SPIN-LATTICE RELAXATION IN CRYSTALS

PART II. CRYSTALS WITH TRIGONAL AND TETRAGONAL STRUCTURE

By H. Szymczak

Institute of Physics of the Polish Academy of Sciences, Warsaw*

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The theory of electron spin-lattice relaxation has been elaborated for crystals with trigonal and tetragonal structure. Single-phonon processes are discussed as well as two relaxation mechanisms: dipole and quadrupole mechanisms. The calculations take into account the elastic anisotropy of the medium. It is shown that the neglection of elastic anisotropy results in considerable errors in the calculation of single-phonon transition probabilities.

1. Introduction

In the previous paper [1] the author has considered the influence of elastic anisotropy of the medium on the probability of single-phonon spin lattice interaction. It has been shown there that the treatment of cubic crystals as an isotropic elastic medium (isotropic approximation) leads to considerable errors. The influence of elastic anisotropy in cubic crystals on spin-lattice relaxation is described by the tensor A_{ij} (with three components A_{11}, A_{12}, A_{44}) introduced in Ref. [1]. For the majority of cubic crystals for which the components c_{ij} of the elastic stiffness tensor are known, the components of the tensor A_{ij} have been calculated. One can expect that in crystals with symmetry lower than cubic the elastic anisotropy of the medium will play a still greater role in spin-lattice processes.

2. Spin-lattice relaxation in crystals with trigonal and tetragonal structure

The processes considered in the present paper are one phonon spin-lattice processes in crystals of trigonal structure (groups D_3, C_{3v}, D_{3d}) and tetragonal structure (groups D_{2d}, D_4, D_{4v}, D_{4h}). Similarly as in Ref. [1] the following two spin-lattice relaxation mechanisms are taken into account:

a) dipole mechanism with the Hamiltonian

$$\mathscr{H}_{sp} = \sum_{ijkl} F_{ijkl} S_i H_j e_{kl} \tag{1}$$

* Address: Instytut Fizyki PAN, Lotników 32/40, 02-668 Warszawa, Poland.

b) quadrupole mechanism with the Hamiltonian

$$\mathscr{H}_{sp} = \sum_{ijkl} G_{ijkl} S_i S_j e_{kl} \tag{2}$$

where e_{kl} is the strain tensor, S_i the spin operator components, F_{ijkl} and G_{ijkl} the components of the magnetoelastic tensor.

The tensors F_{ijkl} and G_{ijkl} are often written in the form of second rank tensors $F_{\alpha\beta}$ and $G_{\alpha\beta}$ ($\alpha, \beta = 1, 2, \ldots, 6$) in the six-dimensional Voigt space.

The probability of transition in unit time of an ion from the i-level to the j-th level with a simultaneous emission of one phonon can be written in the form (see Ref. [1]):

a) in case of the dipole model

$$W_{ij} = \Phi(\omega, T) \sum_{m,n} \Gamma_{mn} \langle i| (\boldsymbol{SH})_m |j\rangle \langle j| (\boldsymbol{SH})_n |i\rangle \tag{3}$$

where

$$\Phi(\omega, T) = \frac{\omega^3 \exp \frac{\hbar\omega}{kT}}{32\pi^2 \varrho \hbar \left(\exp \frac{\hbar\omega}{kT} - 1 \right)}$$

ϱ — is the density of the crystal, ω — the resonance frequency, $\boldsymbol{H}$ — the external magnetic field vector, Γ_{mn} — the second rank tensor in Voigt's space with the components

$$\Gamma_{mnpr} = \sum_{\alpha\beta\gamma\delta} A_{\alpha\beta\gamma\delta} F_{mn\alpha\beta} F_{pr\gamma\delta}$$

$$A_{\alpha\beta\gamma\delta} = \int \sum_{\mu} (\varepsilon_\alpha^\mu \lambda_\beta + \varepsilon_\beta^\mu \lambda_\alpha)(\varepsilon_\gamma^\mu \lambda_\delta + \varepsilon_\delta^\mu \lambda_\gamma) \frac{d\Omega}{(v_k^\mu)^5} \tag{4}$$

$\boldsymbol{k}$, $\boldsymbol{\varepsilon}^\mu$ the wave vector of the phonon and its polarization vector; μ the index enumerating the particular phonon modes ($\mu = 1, 2, 3$); v_k^μ — the velocity of phonons with given k and polarization μ

$$(\boldsymbol{SH})_1 = S_x H_x, \quad (\boldsymbol{SH})_2 = S_y H_y, \quad (\boldsymbol{SH})_3 = S_z H_z$$

$$(\boldsymbol{SH})_4 = S_z H_y + S_y H_z, \quad (\boldsymbol{SH})_5 = S_x H_z + S_z H_x,$$

$$(\boldsymbol{SH})_6 = S_x H_y + S_y H_x$$

b) for the quadrupole model

$$W_{ij} = \Phi(\omega, T) \sum_{mn} \Lambda_{mn} \langle i| (S)_m |j\rangle \langle j| (S)_n |i\rangle \tag{5}$$

where Λ_{mn} — is a second rank tensor in Voigt's space with the components

$$\Lambda_{mnpr} = \sum_{\alpha\beta\gamma\delta} A_{\alpha\beta\gamma\delta} G_{mn\alpha\beta} G_{pr\gamma\delta}$$

$$(S)_1 = S_x^2, \quad (S)_2 = S_y^2, \quad (S)_3 = S_z^2, \quad (S)_4 = S_y S_z + S_z S_y,$$

$$(S)_5 = S_x S_z + S_z S_x, \quad (S)_6 = S_x S_y + S_y S_x.$$

The main problem for both models under consideration is the calculation of the components of the tensor $A_{\alpha\beta\gamma\delta}$. Owing to the symmetry properties of the crystal this tensor may be written as a tensor A_{mn} in six-dimensional Voigt space. In the isotropic approximation the tensor A_{mn} has two independent components A_{11} and A_{12} and can be presented in the form:

$$(A_{mn}) = \begin{Vmatrix} A_{11} & A_{12} & A_{12} & 0 & 0 & 0 \\ A_{12} & A_{11} & A_{12} & 0 & 0 & 0 \\ A_{12} & A_{12} & A_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & A_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & A_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & A_{44} \end{Vmatrix} \tag{6}$$

$$A_{44} = \tfrac{1}{2}(A_{11} - A_{12})$$

If the medium is treated as elastically isotropic, it is possible to calculate the components A_{11} and A_{12}:

$$A_{11} = \frac{16\pi}{15}\left(\frac{3}{v_l^5} + \frac{2}{v_t^5}\right)$$

$$A_{12} = \frac{16\pi}{15}\left(\frac{1}{v_l^5} - \frac{1}{v_t^5}\right) \tag{7}$$

where v_l and v_t are the velocities of the longitudinal and transverse wave, respectively. The easiest way to calculate these velocities is when the direction of propagation of the phonon coincides with the C_3 axis (in trigonal crystals) or the C_4-axis in tetragonal crystals. Then

$$v_l = \left(\frac{C_{33}}{\varrho}\right)^{1/2}$$

$$v_t = \left(\frac{C_{44}}{\varrho}\right)^{1/2} \tag{8}$$

For crystals with trigonal symmetry (D_3, C_{3v}, D_{3d}) the tensor A_{mn} has six independent components and can be written in the form:

$$(A_{mn}) = \begin{Vmatrix} A_{11} & A_{12} & A_{13} & A_{14} & 0 & 0 \\ A_{12} & A_{11} & A_{13} & -A_{14} & 0 & 0 \\ A_{13} & A_{13} & A_{33} & 0 & 0 & 0 \\ A_{14} & -A_{14} & 0 & A_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & A_{44} & A_{14} \\ 0 & 0 & 0 & 0 & A_{14} & \tfrac{1}{2}(A_{11} - A_{12}) \end{Vmatrix} \tag{9}$$

The results of calculations of the components of the tensor A_{mn} for trigonal crystals are given in Table I. The calculations have been made using Eq. (4) and are based on the values of the components of the elastic stiffness tensor given in the papers: [2] for Al_2O_3, $CaCO_3$

TABLE I

Components of the tensor A_{mn} for crystals with trigonal structure (in units 10^{-28} cm^{-5} sec^5)

	Al_2O_3	$CaCO_3$	$NaNO_3$	SiO_2
A_{11}	0.6506	15.55	14.67	10.31
A_{33}	0.5666	28.59	52.82	6.62
A_{12}	−0.3321	−6.77	−4.72	−3.62
A_{13}	−0.2111	−9.39	−12.36	−3.03
A_{14}	0.1095	8.87	−9.25	−2.74
A_{44}	0.6066	17.30	21.60	4.38
A_{66}	0.4913	11.16	9.69	6.97

TABLE II

Components of the tensor A_{mn} for crystals with trigonal structure calculated by means of the isotropic approximation (in units 10^{-28} cm^{-5} sec^5)

	Al_2O_3	$CaCO_3$	$NaNO_3$	SiO_2
A_{11}	0.8979	14.38	33.49	4.07
A_{12}	−0.4005	−5.47	−9.25	−1.22
A_{44}	0.6492	9.92	21.37	2.65

and Na_2NO_3, and [3] for SiO_2. For the sake of comparison the values of these components calculated in the isotropic approximation (Eqs (6)–(8)) are given in Table II. It follows from the comparison of these two tables that the isotropic approximation is not suitable for the description of relaxation phenomena in trigonal crystals. It gives both incorrect values of the particular components of A_{mn} and of their ratios as well. The relationships predicted by the isotropic approximation: $A_{11} = A_{33}$, $A_{12} = A_{13}$, $A_{14} = 0$, $2A_{44} = A_{11} - A_{12}$ are not satisfied for any of the investigated trigonal crystals. Comparatively smallest deviations occur in case of Al_2O_3 crystals.

For crystals with tetragonal symmetry (D_{2d}, D_4, D_{4v}, D_{4h}) the tensor A_{mn} has six independent components and can be written in the form:

$$(A_{mn}) = \begin{Vmatrix} A_{11} & A_{12} & A_{13} & 0 & 0 & 0 \\ A_{12} & A_{11} & A_{13} & 0 & 0 & 0 \\ A_{13} & A_{13} & A_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & A_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & A_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & A_{66} \end{Vmatrix} \tag{10}$$

Table III presents the results of calculations of the components of the tensor A_{mn} for crystals with tetragonal symmetry. These calculations have been made using the values of components of the elastic stiffness tensor given in Ref. [2] for $ZrSiO_4$, Ref. [3] for $BaTiO_3$, Ref. [4] for TiO_2, Ref. [5] for ZnO and CdS; and Ref. [6] for MgF_2.

The values of A_{mn} calculated on the basis of the the same data but using the isotropic approximation are given in Table IV. The comparison of the Tables III and IV implies

Trigonal symmetry, groups C_3, C_{3i}

$$F_{12} = F_{21},\ F_{13} = F_{23},\ F_{61} = -F_{16},\ 2F_{66} = F_{11} - F_{12},\ F_{31} = F_{32}$$

groups C_{3v}, D_3, D_{3d}

$$F_{12} = F_{21},\ F_{13} = F_{23},\ F_{31} = F_{32},\ 2F_{66} = F_{11} - F_{12},$$
$$F_{15} = F_{16} = F_{45} = F_{46} = F_{61} = 0.$$

Tetragonal symmetry, groups C_{4v}, D_{2d}, D_4, D_{4h}

$$F_{12} = F_{21},\ F_{13} = F_{23},\ F_{31} = F_{32}$$
$$F_{14} = F_{15} = F_{16} = F_{41} = F_{45} = F_{46} = F_{61} = 0$$

groups C_4, S_4, C_{4h}

$$F_{12} = F_{21},\ F_{13} = F_{23},\ F_{31} = F_{32},$$
$$F_{14} = F_{15} = F_{41} = F_{46} = 0.$$

Hexagonal symmetry, groups C_6, C_{3h}, C_{6h}

$$F_{12} = F_{21},\ F_{13} = F_{23},\ F_{31} = F_{32},\ F_{61} = -F_{16},\ 2F_{66} = F_{11} - F_{12}$$
$$F_{14} = F_{15} = F_{41} = F_{46} = 0$$

groups D_{3h}, C_{6v}, D_6, D_{6h}

$$F_{12} = F_{21},\ F_{13} = F_{23},\ 2F_{66} = F_{11} - F_{12}.$$

In the general case described by Eq. (11) the tensor Γ_{mn} has 14 independent components:

$$(\Gamma_{mn}) = \begin{Vmatrix} \Gamma_{11} & \Gamma_{12} & \Gamma_{13} & \Gamma_{14} & \Gamma_{15} & \Gamma_{16} \\ \Gamma_{12} & \Gamma_{11} & \Gamma_{23} & -\Gamma_{14} & -\Gamma_{15} & -\Gamma_{16} \\ \Gamma_{13} & \Gamma_{23} & \Gamma_{33} & 0 & 0 & 0 \\ \Gamma_{14} & -\Gamma_{14} & 0 & \Gamma_{44} & \Gamma_{45} & \Gamma_{46} \\ \Gamma_{15} & -\Gamma_{15} & 0 & \Gamma_{45} & \Gamma_{55} & \Gamma_{56} \\ \Gamma_{16} & -\Gamma_{16} & 0 & \Gamma_{46} & \Gamma_{56} & \Gamma_{66} \end{Vmatrix} \tag{12}$$

Analogous calculations can be done in case of the quadrupole mechanism (tensor Λ_{mn}), however, in this case the form of (12) is subject to changes owing to the constraint imposed upon the components of the magnetoelastic tensor G_{mn}:

$$\sum_{m=1}^{3} G_{mn} = 0. \tag{13}$$

The constraint (13) gives rise to a decrease in the number of independent components of the tensor Λ_{mn} to 11, since

$$\Lambda_{13} = \Lambda_{23} = -(\Lambda_{11} + \Lambda_{12}) \qquad \Lambda_{33} = -2\Lambda_{13}. \tag{14}$$

TABLE III

Components of the tensor A_{mn} for crystals with tetragonal structure (in units 10^{-28} cm^{-5} sec^5)

	TiO_2	$ZrSiO_4$	$BaTiO_3$	ZnO	CdS	MgF_2
A_{11}	5.527	102.61	30.32	36.90	298.70	14.92
A_{33}	1.287	192.60	70.19	30.12	196.60	5.61
A_{12}	−3.994	−42.72	−11.06	−21.27	−185.88	−10.00
A_{13}	−0.773	−19.77	−24.84	−13.71	−95.08	−2.85
A_{44}	1.327	264.70	18.61	30.66	261.45	4.54
A_{66}	0.735	188.35	6.69	29.05	242.29	1.98

TABLE IV

Components of the tensor A_{mn} for crystals with tetragonal structure calculated by means of the isotropic approximation (in units 10^{-28} cm^{-5} sec^5)

	TiO_2	$ZrSiO_4$	$BaTiO_3$	ZnO	CdS	MgF_2
A_{11}	1.536	482.07	23.92	44.88	405.93	5.76
A_{12}	−0.703	−213.37	−10.26	−21.45	−197.97	−2.52
A_{44}	1.119	347.72	17.09	33.17	301.95	4.14

that, similarly as in the case of trigonal crystals, the isotropic approximation used for spin-lattice relaxation gives incorrect results also in the case of crystals with tetragonal symmetry. From among all the crystals considered the isotropic approximation is comparatively best describing the ZnO crystal.

After determining the components of the tensor A_{mn} it is possible to determine the tensors Γ_{mn} and Λ_{mn}. The magnetoelastic tensor F_{mn} for cubic, tetragonal, trigonal and hexagonal point symmetry can be written in the following form:

$$(F_{mn}) = \begin{Vmatrix} F_{11} & F_{12} & F_{13} & F_{14} & F_{15} & F_{16} \\ F_{21} & F_{11} & F_{23} & -F_{14} & -F_{15} & -F_{16} \\ F_{31} & F_{32} & F_{33} & 0 & 0 & 0 \\ F_{41} & -F_{41} & 0 & F_{44} & F_{45} & F_{46} \\ -F_{46} & F_{46} & 0 & -F_{45} & F_{44} & F_{41} \\ F_{61} & -F_{61} & 0 & -F_{15} & F_{14} & F_{66} \end{Vmatrix} \tag{11}$$

The components of this tensor satisfy the following relationships for the particular groups of symmetry:

Cubic symmetry, groups O, T_d, O_h

$$F_{11} = F_{33},\ F_{44} = F_{66},\ F_{12} = F_{13} = F_{21} = F_{23} = F_{31} = F_{32}$$
$$F_{14} = F_{15} = F_{16} = F_{41} = F_{45} = F_{46} = F_{61} = 0$$

groups T, T_h

$$F_{11} = F_{33},\ F_{44} = F_{66},\ F_{12} = F_{23} = F_{31},\ F_{13} = F_{21} = F_{32}$$
$$F_{14} = F_{15} = F_{16} = F_{41} = F_{45} = F_{46} = F_{61} = 0.$$

In crystals with low symmetry one should expect the occurrence of strong dependences of the relaxation times on the angle between the external magnetic field and the crystallographic axes.

Such dependences may provide essential source of information about the components of the magnetoelastic tensor provided that the elastic anisotropy of the medium is properly taken into account. In the simplest case of an ion with the effective spin $S = \frac{1}{2}$ and spin Hamiltonian with axial symmetry:

$$\mathscr{H}_s = \beta g_z H_z S_z + \beta g_\perp (H_x S_x + H_y S_y) \tag{15}$$

the expression for the probability of single-phonon transition for the magnetic field in the xy plane ($H_z = 0$, $H_x = H\cos\varphi$, $H_y = H\sin\varphi$) has the form:

$$W_{12} = \Phi(\omega, T)\frac{H^2}{4}\{\tfrac{1}{2}(\Gamma_{11}-\Gamma_{12}-2\Gamma_{66})\sin^2 2\varphi - \Gamma_{16}\sin 4\varphi + (\Gamma_{44}-\Gamma_{55})\sin^2\varphi + \Gamma_{55}+\Gamma_{66}\}. \tag{16}$$

It follows from Eq. (16) that the elastic anisotropy of the medium influences not only the values of W_{12} but also the character of angular dependences. Thus, *e.g.*, in the isotropic approximation for an ion in a crystal in a site with symmetry D_4, $\Gamma_{16} = 0$ whereas in reality $\Gamma_{16} \neq 0$. Similarly for crystals with symmetries D_3, C_{3v}, D_{3d} and ions in sites with the symmetries D_3, C_{3v}, and D_{3d} we have in the isotropic approximation $\Gamma_{11}-\Gamma_{12}-2\Gamma_{66} = 0$.

In reality we have in these conditions:

$$\Gamma_{11}-\Gamma_{12}-2\Gamma_{66} = 8A_{14}F_{14}(F_{11}-F_{12}).$$

3. *Conclusions*

The paper gives a method of taking into account the elastic anisotropy of the medium in the spin-lattice relaxation theory. It is proved that the neglection of anisotropy in the so-called isotropic approximation leads to large errors in the estimation of probabilities of relaxation transitions. These errors prevent accurate determination of components of the magnetoelastic tensor from the measurements of the relaxation times in crystals.

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