SPIN-PHONON INTERACTIONS FOR $\text{PbF}_2\text{:Gd}^{3+}$ — COMPARISON BETWEEN THEORY AND EXPERIMENT

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The results implying from two microscopic models for spin-phonon interactions are analyzed for the case of $\text{PbF}_2\text{:Gd}^{3+}$. It is shown that the two-phonon first-order mechanism predicts significant contributions to the values of the spin-phonon second-order coupling constants and the one-phonon second-order mechanism is less effective.

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1. Introduction

In our previous paper [1] we reported the experimental data on the dynamic orbit-lattice interactions for $\text{PbF}_2\text{:Gd}^{3+}$ single crystals. We demonstrated that the data can be parametrized using the Einstein as well as the Debye schemes. We came also to the conclusion that although the temperature dependence of the second-order spin-lattice coefficients is predominantly caused by spin-phonon interactions, the microscopic origin of these interactions is very much obscure and the application of the existing theories leads to rather insignificant contributions.

At the same time great theoretical effort has been done in order to develop more advanced theories which could account for dynamic contributions to the experimentally observed temperature variations of the spin-hamiltonian parameters for S ground state rare earth ions [2-4]. In view of the above and also in view of the fact that the discussion concerning the comparison between the experimental and theoretical results published in [1] was, as it now seems, based on the calculations which rather greatly underestimated the role of one of the analyzed microscopic models, we intend to report here in detail the data on the effectiveness of the microscopic models based principally on the relativistic approach to the orbit-lattice interactions for the $^8S_{7/2}$ ground state ions.

2. Theoretical framework

It is often assumed that in the many-center problem describing the interaction between a magnetic ion in a crystal lattice deformed by an external stress the displacement of ligands from their equilibrium position caused by both lattice vibrations and the applied stress is small compared to the metal-ligand distance. In consequence, the hamiltonian describing the crystal field can be expanded into a Taylor series with respect to both normal (or symmetric) coordinates and symmetrized components of the strain tensor.

Since the experimental data are very well described by the spin-lattice hamiltonian which is linear in static deformation [5]:

$$\kappa_{S-L} = \sum_{n,i,\alpha} G_{\Gamma i \sigma}^{(n)} 0_{i,\alpha}^{(n)} \varepsilon_{i,\alpha} \quad (1)$$

where $G_{\Gamma i \sigma}^{(n)}$ are the spin-lattice coefficients and the remaining symbols have their usual meaning.

Also because the temperature dependence of $G_{\Gamma i \sigma}^{(n)}$ can be parametrized in the harmonic approximation in expanding the crystal field hamiltonian with respect to normal coordinates, we shall limit ourself only to linear and bilinear terms of the expansion. Treating the interactions between the paramagnetic ion and the crystal field as a perturbation one can construct a variety of different mechanisms which exhibit the same tensorial (and temperature) dependence as the phenomenological hamiltonian describing the spin-lattice interaction.

We shall consider two such mechanisms which were presented in detail in [2, 3]:

1. The two-phonon first-order mechanism in which the orbit-lattice term bilinear in normal coordinates and linear with respect to the $\varepsilon_{\Gamma\gamma}$ component of the strain tensor enters the perturbation calculation in the first order

$$\langle a | V^{(2)}(\Gamma\gamma) | a \rangle. \quad (2)$$

Here $|a\rangle$ describes the electron-phonon states and γ is the component of the Γ irreducible representation determining a symmetrized static deformation.

2. The one-phonon second-order mechanism in which the term $V^{(1)}(\Gamma\gamma)$ linear in both normal coordinates and static deformation and the term $V^{(1)}(0)$ linear in normal coordinates enter as a perturbation in the second order of perturbation calculation

$$\langle a | V^{(1)}(\Gamma\gamma) | b \rangle \langle b | V^{(1)}(0) | a \rangle. \quad (3)$$

Both considered models include the relativistic character of the wave functions describing the energetical spectrum of the $^8S_{7/2}$ ground state ions.

3. The results and comparison with experimental data

The experimental data reported in [1] indicated that the temperature dependence of the second-order spin-lattice coefficients for $\text{PbF}_2:\text{Gd}^{3+}$ can be parametrized in the Einstein as well as the Debye models if the "averaged" frequency for

the optical modes is chosen to be $\omega_E = 2.5 \times 10^{13} \text{ s}^{-1}$. The Einstein model will be analyzed below due to its simplicity. In this model the temperature dependence of the second-order spin-lattice parameters is parametrized by the following function (see for example [1]):

$$G_{\Gamma_{ig}}^{(2)}(T) = G_{\Gamma_{ig}}^{(2)}(RL) + K_{\Gamma_{ig}}^{(2)} \coth \frac{\hbar\omega_E}{2kT}. \quad (4)$$

Here $G_{\Gamma_{ig}}^{(2)}(RL)$ is the temperature independent contribution to the value of $G_{\Gamma_{ig}}^{(2)}$ and $K_{\Gamma_{ig}}^{(2)}$ gives the contribution resulting from zero-point vibrations of the crystal lattice. The values of this latter parameter will be calculated microscopically below and now we quote the values determined experimentally

$$K_{\Gamma_{3g}}^{(2)}(\text{exp}) = (-3.75 \pm 0.5) \times 10^{-3} \text{ cm}^{-1}$$

and

$$K_{\Gamma_{5g}}^{(2)}(\text{exp}) = (14 \pm 1.5) \times 10^{-3} \text{ cm}^{-1}.$$

The contribution to the above constants resulting from the two-phonon first-order mechanism can be deduced from equations (53a) and (53b) given in [2]. Leaving only the terms which are most important we can write these contributions as

$$K_{\Gamma_{3g}}^{(2)}(\text{model 1}) = \frac{8}{3} A^{(2,2)}(\Gamma_{3g}) \left[\frac{-\sqrt{35}}{2325} bcb_2(0, 2) + \frac{\sqrt{6}}{128} abb_2(1, 1) \right] \langle u^2 \rangle_{T=0K}, \quad (5)$$

$$K_{\Gamma_{5g}}^{(2)}(\text{model 1}) = \frac{1}{3\sqrt{70}} A^{(2,2)}(\Gamma_{5g}) \left[-\frac{15\sqrt{6}}{126} bcb_2(0, 2) + \frac{2\sqrt{21}}{7} abb_2(1, 1) \right] \langle u^2 \rangle_{T=0K}. \quad (6)$$

Here $A^{(2,2)}(\Gamma_{ig})$ are the two-phonon dynamic coupling coefficients which expressed in the point-charge model are

$$A^{(2,2)}(\Gamma_{3g}) = \frac{20Ze^2}{R_L^5}, \quad (7)$$

$$A^{(2,2)}(\Gamma_{5g}) = \frac{20Ze^2}{\sqrt{3}R_L^5}. \quad (8)$$

In the above equations R_L is the metal-ligand distance, $\langle u^2 \rangle_{T=0K}$ is the mean square amplitude at $T = 0 \text{ K}$, $b_2(k', k)$ are the relativistic radial integrals and a , b and c are the mixing parameters for the $^8S_{7/2}$ ground state wave function

$$|^8S_{7/2}M\rangle = a|^8S_{7/2}M\rangle + b|^6P_{7/2}\rangle + c|^6D_{7/2}M\rangle + \dots \quad (9)$$

The following values of the parameters appearing in Eqs. (5)–(8) were used in our calculations:

$$R = 0.2357 \text{ nm [6]}, \quad a = 0.9863, \quad b = 0.1632, \quad c = -0.0122 \text{ [7]},$$

$$b_2(0, 2) = 2.24 \times 10^{-17} \text{ cm}^2 \quad \text{and} \quad b_2(1, 1) = 8.687 \times 10^{-19} \text{ cm}^2 \text{ [8]}.$$

Inserting the above values to Eqs. (5) and (6) we obtain the following contributions: $K_{\Gamma_{3g}}^{(2)}(\text{model 1}) = -8.65 \times 10^{-3} \text{ cm}^{-1}$ and $K_{\Gamma_{3g}}^{(2)}(\text{model 1}) = 6.42 \times 10^{-3} \text{ cm}^{-1}$.

Comparing this result with that obtained experimentally we notice that the considered model predicts correct signs and the order of magnitude for both $K_{\Gamma_{3g}}^{(2)}$ coefficients. However, the value of $K_{\Gamma_{3g}}^{(2)}$ is overestimated whereas that of $K_{\Gamma_{3g}}^{(2)}$ is underestimated. It should be pointed out here that in the calculations of the two-phonon coupling coefficients $A^{(2,2)}(\Gamma_{ig})$ we neglected the fact that the $4f^7$ electrons of Gd^{3+} can be screened from direct action of the crystal field set up by neighboring charges of the electrons on the outer $5s$ and $5p$ subshells. The magnitude of the screening effects has not yet been calculated microscopically and we can only use some estimations given, for example, by Willemsen and Hommels [9]. According to the above authors the screening factor δ_2 for the second-order crystal field terms is equal to 0.77. Taking into account the screening effects we may claim that the model under discussion, considering even the most unfavorable estimation, gives the contribution amounting above 10% of that observed experimentally.

For the one-phonon second-order mechanism the contributions to $K_{\Gamma_{3g}}^{(2)}$ can be calculated according to equation (3.23) in [3] and the procedure allowing the estimation of the proper orbit–lattice parameters given in [4]. The corresponding analytical formulas are very complex and too long to be concisely rewritten here and therefore we give only the final result for the specific case of $\text{PbF}_2\text{:Gd}^{3+}$:

$$K_{\Gamma_{3g}}^{(2)}(\text{model 2}) = -0.2 \times 10^{-3} \text{ cm}^{-1}$$

and

$$K_{\Gamma_{3g}}^{(2)}(\text{model 2}) = 0.3 \times 10^{-3} \text{ cm}^{-1}.$$

As expected, the model considered now gives much smaller contributions than the model discussed previously. Nevertheless, their magnitude is sufficiently large to be taken into account in the overall summation of all contributions to the coupling coefficients describing the spin–phonon interactions.

4. Final remarks

The inclusion of the relativistic character of the wave functions for the $^8S_{7/2}$ ground state ions leads to significant contributions to the coupling constants describing the interaction between the paramagnetic ion and the lattice vibration for

the two-phonon first-order mechanism. These contributions have the correct order of magnitude and their signs are consistent with what is measured experimentally. The one-phonon second-order mechanism is about an order in magnitude less effective. It is conceivable that the consistency between the theory and the experiment could be improved if one could take into account, microscopically, more realistic models than the point-charge one.

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