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M Velter-Stefanescu and D P Lazar

Institute of Atomic Physics, IFTM, PO Box MG-6, Magurele, R-76900 Bucharest, Romania

Abstract. The theoretical angular dependence of the direct-process relaxation rate T_1^{-1} of the trigonal Yb^{3+} ions (T$_4$ centres) in a SrF$_2$ single crystal was determined and compared with the experimental dependence. The theoretical estimation was made according to the Van Vleck–Kronig mechanism in the formalism of the dynamical spin Hamiltonian developed by Kumar and Ray.

1. Introduction

Electron spin resonance studies have shown that, in certain Yb-doped SrF$_2$ single crystals, all Yb^{3+} ions occur as trigonal centres (the so-called T$_4$ centres [1, 2]) having the following g components: $g_\parallel = 2.813$ and $g_\perp = 3.746$. In previous papers [3–5] we have presented our experimental results obtained from the spin–lattice relaxation measurements for both Q (35 GHz) and X (9 GHz) bands. For $g_\parallel$ lines, the overall low-temperature (2 K $< T <$ 12 K) relaxation data of the Yb^{3+} ions in SrF$_2$ can be described by [4]

$$T_1^{-1} = 142.2/[\exp(12.5/T) - 1] + 7.731 B^5 \coth(h\nu/2kT)$$
$$+ 0.197 \times 10^9 \exp(-111.67/T) \tag{1}$$

where the magnetic field B is expressed in teslas. In the Q band the second term corresponding to a direct process becomes dominant at very low temperatures ($T < 6$ K).

The present paper is concerned with the theoretical estimation of the angular dependence of the direct-process relaxation rate in agreement with the Van Vleck–Kronig [6, 7] mechanism, on the base of the wavefunctions [8] obtained in the point-charge approximation, and as a final result we compare the theoretical angular dependence obtained with the experimental dependence.

2. Theory

According to the Van Vleck–Kronig relaxation mechanism, the symmetric vibration modes of the complex formed around the paramagnetic ion by the nearest-neighbour (NN) ligand ions are most important for relaxation processes. The complex around the Yb^{3+} ion in SrF$_2$ is of XY$_8$ type and the symmetric modes which are to be considered are Γ_{1g}, Γ_{3g} and $2\Gamma_{5g}$ [9]. It has been shown by Ray *et al* [10] that for Kramers doublets, in cubic crystals,

the contribution to the relaxation rate of the direct process from the Γ_{1g} mode is isotropic, whereas the Γ_{3g} and Γ_{5g} modes give rise to anisotropy.

The anisotropy of the relaxation rate for Yb^{3+} in SrF_2, in the formalism of the dynamical spin Hamiltonian developed by Kumar and Ray [11], follows the function

$$T_1^{-1} \sim C_2^2 + (C_3^2 - C_2^2)(l^4 + m^4 + n^4) \tag{2}$$

where l, m and n are the direction cosines of the magnetic field with respect to the crystal axes. The constants C_2 and C_3 of the dynamical spin Hamiltonian, deduced from the effective point-charge model, are given by

$$
\begin{aligned}
C_2 &= (192\sqrt{6}/7\Delta_c)(Ze^2/R^4)(3\alpha_J \langle r^2 \rangle + 50\beta \langle r^4 \rangle/R^2 + 735\gamma_J \langle r^6 \rangle/R^4) \\
C_3 &= (64\sqrt{6}/7\Delta_c)(Ze^2/R^4)(16\alpha_J \langle r^2 \rangle + 125\beta_J \langle r^4 \rangle/R^2 + 980\gamma_J \langle r^6 \rangle/R^4).
\end{aligned}
\tag{3}
$$

Here Ze is the effective charge of the NN ligands, R is the distance between the NN ligands and the magnetic Yb^{3+} ion, $\langle r^n \rangle$ are the mean nth powers of the radii of the magnetic electron, α_J, β_J and γ_J are the Stevens multiplicative factors of operator equivalents [12] for the ground states of the Yb^{3+} ion, and Δ_c is the separation of the excited state Γ_8 from the ground state Γ_7. Using the Hartree–Fock $\langle r^n \rangle$-values of Freeman and Watson [13], namely $\langle r^2 \rangle = 0.613$ au, $\langle r^4 \rangle = 0.96$ au and $\langle r^6 \rangle = 3.104$ au, as well as $R_1 = (\sqrt{3}/4)a_0 = 4.733$ au, one obtains

$$T_1^{-1} \sim 1 + 2.16(l^4 + m^4 + n^4). \tag{4}$$

On the other hand, for the trigonal T_4 centre, owing to the presence of the charge-compensating next-nearest-neighbour (NNN) F^- ion, the total angular momentum J of the Yb^{3+} ion is oriented along the $\langle 111 \rangle$ direction, and there is another anisotropy source, namely the matrix elements resulting from the states admixture determined by the magnetic field [14] and having the typical form

$$(1/\Delta_i)\langle a|\mathbf{B} \cdot \mathbf{J}|i\rangle \tag{5}$$

where $|a\rangle$ is a state of the ground Kramers doublet and $|i\rangle$ is a state of the higher doublets at Δ_i in the ground-state multiplet. In the reference system having the z axis along the $\langle 111 \rangle$ direction, and with $\mathbf{B} \in (110)$ plane, the above matrix element may be written

$$(B/\Delta_i)\langle a|J_z \cos\theta + J_x \sin\theta|i\rangle \tag{6}$$

where θ is the angle between the field B and the axis z.

We note that the states $|a\rangle$ and $|i\rangle$ are degenerate in zero magnetic field. Since the use of perturbation theory requires this degeneracy to be first removed, $|a\rangle$ and $|i\rangle$ should be replaced by the eigenfunctions of the Zeeman perturbation $g\beta \mathbf{B} \cdot \mathbf{J}$ at the particular angle of interest [15].

However, to obtain a less complicated final expression for $T_1^{-1}(\theta)$, in our theoretical estimation we used the zero-order wavefunctions and considered independently the first two excited-state contributions. Thus, using this scheme for the calculation, finally one obtains

$$T_1^{-1} \sim B_\theta^2 \sum_i \Delta_{\Gamma_i'}^{-2} \left| \sum_q \langle \Gamma_7' - |J_z \cos\theta + J_x \sin\theta|\Gamma_i' q\rangle \right|^2. \tag{7}$$

Here B_θ is the resonance magnetic field for a particular angle θ, the subscript i distinguishes between the two excited states $\Gamma'_{8,1}$ and $\Gamma'_{8,2}$ at $\Delta_{\Gamma'_i}$ above the ground state Γ'_7 of the trigonal centre and $q = +, -$ labels the two orbitally degenerate states belonging to each Γ'_i [8].

If we combine equations (4) and (7), the resulting expression for the angular dependence of the direct process relaxation rate can be written in the form

$$T_1^{-1} \sim [1 + 2.16(l^4 + m^4 + n^4)]B_\theta^2 \sum_i \Delta_{\Gamma'_i}^{-2} \left| \sum_q \langle \Gamma'_7 - |J_z \cos\theta + J_x \sin\theta | \Gamma'_i q \rangle \right|^2 . \tag{8}$$

Replacing B_θ^2 by g^{-2}, where $g^2 = g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta$, and calculating the matrix elements using the wavefunctions given in table 1, we obtain

$$T_1^{-1} \sim g^{-2}[1 + 2.16(l^4 + m^4 + n^4)](3.6\cos^2\theta + 3.1\sin\theta\cos\theta + 7.13\sin^2\theta). \tag{9}$$

Table 1. Calculated wavefunctions and trigonal field splittings ($^2F_{7/2}$ manifold) of Yb^{3+} ions in SrF_2 for $Z_2/Z_1 = 0.26$, the ratio of the effective charges of the compensating NNN to the NN F^- ions [8]: $|\Gamma'_i\pm\rangle = \pm\lambda|\pm\frac{7}{2}\rangle + \mu|\pm\frac{1}{2}\rangle \pm \nu|\mp\frac{5}{2}\rangle$, $i = 6; 7; 8,1$ $|\Gamma'_{8,2}\pm\rangle = |\pm\frac{3}{2}\rangle$.

State	λ	μ	ν	$\Delta_{\Gamma'_i}$ (cm^{-1})
Γ'_7	0.5504	0.7971	−0.2481	0 (ground state)
$\Gamma'_{8,2}$	—	—	—	77.58
$\Gamma'_{8,1}$	0.7662	−0.3643	0.5292	87.41
Γ'_6	0.3314	−0.4814	−0.8114	137.45
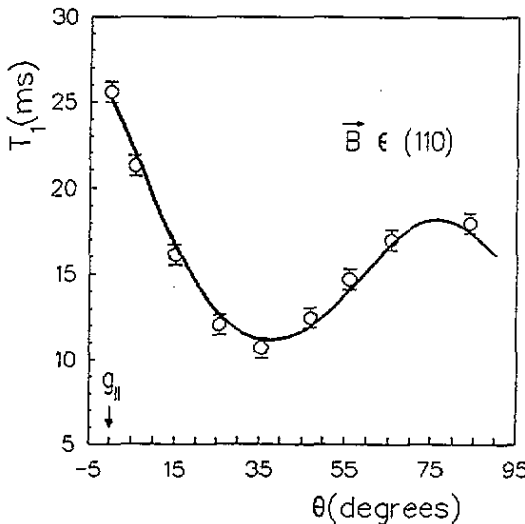
Figure 1. The angular variation in T_1 for Yb^{3+} in trigonal sites in SrF_2 (4.2 K; Q band). The magnetic field is applied at an angle θ with respect to a $\langle 111 \rangle$ axis in a $\langle 110 \rangle$ plane. The full curve represents the theoretical prediction given by equation (9).

3. Results

Spin–lattice relaxation measurements were carried out in the 35 GHz microwave band [3] using a home-made homodyne EPR spectrometer, by the 'inspection pulses' method [16, 17].

The angular variation in the experimental relaxation time T_1 obtained at 4.2 K by rotating the magnetic field in a (110) plane away from a $\langle 111 \rangle$ direction is shown in figure 1. The full curve in this figure is the result of the fit made with the function (9). The good agreement, within the experimental errors, demonstrates the correct estimation of both the angular dependence of the direct process rate and the wavefunctions corresponding to the energy level scheme of Yb^{3+} in trigonal symmetry derived from crystal-field theory taking the experimental g-values and experimental trigonal splitting $\Delta_{\Gamma'_{8,2}}$ into account [8].

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