spin–lattice Hamiltonian) appear. In a previous work we measured these coefficients related to tetragonal ($G_{3g}^{(2)}$) and trigonal ($G_{5g}^{(2)}$) deformations of the crystal as a function of temperature for Gd^{3+} in ThO_2 and in CeO_2 [1]. The observed temperature variation was assumed to be due to the interaction of the Gd^{3+} ions with the lattice vibrations In this work we report experimental values which support this explanation. We measure the spin–lattice coefficients $G_{3g}^{(2)}$ and $G_{5g}^{(2)}$ for Gd^{3+} in CaF_2 and CdF_2 between 4.2 and 290 K using the techniques described in ref. [1]: The CaF_2 and CdF_2 samples, doped with 0.1 at.% of Gd^{3+} were provided by Optovac Inc., USA. To obtain the values of $G_{3g}^{(2)}$ and $G_{5g}^{(2)}$ from the experimental data, we used the values of the elastic constants of CaF_2 and CdF_2 that have been measured as a function of temperature [2, 3]. Our experimental results are shown in fig. 1 as a function of temperature together with the values for Gd^{3+} in ThO_2 and in CeO_2. Data of the elastic constants of these crystals are available only for ThO_2 at room temperature [4]. In order to obtain the values given in fig. 1 we used for CeO_2 the same elastic constants as for ThO_2 and we assumed that their temperature variation is similar to that observed for other crystals with fluorite structure.

Fig. 1 shows both $G_{3g}^{(2)}$ and $G_{5g}^{(2)}$ versus T for all the crystals studied. Gd^{3+} replaces cations of different size and charge in the fluorine (divalent) and oxygen (tetravalent) coordination. It can be seen that the slopes of $G_{3g}^{(2)}$ and $G_{5g}^{(2)}$ as a function of temperature have opposite signs. However, for each coefficient the sign remains the same for all the compounds, and their absolute change is in all cases of the same order of magnitude despite their different values at 0 K.

The temperature variation of the spin–lattice coefficients cannot be due to the change of the elastic constants of the crystal at the impurity site, as can

Table 1
Values of the constants $G_i^{(2)}$(RL) and $K_i^{(2)}$ (units in m^{-1})

	$G_{3g}^{(2)}$(RL)	$K_{3g}^{(2)}$	$G_{5g}^{(2)}$(RL)	$K_{5g}^{(2)}$
CaF_2	−20.0 ±0.1	−0.71±0.04	−12.9±0.3	0.87±0.11
CdF_2	−19.7 ±0.1	−1.17±0.02	− 9.7±0.1	1.02±0.03
ThO_2	− 1.33±0.13	−0.41±0.06	− 8.1±0.1	0.78±0.04
CeO_2	−21.7 ±0.1	−0.51±0.06	− 1.2±0.1	0.56±0.03

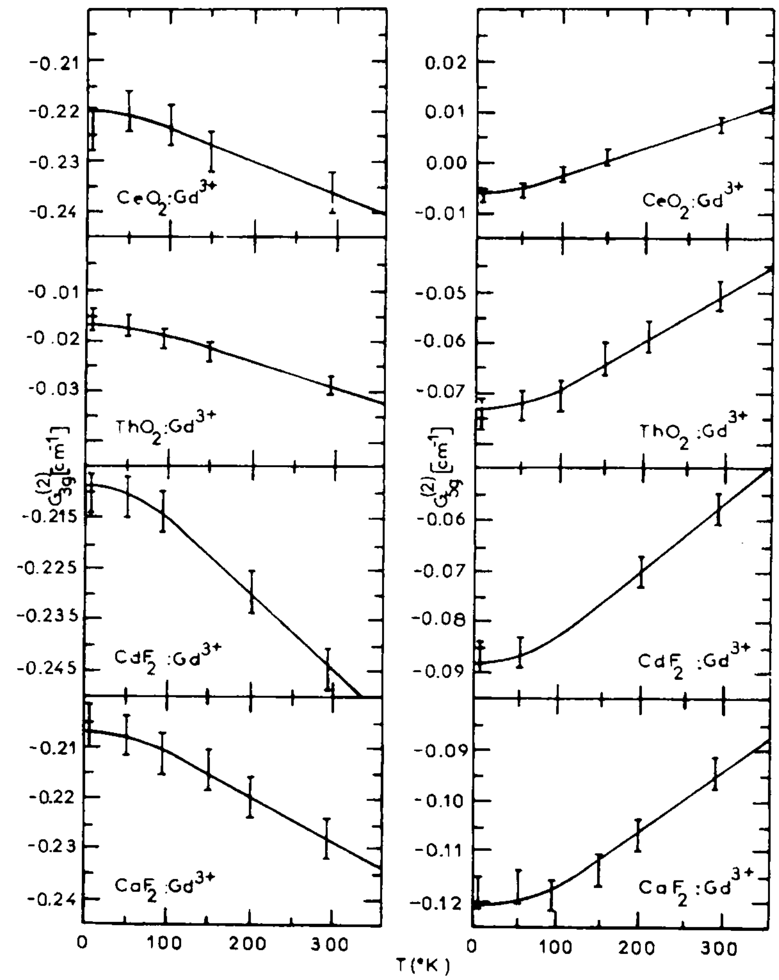

Fig. 1. Temperature dependence of the second-order tetragonal and trigonal spin–lattice coefficients $G_{3g}^{(2)}$ and $G_{5g}^{(2)}$ in CeO_2, ThO_2, CdF_2 and CaF_2. The solid line is obtained by a least-squares fit of eq. (1) with the experimental data.

be observed from the sign change of $G_{5g}^{(2)}$ of Gd^{3+} in CeO_2.

We attribute the temperature dependence of $G_{3g}^{(2)}$ and $G_{5g}^{(2)}$ of Gd^{3+} in cubic crystals to the interaction of the ions with the lattice vibrations. Assuming an Einstein model, the temperature variation of the spin–lattice coefficients is given by [1]:

$$G_i^{(2)}(T) = G_i^{(2)}(\mathrm{RL}) + K_i^{(2)} \coth\left(\frac{\hbar\omega}{2kT}\right), \qquad (1)$$

where $G_i^{(2)}(T)$ and $G_i^{(2)}(\mathrm{RL})$ are the values of $G_{3g}^{(2)}$ and $G_{5g}^{(2)}$ at temperature T and for a rigid lattice respectively and $K_i^{(2)}$ is a constant depending on the interaction. By a least-squares analysis we obtained a good fit of experimental data with eq. (1) assuming $\omega = 2 \times 10^{13}\ \mathrm{sec}^{-1}$. The values of $G_i^{(2)}(\mathrm{RL})$ and $K_i^{(2)}$ are given in table 1.

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