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Anisotropy of conduction-electron-induced spin–lattice relaxation in NMR

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Abstract. The general form of the angular dependence of the nuclear spin–lattice relaxation rate is calculated for relaxation due to the various magnetic interactions between the nuclei and conduction electrons in crystalline, metallic materials. The forms of angular dependence for each crystal symmetry class are identical with those of the relaxation rate, in the high-temperature (fast-diffusion) limit, due to nuclear–nuclear dipolar coupling, when at least one of the interacting nuclear species takes part in translational diffusion.

1. Introduction

The magnetic electron–nuclear interaction in metallic conductors gives rise to a frequency shift (Knight shift) of the nuclear magnetic resonance and also provides a contribution to the nuclear spin relaxation rate. Since these arise from the same interaction there is an intimate relation between the square of the Knight shift and the spin–lattice relaxation rate, the Korringa relation, which takes a particularly simple form for the case of the Fermi contact part of the interaction in cubic metals (Abragam 1961).

Both the Knight shift and the relaxation rate can depend on the direction of the applied static magnetic field with respect to the crystal axes. (Amorphous and liquid metals are excluded from the present considerations.) The Knight shift (and the chemical shift in non-metals) is a second-order tensor and the orientation of the principal axes of the tensor determines the angular dependence of the shift on the magnetic field direction (Abragam 1961) and the number of independent components of the tensor depends on the crystal symmetry (Buckingham and Malm 1971). The anisotropy of the electron–nuclear contribution to the nuclear relaxation rate is more involved than in the case of the Knight shift because the relaxation rate involves the squares of matrix elements whereas the Knight shift depends linearly on the appropriate matrix elements.

The anisotropy of the relaxation rate has been considered within the tight-binding approximation for the electron states by Obata (1963) for the case of cubic symmetry and this work was extended to hexagonal symmetry by Narath (1967). In the present work we consider the general problem of the anisotropy of the relaxation rate for all crystal symmetry classes and derive the results without assuming the tight-binding approximation to hold. We do not attempt to calculate the values of the coefficients of the angular terms from the electronic structure of the metal.

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2. Spin–lattice relaxation contributions

Following Obata (1963), the Hamiltonian of a nucleus of spin I at the origin interacting with an electron with spin s at \mathbf{r} , in the absence of spin–orbit coupling, is

$$H = \gamma_e \gamma_n \hbar^2 (I_+ \Phi_-(\mathbf{r}) + I_- \Phi_+(\mathbf{r}) + I_z \Phi_0(\mathbf{r})) \quad (2.1)$$

where the direction of spin quantisation is along the external field, chosen as the z axis, and

$$\begin{aligned} \Phi_{\pm}(\mathbf{r}) = s_{\pm} [& (4\pi/3)\delta(\mathbf{r}) - (c_0/4r^3)Y_2^0(\Omega)] + s_{\mp} (c_1/r^3)Y_2^{\pm 2}(\Omega) \\ & \mp s_z (c_1/r^3)Y_2^{\pm 1}(\Omega) + (I_{\pm}/2r^3) \end{aligned} \quad (2.2a)$$

$$\begin{aligned} \Phi_0(\mathbf{r}) = (c_1/r^3) (s_+ Y_2^{-1}(\Omega) - s_- Y_2^1(\Omega)) + s_z [& (8\pi/3)\delta(\mathbf{r}) + (c_0/r^3)Y_2^0(\Omega)] + I_z/r_3 \\ c_0^2 = 16\pi/5 \quad c_1^2 = 6\pi/5 \end{aligned} \quad (2.2b)$$

The terms involving $\delta(\mathbf{r})$ are the contact interaction, the terms involving the spherical harmonics $Y_2^q(\Omega)$ are the non-contact dipolar interactions and the terms involving the orbital angular momentum operator I are the orbital interactions. The direction Ω is the direction of the electron site \mathbf{r} relative to the magnetic field direction.

In addition to the above terms, other contributions to the relaxation can arise from core polarisation or polarisation of conduction electron s bands lying below the Fermi level, and by non- s electrons at the Fermi level. These terms are not included in the present analysis since the relaxation due to them is isotropic with respect to the magnetic field direction.

In high magnetic fields the nuclear spin–lattice relaxation rate R_1 is independent of the magnitude of the nuclear spin I (Abragam (1961), p 362) and therefore it is sufficient to consider the case $I = \frac{1}{2}$. The relaxation rate is then twice the transition probability per unit time of the nucleus having a spin flip from $-\frac{1}{2}$ to $+\frac{1}{2}$. Such a transition only involves the I_+ -term in equation (2.10) and, therefore, within first-order time-dependent perturbation theory, and assuming the high-temperature limit for the Fermi–Dirac distribution of occupation of electron states $|k\rangle$, the expression for R_1 is (Obata 1963)

$$R_1 = \frac{4\pi}{\hbar} (\gamma_e \gamma_n \hbar^2)^2 k_B T \sum_{\sigma\sigma'} \sum_{kk'} |\langle k\sigma | \Phi_-(\mathbf{r}) | k'\sigma' \rangle|^2 \delta(E_k - E_{k'}) \delta(E_k - E_F) \quad (2.3)$$

where k_B is Boltzmann's constant, T is the temperature, E_F is the Fermi energy and σ is the electron spin magnetic quantum number.

The anisotropy of R_1 with respect to the orientation of the applied magnetic field relative to crystal axes is determined by the matrix elements in equation (2.3). It is therefore sufficient in analysing the anisotropy of R_1 just to consider the angular dependence of the expression

$$A_{kk'} = \sum_{\sigma\sigma'} |\langle k\sigma | \Phi_-(\mathbf{r}) | k'\sigma' \rangle|^2 \quad (2.4)$$

since the angular dependence arises from the terms depending on \mathbf{r} in equation (2.2).

Evaluating the summations over σ and σ' in equation (2.4) using the expression

(2.2a) for $\Phi_-(\mathbf{r})$ yields

$$\begin{aligned}
 A_{kk'} = & |\langle \mathbf{k} | (4\pi/3) \delta(\mathbf{r}) | \mathbf{k}' \rangle|^2 + |\langle \mathbf{k} | (c_1/r_3) Y_2^{-2}(\Omega) | \mathbf{k}' \rangle|^2 \\
 & + \frac{1}{2} |\langle \mathbf{k} | (c_1/r_3) Y_2^{-1}(\Omega) | \mathbf{k}' \rangle|^2 + \frac{1}{18} |\langle \mathbf{k} | (c_0/r^3) Y_2^0(\Omega) | \mathbf{k}' \rangle|^2 \\
 & + \frac{1}{2} |\langle \mathbf{k} | (l_-/r^3) | \mathbf{k}' \rangle|^2 \\
 & - 2 \operatorname{Re} [\langle \mathbf{k} | (4\pi/3) \delta(\mathbf{r}) | \mathbf{k}' \rangle \langle \mathbf{k} | (c_0/4r^3) Y_2^0(\Omega) | \mathbf{k}' \rangle^*].
 \end{aligned} \tag{2.5}$$

The first term is the contact interaction, the next three terms are the dipolar interaction, the fifth term is the orbital interaction and the final term is a cross term between the contact and dipolar interactions. Each term in the summation over σ and σ' involves contributions from only one of s_- , s_+ or both s_z and l in equation (2.2a) and so cross terms between the contact and orbital terms do not occur. The cross terms between the dipolar and orbital terms cancel, so the only cross term in equation (2.5) is between the contact and dipolar interactions.

3. Anisotropy of the contributions

3.1. Contact interaction

The contact interaction is isotropic for all crystal symmetries since it only involves the value of the Bloch state wavefunctions at the nuclear site. The insertion of the first term of equation (2.5) into equation (2.3) leads to the familiar expression for the relaxation rate (Abragam 1961).

3.2. Dipolar interaction

Each of the three dipolar terms in equation (2.5) is of the form

$$A_{kk'}^{(d)}(q) = a_q |\langle \mathbf{k} | Y_2^q(\Omega) / r^3 | \mathbf{k}' \rangle|^2 \tag{3.1}$$

where a_q are real constants. The spherical harmonics $Y_2^q(\Omega)$ relative to the magnetic field direction may be written in terms of spherical harmonics $Y_2^{q'}(\Omega_1)$ relative to the crystal axes as

$$Y_2^q(\Omega) = \sum_{q'=-2}^2 Y_2^{q'}(\Omega_1) R_{q'q}^{(2)}(\varphi, \theta) \tag{3.2}$$

where $R_{q'q}^{(2)}(\varphi, \theta)$ is a rotation matrix (Messiah 1965) and θ, φ are the polar angles of the field direction relative to the crystal axes. The expression (3.1) then becomes

$$A_{kk'}^{(d)}(q) = a_q \sum_{q', q''=-2}^2 R_{q'q}^{(2)*}(\varphi, \theta) J_{q'q''}^{(d)} R_{q''q}^{(2)}(\varphi, \theta) \tag{3.3}$$

where $J_{q'q''}^{(d)}$ is defined by

$$J_{q'q''}^{(d)} = \langle \mathbf{k} | Y_2^{q'}(\Omega_1) | \mathbf{k}' \rangle^* \langle \mathbf{k} | Y_2^{q''}(\Omega_1) | \mathbf{k}' \rangle. \tag{3.4}$$

The quantities $J_{q'q''}^{(d)}$ are independent of the field direction and the field dependence is contained in the rotation matrices.

The angular dependence of the expression (3.3) for the various crystal classes has been evaluated by Sholl (1986) (hereinafter referred to as I) in connection with the spectral density functions for nuclear spin relaxation due to nuclear–nuclear dipolar interactions modulated by translational diffusion. It was shown there that the number of independent non-zero elements $J_{qq'}$ depends on the crystal class and varies from 2 for

cubic crystals to 15 for triclinic crystals. The angular dependence of equation (3.3) was also calculated for each crystal class. These results are also directly applicable to equations (3.3) and (3.4).

The angular dependence of the electron–nuclear dipolar contribution to the relaxation rate (2.3) follows from the angular dependence of the dipolar terms in equation (2.5) which is a sum of terms of the form (3.1). The linear combination of the terms for different q arising from (3.1) is, as expected, the same as that for the nuclear–nuclear relaxation due to translational diffusion of unlike spins (Abragam 1961). Since the energy dependence of a nuclear spin flip has been neglected in equation (2.3) as being negligible compared with the electron energies E_k , it is the ‘extreme narrowing’ case of the general theory that is relevant here. In this case the angular dependence simplifies and the angular anisotropy has been evaluated in I. The general forms of the angular dependence of the dipolar contribution to R_1 for the crystal classes are the following.

$$\text{Cubic: } A_1 \quad (3.5a)$$

$$\text{Hexagonal, trigonal, tetragonal: } A_1 + A_2 \sin^2 \theta \quad (3.5b)$$

$$\text{Orthorhombic: } A_1 + \sin^2 \theta (A_2 + A_3 \cos 2\varphi) \quad (3.5c)$$

$$\text{Monoclinic: } A_1 + \sin^2 \theta (A_2 + A_3 \cos 2\varphi + A_4 \sin 2\varphi) \quad (3.5d)$$

$$\begin{aligned} \text{Triclinic: } A_1 + \sin^2 \theta (A_2 + A_3 \cos 2\varphi + A_4 \sin 2\varphi) \\ + \sin 2\theta (A_5 \cos \varphi + A_6 \sin \varphi). \end{aligned} \quad (3.5e)$$

The parameters A_i can be related to linear combinations of terms contributing to R_1 arising from equations (3.1), (3.3) and (3.4) in a similar way to the results in I.

3.3. Orbital interaction

The orbital contribution to $A_{kk'}$ (equation (2.5)) is

$$A_{kk'}^{(o)} = \frac{1}{2} |\langle \mathbf{k} | l_- / r^3 | \mathbf{k}' \rangle|^2. \quad (3.6)$$

It is useful in discussing this term to introduce the spherical tensors L_1^q defined by (Narath 1967)

$$L_1^{\pm 1} = \mp 2^{-1/2} l_{\pm} \quad L_1^0 = l_z \quad (3.7)$$

since L_1^q transform under a rotation of axes in the same way as the spherical harmonics Y_1^q . Analogously to equation (3.2), the L_1^q therefore satisfy

$$L_1^q(\Omega) = \sum_{q'=-1}^1 Y_1^{q'}(\Omega_1) R_{q'q}^{(1)}(\varphi, \theta) \quad (3.8)$$

and $A_{kk'}^{(o)}$ becomes

$$A_{kk'}^{(o)} = \sum_{q', q''=-1}^1 R_{q'-1}^{(1)*}(\varphi, \theta) J_{q'q''}^{(o)} R_{q''-1}^{(1)}(\varphi, \theta) \quad (3.9)$$

$$J_{q'q''}^{(o)} = \langle \mathbf{k} | L_1^{q'} | \mathbf{k}' \rangle \langle \mathbf{k} | L_1^{q''} | \mathbf{k}' \rangle^*. \quad (3.10)$$

Similarly to the case of equations (3.3) and (3.4), the angular dependence of $A_{kk'}^{(o)}$ is contained in the rotation matrices.

The $J_{qq'}^{(o)}$ satisfy the relations $J_{qq'}^{(o)} = (-1)^{q-q'} J_{-q-q'}^{(o)*} = J_{q'q}^{(o)*}$ and $J_{qq}^{(o)}$ is real. There are

therefore at most six independent parameters which may be taken as $J_{00}^{(o)}$, $J_{11}^{(o)}$ real and $J_{-10}^{(o)}$, $J_{-11}^{(o)}$ complex. This is to be compared with 15 independent parameters for $J_{qq'}^{(d)}$. Using the expressions for $R_{q'q}^{(1)}(\varphi, \theta)$ (Messiah 1965), equation (3.9) becomes

$$A_{kk'}^{(o)} = J_{11}^{(o)} + \frac{1}{2}(J_{00}^{(o)} - J_{11}^{(o)}) \sin^2 \theta + \frac{1}{2} \sin^2 \theta \operatorname{Re}(J_{-11}^{(o)} \exp(2i\varphi)) - (1/\sqrt{2}) \sin 2\theta \operatorname{Re}(J_{-10}^{(o)} \exp(i\varphi)). \quad (3.11)$$

The number of independent non-zero $J_{q'q}^{(o)}$ depends on the crystal symmetry and the results for each crystal class can be evaluated in a similar way to the corresponding analysis in I. For the cubic, hexagonal, trigonal and tetragonal classes the only non-zero parameters are $J_{00}^{(o)}$ and $J_{11}^{(o)}$ and these are equal for the cubic class. For the orthorhombic and monoclinic classes $J_{-11}^{(o)}$ is also non-zero and is real for the orthorhombic and complex for monoclinic classes. For the triclinic class all six parameters are required.

The resulting angular dependence of the orbital interaction contribution to the relaxation rate is then identical in form to the dipolar case given by equations (3.5).

3.4. Contact dipolar term

The only cross term in the relaxation arises from the contact dipolar term in equation (2.5), which is

$$A_{kk'}^{(c)} = -2 \operatorname{Re} \langle \mathbf{k} | (4\pi/3) \delta(\mathbf{r}) | \mathbf{k}' \rangle \langle \mathbf{k} | (c_0/4r^3) Y_2^0(\Omega) | \mathbf{k}' \rangle^*. \quad (3.12)$$

The angular dependence of this term arises from the spherical harmonic and using equation (3.2) it may be written as

$$A_{kk'}^{(c)} = 2 \operatorname{Re} \sum_{q'=-2}^2 R_{q'0}^{(2)}(\varphi, \theta) J_{q'}^{(c)} \quad (3.13)$$

$$J_{q'}^{(c)} = -\langle \mathbf{k} | (4\pi/3) \delta(\mathbf{r}) | \mathbf{k}' \rangle \langle \mathbf{k} | (c_0/4r^3) Y_2^{q'}(\Omega_1) | \mathbf{k}' \rangle^* \quad (3.14)$$

where $J_{-q}^{(c)} = J_q^{(c)*}$. Substituting the expressions for the rotation matrices gives

$$A_{kk'}^{(c)} = 2 \operatorname{Re}[J_0^{(c)}(3 \cos^2 \theta - 1) - \sqrt{6} J_1^{(c)} \sin 2\theta \exp(-i\varphi) + \sqrt{6} J_2^{(c)} \sin^2 \theta \exp(-2i\varphi)]. \quad (3.15)$$

Since the $J_q^{(c)}$ are complex there are six independent parameters but only five of these contribute to $A_{kk'}^{(c)}$ since $\operatorname{Im} J_0^{(c)}$ does not occur.

The effect of crystal symmetry on the $J_q^{(c)}$ is that all of the terms vanish for cubic symmetry, all but $J_0^{(c)}$ vanish for the hexagonal, trigonal and tetragonal classes, for the monoclinic and orthorhombic classes $J_0^{(c)}$ and $J_2^{(c)}$ are non-zero with $J_2^{(c)}$ real for the orthorhombic class while all terms are required for the triclinic class. These conditions result in the angular dependence of the cross term being of the same form as for the dipolar and orbital contributions, as given by equation (3.5), except for two differences. Firstly, the isotropic term A_1 for cubic symmetry is zero for the cross term and, secondly, the $A_1 + A_2 \sin^2 \theta$ term in equations (3.5b) to (3.5e) specialises to $J_0^{(c)}(3 \cos^2 \theta - 1)$ for the cross term.

The electron–nuclear dipolar term is usually expected to be small compared with the orbital term, and often also compared with the contact term. However, the cross term, containing a matrix element from each of the contact and dipolar terms, may be larger than the dipolar term. Similar considerations also apply to an entirely analogous cross term between the core-polarisation and dipolar terms.

4. Discussion

The results obtained in the previous section are consistent with those of Obata (1963) and Narath (1967) for cubic and hexagonal systems within the tight-binding approximation for the electron states. The present work is a generalisation of their results to arbitrary crystal symmetry and the theory has been developed without any assumptions concerning the form of the electron states except for the neglect of spin-orbit coupling.

The key result is that, for all of the electron-nuclear contributions to a nuclear relaxation rate, the anisotropy of the relaxation rate as a function of direction of the magnetic field relative to axes fixed in the crystal depends only on the crystal symmetry class and the expressions are given by equations (3.5a) to (3.5e). These expressions are also the same as the 'extreme narrowing' or high-temperature limit of nuclear relaxation due to time-dependent nuclear-nuclear dipolar coupling between diffusing nuclei. In cases where nuclei are being relaxed due to both electron-nuclear interactions and nuclear-nuclear dipolar interactions due to diffusive motions simultaneously, it would not therefore be possible to separate the two effects on the basis of the angular dependence of the relaxation rate in the 'extreme narrowing' limit. This would not, however, be the case at lower temperatures where the angular dependence of the nuclear diffusional contribution to the relaxation rate involves additional terms (Sholl 1986). In principle, knowledge of the anisotropy of the Knight shift can be of help in separating the contributions using the Korringa relation, but, without knowledge of which are the dominant contributions to the electron-nuclear interactions, the analysis cannot be carried through in general. Simultaneous nuclear relaxation due to the electron-nuclear interaction and the diffusive nuclear-nuclear interaction is of considerable interest when NMR is used to study diffusion in metals (see, for example, Schone *et al* (1986) for a study of orthorhombic niobium hydride).

Experimental observations of the anisotropy of R_1 in metals are rather sparse, certainly compared with the more straightforward observation of anisotropy of the Knight shift. The expression (3.5b) is in agreement with the experimental results for hexagonal titanium (Narath 1967) and hexagonal scandium (Fradin 1968). Attempts to measure the anisotropy in tetragonal tin have so far proved rather inconclusive (McLachlan 1968). Relaxation in single crystals of the hexagonal semiconductor tellurium has been investigated by Koma *et al* (1968), but no measurements of angular dependence were reported.

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