APPLICATION OF THE HOUSTON METHOD TO THE CALCULATION OF SPIN-LATTICE RELAXATION FOR CUBIC CRYSTALS

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The calculation of spin-lattice relaxation time for one-phonon processes for paramagnetic ions are performed by taking into account the elastic anisotropy of a crystal. Houston's method for the approximation of the integral over the unit sphere of any function which is invariant under the operations of the cubic symmetry group, in terms of its values along certain directions is used. The results are compared with the solutions obtained by numerical integration and are shown to be a good approximation of the numerical method.

1. Introduction

The spin interactions of paramagnetic ions with lattice vibrations (the spin-lattice interaction) are the esssential mechanism of relaxation in paramagnetic resonance, which is responsible for the absorption of energy. The theory of this interaction is sufficiently well elaborated, but only a few papers have taken into account the elastic anisotropy of the crystal. Although the long-wavelength approximation and Debye's model of the lattice are valid for one-phonon processes at all temperatures [1], the isotropic approximation, as showed Bates and Szymczak [2], leads to significant errors.

Since the anisotropy of elastic properties of crystals is taken into account, some integrals for the phonon wave vector must be calculated over all directions. These integrals are very similar to the integral used in calculations of the Debye temperature from the elastic constants of a crystal (see for example the review article by Allers [3]). Most of the methods described there can be applied to our problem. The only difference is that in calculating the Debye temperature the integrand contains velocities of the phonon modes in the -3 power, whereas in our case these velocities appear in the -5 power together with some linear combinations of the phonon wave vector and polarization vectors of each of the phonon modes.

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In this paper Houston's method extended by Betts et al. [4] and applied to the calculations of the Debye temperature will be adapted to the calculation of spin-lattice relaxation. The results obtained will be compared with the numerical solutions given by Szymczak [5, 2].

2. The spin-lattice interaction

The Hamiltonian for the interaction of the effective spin S of a magnetic ion with the surrounding lattice vibrations described by the strain tensor ε_{ij} can be written in the quadrupolar approximation as:

$$H_{sp} = \sum_{ijkl} G_{ijkl} S_i S_j \varepsilon_{kl}, \tag{1}$$

where G_{ijkl} is the magneto-elastic tensor and i, j, k, l label the x, y, z components of tensors.

Since the strain tensor ε_{ij} is symmetric (which corresponds to neglecting rotations) it contains only 6 independent components and can be written in the Voigt notation as the 6-dimmensional vector ε_λ, $\lambda = 1, ..., 6$, where $\varepsilon_1 = \varepsilon_{xx}$, $\varepsilon_2 = \varepsilon_{yy}$, $\varepsilon_3 = \varepsilon_{zz}$, $\varepsilon_4 = \varepsilon_{yz}$, $\varepsilon_5 = \varepsilon_{zx}$, $\varepsilon_6 = \varepsilon_{xy}$. In the following, the indexes of vectors and tensors in the Voigt notation will be denoted by greek letters.

The probablility W_{ab} of a transition of the ion from the state $|a\rangle$ to the state $|b\rangle$ with the simulatenous emission of one phonon of energy $\hbar\omega$ is given by

$$W_{ab} = \frac{2\pi}{\hbar^2} |\langle a, n|H_{sp}|b, n+1\rangle|^2 \varrho(\omega = \omega_{ab}), \tag{2}$$

where n is the number of phonons, $\varrho(\omega)$ — the density of phonon states.

Expressing ε_{ij} by the creation and annihilation operators of a phonon and taking $\varrho(\omega)$ from the Debye model we shall obtain [5]:

$$W = \frac{\omega^3}{32\pi^2 \varrho \hbar} \left(\frac{1}{\exp\dfrac{\hbar\omega}{kT} - 1} + 1 \right) \sum_{\substack{ijkl \\ mnpr}} A_{ijkl} G_{mnij} G_{prkl} \langle a|S_m S_n|b\rangle \langle b|S_p S_r|a\rangle, \tag{3}$$

where

$$A_{ijkl} = \int \sum_{s=1}^{3} (\lambda_i \Lambda_j^s + \lambda_j \Lambda_i^s)(\lambda_k \Lambda_l^s + \lambda_l \Lambda_k^s)/v_s^5 d\Omega, \tag{4}$$

T and ϱ are the temperature and the density of a crystal, respectively, s is labeling the phonon modes, λ_i and Λ_i^s are the direction cosines of propagation and polarization vectors respectively, v_s — velocity of phonon modes and integration is taken over the spatial angle Ω of directions of phonon wave-vectors.

Owing to the symmetry of tensor A in i, j and k, l indexes, this tensor may be written in the Voigt notation as $A_{\lambda\mu}$. For cubic crystals tensor $A_{\lambda\mu}$ has the form

$$[A_{\lambda\mu}] = \begin{vmatrix} A_{11} & A_{12} & A_{12} & 0 & 0 & 0 \\ A_{12} & A_{11} & A_{12} & 0 & 0 & 0 \\ A_{12} & A_{12} & A_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & A_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & A_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & A_{44} \end{vmatrix} \tag{5}$$

The $G_{\lambda\mu}$ tensors are known from experiment, so the main problem is to evaluate $A_{\lambda\mu}$. In order to calculate integrals (4), it is necessary to know v_s and Λ^s for all directions of λ. In the long-wavelength approximation they can be found from the secular equation

$$\sum_j T_{ij}\Lambda_j^s = v_s^2 \Lambda_i^s, \tag{6}$$

where matrix T_{ij} for cubic crystals has the form

$$T_{ij} = \beta\lambda_i\lambda_j + \gamma\delta_{ij} + (\alpha-\beta)\lambda_i^2\delta_{ij} \tag{7}$$

$$\alpha = (c_{11}-c_{44})/\varrho, \quad \beta = (c_{12}+c_{44})/\varrho, \quad \gamma = c_{44}/\varrho$$

and $c_{\lambda\mu}$ is the tensor of elastic moduli.

3. Isotropic approximation

If the crystal is treated as an isotropic elastic continuum which is equivalent to set $\alpha = \beta$ in Eq. (7), then the phonon spectra are simple and the integrals can by solved directly. One obtains

$$A_{11} = \tfrac{16}{15}\pi(3v_l^{-5}+2v_t^{-5})$$

$$A_{12} = \tfrac{16}{15}\pi(v_l^{-5}-v_t^{-5})$$

$$A_{44} = \tfrac{1}{2}(A_{11}-A_{12}), \tag{8}$$

where v_l and v_t are the sound velocities in a crystal for pure longitudinal and transversal waves, given by the equations $\varrho v_l^2 = c_{11}$, $\varrho v_t^2 = c_{44}$.

For most real crystals $\alpha \neq \beta$ and then it is necessary to solve Eq. (6) for each direction of λ. The integrals $A_{\lambda\mu}$ may be then calculated only numerically [5–7], but the results are valid only for the particular crystals.

The analytical methods of approximation have more general validity than the direct method [2]. The main problem in our calculations is the diagonalisation of the T_{ij} matrix in integration. Such a problem occurred in the calculation of the Debye θ from the elastic constants and some methods of approximation of the integral over the angles are elaborated. Comparing these methods with the results of numerical integration Wanner [8] has shown, that Houston's and Fedorov's [9] method gave the best agreement. The Fedorov's method has already been applied to the spin-lattice relaxation calculations by Bates and Szymczak [2]. Houston's method will be adapted in this paper.

4. Houston's method

This method was first derived by Houston [10] for an approximate determination of the spectrum of phonon frequency in cubic crystals. It is based on the fact that there exist in a crystal certain directions along which the secular equation (6) can be solved exactly. So we can express our functions of v_s and Λ^s, and in fact any function f which is invariant under the operations of the cubic symmetry group, in terms of the Kubic harmonics (see [4]) by comparison of their values with the values of our function for as many directions as harmonics we wish to have in the expansion. Then we can easily integrate the combination of the Kubic harmonics. Houston gave the formula for 3 principal directions in a crystal

$$F = \iint f \sin\theta \, d\theta \, d\varphi = (4\pi/35 \times [10f(100) + 16f(110) + 9f(111)], \qquad (9)$$

where $f(100)$, $f(110)$, $f(111)$ are the values of function f in the [100], [110], [111] directions respectively. The small letters will be used to sign here and in the following the values of function in particular directions, and capital letters — the integrals of corresponding functions. Betts, Bhatia and Wyman [4] extended this formula to the 6 directions

$$F = \frac{4\pi}{1081080} \left[117603f(100) + 76544f(110) + 17496f(111) \right.$$

$$\left. + 381250f(210) + 311040f(211) + 177147f(221) \right]. \qquad (10)$$

5. Application

To apply this method to the approximation of A_{11}, A_{12}, A_{44} it is necessary to express to the integrands the appropriate symmetry.

$$A_{11} = A_{22} = A_{33} = \tfrac{1}{3}(A_{11} + A_{22} + A_{33})$$

$$= \int \tfrac{4}{3} \sum_{s=1}^{3} \left[(\lambda_x \Lambda_x^s)^2 + (\lambda_y \Lambda_y^s)^2 + (\lambda_z \Lambda_z^s)^2 \right] \frac{d\Omega}{v_s^5},$$

$$A_{12} = A_{13} = A_{23} = \tfrac{1}{3}(A_{12} + A_{13} + A_{23})$$

$$= \int \tfrac{4}{3} \sum_{s=1}^{3} \left[(\lambda_x \Lambda_x^s \lambda_y \Lambda_y^s) + (\lambda_x \Lambda_x^s \lambda_z \Lambda_z^s) + (\lambda_y \Lambda_y^s \lambda_z \Lambda_u^s) \right] \frac{d\Omega}{v_s^5},$$

$$A_{44} = A_{55} = A_{66} = \tfrac{1}{3}(A_{44} + A_{55} + A_{66})$$

$$= \int \tfrac{1}{3} \sum_{s=1}^{3} \left[(\lambda_x \Lambda_y^s + \lambda_y \Lambda_x^s)^2 + (\lambda_x \Lambda_z^s + \lambda_z \Lambda_x^s)^2 + (\lambda_y \Lambda_z^s + \lambda_z \Lambda_y^s)^2 \right] \frac{d\Omega}{v_s^5}. \qquad (11)$$

The following expressions for the integrand values for the required direction are obtained and can be introduced directly into Eq. (9) or (10) instead of f giving values of A_{11}, A_{12}, A_{44} respectively.

[100] direction

$$v_1 = [\alpha + \gamma]^{1/2}, \quad v_2 = [\gamma]^{1/2}$$

$$a_{11}(100) = \tfrac{4}{3} \times v_1^{-5}, \quad a_{12}(100) = 0, \quad a_{44}(100) = \tfrac{1}{3} \times 2v_2^{-5}$$

[110] direction

$$v_1 = [\gamma + \tfrac{1}{2}(\alpha + \beta)]^{1/2}, \quad v_2 = [\gamma + \tfrac{1}{2}(\alpha - \beta)]^{1/2}, \quad v_3 = [\gamma]^{1/2}$$

$$a_{11}(110) = \tfrac{4}{3} \times \tfrac{1}{2}(v_1^{-5} + v_2^{-5}), \quad a_{12}(110) = \tfrac{4}{3} \times \tfrac{1}{4}(v_1^{-5} - v_2^{-5}), \quad a_{44}(110) = \tfrac{1}{3}(v_1^{-5} + v_3^{-5})$$

[111] direction

$$v_1 = [\gamma + \tfrac{1}{3}(\alpha + 2\beta)]^{1/2}; \quad v_2 = [\gamma + \tfrac{1}{3}(\alpha - \beta)]^{1/2}$$

$$a_{11}(111) = \tfrac{4}{3} \times \tfrac{1}{3}(v_1^{-5} + 2v_2^{-5}), \quad a_{12}(111) = \tfrac{4}{3} \times \tfrac{1}{3}(v_1^{-5} - v_2^{-5}),$$

$$a_{44}(111) = \tfrac{1}{3} \times \tfrac{2}{3}(2v_1^{-5} + v_2^{-5}) \tag{12}$$

[210] direction

$$\Delta = \sqrt{9\alpha^2 + 16\beta^2}, \quad v_1 = \left[\gamma + \frac{\alpha}{2} + \frac{\Delta}{10}\right]^{1/2}, \quad v_2 = \left[\gamma + \frac{\alpha}{2} - \frac{\Delta}{10}\right]^{1/2}, \quad v_3 = [\gamma]^{1/2}$$

$$a_{11}(210) = \tfrac{4}{3} \times \tfrac{1}{10}\left[5(v_1^{-5} + v_2^{-5}) + \frac{9\alpha}{\Delta}(v_1^{-5} - v_2^{-5})\right],$$

$$a_{12}(210) = \tfrac{4}{3} \times \tfrac{4}{5}\left[\frac{\beta}{\Delta}(v_1^{-5} - v_2^{-5})\right],$$

$$a_{44}(210) = \tfrac{1}{3} \times \tfrac{1}{10}\left[5(v_1^{-5} + v_2^{-5}) + \frac{16\beta - 9\alpha}{\Delta}(v_1^{-5} - v_2^{-5}) + 10v_3^{-5}\right].$$

[211] direction

$$\Delta = \sqrt{9\alpha^2 + 33\beta^2 - 6\alpha\beta}, \quad v_1 = [\gamma + \tfrac{1}{12}(5\alpha + \beta + \Delta)]^{1/2},$$

$$v_2 = [\gamma + \tfrac{1}{12}(5\alpha + \beta - \Delta)]^{1/2}, \quad v_3 = [\gamma + \tfrac{1}{6}(\alpha - \beta)]^{1/2}$$

$$a_{11}(211) = \tfrac{4}{3} \times \tfrac{1}{12}\left[5(v_1^{-5} + v_2^{-5}) + \frac{9\alpha - 3\beta}{\Delta}(v_1^{-5} - v_2^{-5}) + 2v_3^{-5}\right],$$

$$a_{12}(211) = \tfrac{4}{3} \times \tfrac{1}{24}\left[(v_1^{-5} + v_2^{-5}) + \frac{33\beta - 3\alpha}{\Delta}(v_1^{-5} - v_2^{-5}) - 2v_3^{-5}\right],$$

$$a_{44}(211) = \tfrac{1}{3} \times \tfrac{1}{3}\left[2(v_1^{-5} + v_2^{-5}) + \frac{9\beta - 3\alpha}{\Delta}(v_1^{-5} - v_2^{-5}) + 2v_3^{-5}\right].$$

[221] direction

$$\Delta = \sqrt{9\alpha^2 + 48\beta^2 + 24\alpha\beta}\,, \quad v_1 = \left[\gamma + \tfrac{1}{18}(5\alpha + 4\beta + \Delta)\right]^{1/2},$$

$$v_2 = \left[\gamma + \tfrac{1}{18}(5\alpha + 4\beta - \Delta)\right]^{1/2}, \quad v_3 = \left[\gamma + \tfrac{4}{9}(\alpha - \beta)\right]^{1/2}$$

$$a_{11}(221) = \tfrac{4}{3}\times\tfrac{1}{18}\left[5(v_1^{-5} + v_2^{-5}) + \frac{9\alpha + 12\beta}{\Delta}(v_1^{-5} - v_2^{-5}) + 8v_3^{-5}\right],$$

$$a_{12}(221) = \tfrac{4}{3}\times\tfrac{1}{9}\left[(v_1^{-5} + v_2^{-5}) + \frac{3\alpha + 12\beta}{\Delta}(v_1^{-5} - v_2^{-5}) - 2v_3^{-5}\right],$$

$$a_{44}(221) = \tfrac{1}{3}\times\tfrac{1}{18}\left[17(v_1^{-5} + v_2^{-5}) + \frac{3\alpha + 36\beta}{\Delta}(v_1^{-5} - v_2^{-5}) + 2v_2^{-5}\right].$$

The values of $A_{\lambda\mu}$ have been calculated for some crystals using consequently the isotropic approximation (Eq. (8)), the 3-term formula (Eq. (9), (12)) and finally the 6-term formula (Eq. (10) and (12)). These results are collected in Table I and compared there with

TABLE I

Values of the tensor components A_{11}, A_{12} and A_{14} for some cubic crystals in units of 10^{-18} s^5 m^{-5}

Crystal	η	Tensor compo-nent	Method of calculation						
			numerical	isotropic		3-term		6-term	
MgAl$_2$O$_4$	2.43	A_{11}	3.01	0.749	75%	3.92	30%	2.94	2.3%
		A_{12}	−1.37	−0.218	84%	−1.86	36%	−1.33	2.7%
		A_{44}	0.678	0.484	28%	0.599	12%	0.685	1.1%
MgO	1.55	A_{11}	1.35	0.694	48%	1.49	10%	1.34	0.4%
		A_{12}	−0.568	−0.213	62%	−0.646	14%	−0.565	0.6%
		A_{44}	0.518	0.454	12%	0.488	6%	0.519	0.2%
Y$_3$AL$_5$O$_{12}$	1.03	A_{11}	2.43	2.31	5%	2.46	1%	2.43	0.0%
		A_{12}	−1.04	−0.97	6%	−1.05	1%	−1.04	0.0%
		A_{44}	1.66	1.64	1%	1.65	0.7%	1.66	0.1%
SrF$_2$	0.81	A_{11}	30.8	42.4	41%	28.9	6%	30.8	0.2%
		A_{12}	−13.423[1]	−20.0	49%	−12.5	7%	−13.4	0.2%
		A_{44}	29.1	31.7	9%	30.5	5%	29.1	0.1%
PbS	0.51	A_{11}	114.1	346.0	202%	89.5	22%	111.7	2.1%
		A_{12}	−43.8	−166.0	279%	−33.6	24%	−42.6	2.8%
		A_{44}	194	256	32%	231	20%	198	2.1%
KCl	0.31	A_{11}	53.5	355	563%	33.2	38%	48.5	9.3%
		A_{12}	−15.5	−174	1022%	−9.31	40%	−14.1	9.5%
		A_{44}	163	264	62%	233	43%	177	8.3%

[1] In Szymczak's calculations [5, 2] the value of A_{12} for SrF$_2$ was misprinted by the tape-reader, the correct value ought to be −13.423 instead of −5.423.

those obtained by Szymczak [5] by numerical integration. The deviations from values obtained numerically are given in percents next to each value. Table I contains also values of the anisotropy coefficient $\eta = 2c_{44}/(c_{11}-c_{12})$. The deviation of η from unity is a measure of elastic anisotropy ($\alpha = \beta$ for $\eta = 1$). The values of ϱ and $c_{\lambda\mu}$ have been taken from Szymczak's calculations.

It can be see in the table, that the disagreement between the 6-term method and numerical results is less than 10% and for crystals with $0.5 < \eta < 2.5$ even less than 3%. The agreement between these two methods is good. The 3-term method, however simpler in calculation, gives agreement only to 40%. It can be seen also that the isotropic approximation may yield values 10 times too large (A_{12} for KCl).

6. Other applications

The interaction of an ion with its surroundings may be also expressed by the orbit--lattice Hamiltonian

$$H_{ol} = \sum_{\Gamma,\gamma,l} V(\Gamma, l)O_{\gamma}(\Gamma, l)\varepsilon_{\gamma}(\Gamma), \tag{13}$$

where $O_{\gamma}(\Gamma, l)$ is an orbital operator of order l which transforms like the γ-th member of the term Γ. $V(\Gamma, l)$ and $\varepsilon_{\gamma}(\Gamma)$ are the orbit-lattice coupling coefficient and strain respectively.

This formalism in comparison with Hamiltonian (1) gives the possibility of taking into account also the strains of rotational symmetry for the representation $\Gamma = T$. Analogous calculations to the ones presented above lead to integrals similar to $A_{\lambda\mu}$. Such integrals can be expressed for cubic crystals in terms of the $A_{\lambda\mu}$ tensor [2]. Even the use of rotational symmetry leads to the integral of type [7]

$$\int \sum_{s=1}^{3} (\lambda_{\gamma}\Lambda_y^s - \lambda_y\Lambda_x^s)^2 \frac{d\Omega}{v_s^5} = (A_{44}-A_{12})$$

and does not introduce any new coefficients.

7. Conclusions

Is has been shown that Houston's method may by applied not only to the calculations of the Debye temperature, but also to many other problems for example to the calculation of spin-lattice relaxation. The expression (12) obtained with the aid of this method can be used for all crystals of cubic symmetry. For the crystals of symmetry lower than cubic calculations of $A_{\lambda\mu}$ coefficients [11] may be done using the analogous method derived by Betts et al. [12].

The components of the $A_{\lambda\mu}$ tensor are also required for calculations of the many--phonon relaxation process [2], and can appear in all calculations of spin-lattice processes when the elastic anisotropy of a crystal is considered.

REFERENCES

[1] R. Orbach, H. J. Stapelton, *Electron Paramagnetic Resonance*, Ed. S. Geschwind, Plenum Press New York 1972, p. 121.

[2] C. A. Bates, H. Szymczak, *J. Phys. C* **8**, 2502 (1975).

[3] G. A. Alers, *Physical Acoustic*, Ed. W. P. Mason, Academic Press, New York 1965, Vol. IIIB, Ch. 1.

[4] D. D. Betts, A. B. Bhatia, M. Wyman, *Phys. Rev.* **104**, 37 (1956).

[5] H. Szymczak, *Acta Phys. Pol.* **A42**, 19 (1972).

[6] P. L. Donoho, *Phys. Rev.* **A133**, 1080 (1964).

[7] J. M. Baker, D. van Ormondt, *J. Phys. C* **7**, 2060, (1974).

[8] R. Wanner, *Canad. J. Phys.* **48**, 1270 (1970).

[9] F. J. Fedorov, *Theory of Elastic Waves in Crystals*, Plenum Press, New York 1968.

[10] W. V. Houston, *Rev. Mod. Phys.* **20**, 161 (1948).

[11] H. Szymczak, *Acta Phys. Pol.* **A43**, 649 (1973).

[12] D. D. Betts, A. B. Bhatia, G. K. Horton, *Phys. Rev.* **104**, 43 (1956).