Nuclear quadrupolar relaxation by translational diffusion in solids: I. Mean field theory

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Received 18 February 1982

Abstract. The theory of nuclear quadrupolar relaxation due to translational diffusion in crystalline solids is investigated. Unlike the case of dipolar relaxation, it is often necessary to take into account three-particle, as well as two-particle, probability functions in the expression for the spectral densities of the quadrupolar interaction. In particular, the nuclear relaxation of a particle diffusing on a cubic lattice, due to the relative translational motion of other identical particles on the same lattice, is evaluated according to the mean field theory which includes, in an average way, the effects of spatial correlations between the motions of particles. Formal expressions are obtained for the three-particle probability function for nearest-neighbour jumps on sc, FCC and BCC lattices. Analytical formulae are derived for the spectral density functions in the low-temperature limit and demonstrate the greater importance of three-particle effects as the concentration of particles increases. In a subsequent paper, the mean field theory is applied to the quadrupolar relaxation of deuterons in transition metal deuterides.

1. Introduction

A nucleus which possesses an electric quadrupole moment is capable of interacting with fluctuating electric field gradients produced in solids by, for example, lattice vibrations (Van Kranendonk 1954) or the diffusion of point defects (Reif 1955). Since this quadrupolar interaction may be much more effective in producing nuclear spin relaxation than the nuclear magnetic dipole–dipole interaction, it can be the dominant relaxation mechanism in ionic crystals (Cohen and Reif 1957). Although the most important contribution to spin–lattice relaxation in metals is usually that arising from the interaction between the nuclear spins and the conduction electrons, this is not necessarily the case for all conductors. In transition metal hydrides and deuterides, for example, quadrupolar relaxation due to the diffusion of interstitial hydrogen or deuterium can be an important mechanism (see, for example, Schreiber and Cotts 1963, Weaver 1974).

Quadrupolar relaxation due to translational diffusion in solids can occur in several different ways. Firstly, stationary nuclear spins may relax due to the fluctuating field gradients generated by mobile impurities, a situation which occurs for metal nuclei in transition metal hydrides. Secondly, mobile nuclei may relax because they diffuse between sites at which the field gradients differ in magnitude or orientation, e.g. the interstitial sites in body centred cubic (BCC) and body centred tetragonal metal hydrides. A third case is the quadrupolar relaxation of a mobile nucleus due to the field gradient variations produced by the diffusion of surrounding charged particles as well as by the
motion of the nucleus in question. This situation applies to the relaxation of deuterium nuclei which are diffusing amongst the sites of an interstitial lattice in a face centred cubic (FCC) crystal. Since these interstitial sites possess cubic symmetry with respect to both the atoms of the FCC crystal and the surrounding interstitial sites, the average field gradients experienced by the deuterium nuclei are zero if the deuterium ions are distributed randomly amongst the sites of the interstitial lattice. However, at any instant the field gradients are likely to be non-zero due to a non-cubic arrangement of the other deuterium ions which occupy some of the surrounding interstitial sites.

Although the first two cases above have been considered theoretically (Fedders 1974, 1977, 1978), an adequate theory has not been developed for the third case. As shown by treatments of the corresponding situation for liquids (Sholl 1967, 1974, Warren 1974), complications arise when both the relaxing nucleus and the surrounding particles are mobile and the presence of the surrounding particles can affect the motion of the relaxing nucleus.

As discussed in a subsequent paper (Barton and Seymour 1982 hereafter referred to as II), there are substantial differences between the experimental spin-lattice relaxation results for deuterons in the FCC phase of transition metal deuterides and the data for protons in the corresponding hydrides. Motivated by the need for a more detailed interpretation of these results for cubic transition metal deuterides, the aim of this paper is to develop the theory of the nuclear quadrupolar relaxation of a particle diffusing on a cubic lattice, due to the relative translational motion of other identical particles on the same lattice. This meaning of lattice is implied when this word is used in the following sections.

In § 2 the general theory of quadrupolar relaxation due to fluctuating field gradients in crystalline solids is summarised and the probability function which appears in the expression for the field gradient correlation functions is discussed in terms of two- and three-particle components. An integral equation for the three-particle probability function within the mean field theory is derived in § 3 and formal solutions of this equation are obtained for nearest-neighbour jumps on cubic lattices. In § 4 exact low-temperature expressions for the three-particle probability function and the spectral density functions for quadrupolar relaxation are determined.

2. General theory

The Hamiltonian describing the nuclear electric quadrupolar interaction may be expressed in the form (Cohen and Reif 1957, Sholl 1967)

\[ H_Q(t) = \sum_{p=\pm 2}^{2} Q^{(p)} F^{(-p)} \]  

(2.1)

where

\[ Q^{(0)} = \beta [3I_z^2 - I(I + 1)] \]  

(2.2)

\[ Q^{(\pm 1)} = \frac{\beta \sqrt{6}}{2} (I_z I_+ + I_+ I_z) \]  

(2.3)

\[ Q^{(\pm 2)} = \frac{\beta \sqrt{6}}{2} I_z^2 \]  

(2.4)
with

\[ \beta = eQ/2I(2I - 1) \]  

(2.5)

and

\[ F^{(0)} = \frac{1}{2}(V_{zz} - \frac{1}{2}V^{2}V) \]  

(2.6)

\[ F^{(\pm)} = 6^{-1/2}(V_{zz} \pm iV_{yz}) \]  

(2.7)

\[ F^{(\pm)} = \frac{1}{2}6^{-1/2}(V_{xx} - V_{yy} \pm 2iV_{xy}). \]  

(2.8)

In the above equations \( I \) is the nuclear spin, \( Q \) the nuclear quadrupole moment, \( V \) the time-dependent potential at the nucleus and \( V_{ij} = \partial^2V/\partial x_i \partial x_j \) is the second derivative of \( V \) with respect to a given set of orthogonal axes.

It is commonly assumed that the field gradient components at a nucleus located at the origin may be represented as sums over all other particles on the lattice of the appropriate derivatives of the potential at the origin \( \nu(\mathbf{r}_i) \) due to the particle at \( \mathbf{r}_i \). In the case of a conductor, the effect of linear screening of the bare potential of the particle at \( \mathbf{r}_i \) by the conduction electrons may be included in \( \nu(\mathbf{r}_i) \). Then, if \( \nu \) is a central potential, equations (2.6)–(2.8) may be written as

\[ F^{(\rho)} = \sum_{i} U_{\rho}(\mathbf{r}_i) \]  

(2.9)

where

\[ U_{\rho}(\mathbf{r}_i) = (\mathbf{\hat{r}} \cdot \mathbf{\hat{z}})^{1/2} \sigma \nu_2(\mathbf{r}_i)(-1)^{|\rho|} \nu^{(\rho)} Y_{2\rho}(\mathbf{\Omega}_i) \]  

(2.10)

and

\[ \nu_2(\mathbf{r}) = r(d/dr)[(1/r)(d\nu(r)/dr)]. \]  

(2.11)

\( Y_{2\rho} \) are the spherical harmonics normalised to unity and \( \mathbf{\Omega}_i \) is the direction of \( \mathbf{r}_i \) relative to the \( z \) axis (generally chosen to coincide with the direction of the applied magnetic field). The factor \( \sigma \) is included in equation (2.10) to account for the effects of the core electrons of the particle at the origin on the field gradient at its nucleus. Only when this field gradient arises from charges external to the core does \( \sigma \) become \( 1 - \gamma_{\infty} \) where \( \gamma_{\infty} \) is the Sternheimer antisheilding factor.

If the temporal correlation functions of the fluctuating field gradient functions \( F^{(\rho)} \) are defined by

\[ G^{(\rho)}(t) = \langle F^{(\rho)}(t')F^{(\rho)\ast}(t' + t) \rangle \]  

(2.12)

where the angular brackets denote an ensemble average, then the nuclear spin relaxation arising from the fluctuating field gradients may be expressed in terms of the temporal Fourier transforms \( J^{(\rho)}(\omega) \) of these correlation functions, i.e.

\[ J^{(\rho)}(\omega) = \int_{-\infty}^{\infty} G^{(\rho)}(t) \exp(-i\omega t) \, dt \]

\[ = 2 \text{Re} \int_{0}^{\infty} G^{(\rho)}(t) \exp(-i\omega t) \, dt. \]  

(2.13)

The final step follows because \( G^{(\rho)}(t) \) is an even function of the time \( t \) (Abragam 1961).
The relaxation produced by a quadrupolar interaction is not, in general, described by a simple exponential decay, but by the sum of two or more decaying exponentials (Hubbard 1970). However, there are circumstances in which relaxation according to a single exponential behaviour does occur and hence the concept of a relaxation time is valid, namely if (1) the nucleus has spin $I = 1$, or (2) the field gradients fluctuate much more rapidly than the nuclear Larmor precession period (the extreme narrowing approximation) (Abragam 1961). Moreover, provided that the concept of a spin temperature is applicable, nuclear spin–lattice relaxation (but not spin–spin relaxation) may be described in terms of a single relaxation time even when the two conditions mentioned above are not satisfied (Abragam 1961). The existence of a spin temperature requires spin–spin relaxation to be much more rapid than spin–lattice relaxation and any residual inequality in the spacing of nuclear energy levels due, for example, to quadrupolar interactions, to be smaller than the dipolar linewidth (Andrew and Tunstall 1961).

When the relaxation can be described by a single exponential decay of the nuclear magnetisation, the associated relaxation time may be expressed in terms of the spectral density functions $J^{\rho}(\omega)$ defined by equation (2.13). If the fluctuating dipolar and quadrupolar interactions can be regarded as perturbations of the nuclear Zeeman energy levels, then the spin–lattice relaxation rate $T^{-1}_1$, the spin–lattice relaxation rate in the rotating frame $T^{-1}_\rho$, and the spin–spin relaxation rate $T^{-1}_2$ produced by the quadrupolar interaction for the case of a single nuclear species in the motionally narrowed regime are given by (Abragam 1961, Wolf 1979)

\[
T^{-1}_1 = \frac{3}{20} \left( \frac{eQ}{\hbar} \right)^2 \frac{2I + 3}{I^2(2I - 1)} \left[ J^{(1)}(\omega_0) + 4J^{(2)}(2\omega_0) \right]
\]

(2.14)

\[
T^{-1}_\rho = \frac{3}{40} \left( \frac{eQ}{\hbar} \right)^2 \frac{2I + 3}{I^2(2I - 1)} \left[ 3J^{(0)}(2\omega_1) + 5J^{(1)}(\omega_0) + 2J^{(2)}(2\omega_0) \right]
\]

(2.15)

\[
T^{-1}_2 = \frac{3}{40} \left( \frac{eQ}{\hbar} \right)^2 \frac{2I + 3}{I^2(2I - 1)} \left[ 3J^{(0)}(0) + 5J^{(1)}(\omega_0) + 2J^{(2)}(2\omega_0) \right]
\]

(2.16)

where $\omega_0$ and $\omega_1$ are the Larmor precession frequencies in the applied static and radio-frequency magnetic fields respectively. As emphasised by Wolf (1979), the form of the above equations for quadrupolar relaxation rates is identical to that of the corresponding equations for the relaxation rates produced by dipole–dipole interactions. This similarity arises from the fact that the quadrupole–charge and dipole–dipole interactions involve the spin operators in the same way.

In order to obtain values for the relaxation rates given by equations (2.14)–(2.16), it is necessary to evaluate the correlation functions $G^{\rho}(t)$ and their Fourier transforms $J^{\rho}(\omega)$. Using equations (2.9) and (2.10) in equation (2.12) yields

\[
G^{\rho}(t) = \frac{4}{5} \pi \sigma^2 \sum_{r_1, r_2} v_2(r_1) v_2(r_2) Y_{2\rho}(\Omega) Y_{2\rho}^*(\Omega) P(r_1, r_2, t)
\]

(2.17)

where $P(r_1, r_2, t)$ is the probability of finding particles at $r_1$ initially and at $r_2$ a time $t$ later given there is a particle at the origin throughout this time interval. The position vectors $r_1$ and $r_2$ are defined relative to the origin which is a moving particle rather than a fixed point in the lattice. The prime on the summations indicates that terms for which $r_j = 0$ or $r_i = 0$ are to be omitted.

As may be seen in § 3, it is convenient to consider the double spatial Fourier transform of $P(r_1, r_2, t)$. With this in mind, equation (2.17) may be written as

\[
G^{\rho}(q) = \frac{4}{5} \pi \sigma^2 N^{-2} \sum_{q, q'} T^{\rho}(q, q', t) T^*_{\rho}(q')
\]

(2.18)
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where (see the Appendix)

\[
P(q, q', t) = \sum_{i,j} P(r_i, r_j, t) \exp(-iq \cdot r_i + iq' \cdot r_j) \tag{2.19}
\]

and

\[
T_p(q) = \sum_i v_2(r_i) Y_{2p}(\Omega_i) \exp(iq \cdot r_i). \tag{2.20}
\]

The \(q\) and \(q'\) summations in equation (2.18) are over the first Brillouin zone of the crystal lattice and \(N\) is the number of lattice points in the crystal. The expression for the \(J^{(q)}(\omega)\) is therefore

\[
J^{(q)}(\omega) = \frac{\alpha}{4} \pi \sigma^2 N^{-2} \sum_{q,q'} T_p(q) P^{R}(q, q', \omega) T^{*}_p(q') \tag{2.21}
\]

where \(P^{R}(q, q', \omega)\) is the real part of \(P(q, q', \omega)\) which is given by

\[
P(q, q', \omega) = 2 \int_0^\infty P(q, q', t) \exp(-i\omega t) \, dt. \tag{2.22}
\]

The probability function \(P(r_i, r_j, t)\) may be expressed as the sum of two separate terms, namely

\[
P(r_i, r_j, t) = cP_1(r_i, r_j, t) + c^2 \sum_{k \neq i} P_2(r_k, r_j, t) \tag{2.23}
\]

where \(c\) denotes the fraction of lattice sites which are occupied. \(P_1(r_i, r_j, t)\) is the probability of finding a particle at \(r_i\) a time \(t\) after the same particle was at \(r_j\) and \(P_2(r_k, r_j, t)\) is the probability that a particle initially at \(r_k\) moves to \(r_j\) in a time \(t\) given there was another particle at \(r_k\) initially (see figure 1). Both \(P_1(r_i, r_j, t)\) and \(P_2(r_k, r_j, t)\) contain the condition that a further particle is located at the origin during the time \(t\). Thus the first term in equation (2.23) is a two-particle function describing the diffusion of a particle from \(r_i\) to \(r_j\) relative to the particle at the origin, whereas the second term is a three-particle function which describes the diffusion of a particle initially at \(r_i\) to any site of the lattice except \(r_j\) or the origin and some other particle diffusing to \(r_j\). A useful exact result for \(P(r_i, r_j, t)\) is the condition at \(t = 0\),

\[
P(r_i, r_j, 0) = c\delta_{r_i,r_j}(1 - \delta_{r_i,0}) + c^2(1 - \delta_{r_i,0})(1 - \delta_{r_j,0})(1 - \delta_{r_i,r_j}) \tag{2.24}
\]

where the first and second terms are the two-particle and three-particle functions respectively at \(t = 0\).

The three-particle function \(\sum_{k \neq i} P_2(r_k, r_j, t)\) may be written as a function of \(r_i, r_j\) and \(t\) which will be denoted by \(P_3(r_i, r_j, t)\). Then the spatial and temporal Fourier transform of equation (2.23), which is required for the evaluation of the \(J^{(q)}(\omega)\) from equation (2.21), is

\[
P(q, q', \omega) = cP_1(q, q', \omega) + c^2P_2(q, q', \omega) \tag{2.25}
\]

where \(P_1(q, q', \omega)\) and \(P_2(q, q', \omega)\) are defined by relations analogous to equations (2.19) and (2.22) for \(P(q, q', \omega)\).

The two-particle probability function, \(P_1(r_i, r_j, t)\) or \(P_1(q, q', \omega)\), occurs in the theory of nuclear spin relaxation due to dipole–dipole interactions between diffusing particles and the resulting correlation functions and relaxation rates for particles undergoing nearest-neighbour jumps on cubic lattices have been evaluated for several different jumping models (see, for example, Barton and Sholl 1976, Fedders and Sankey 1978).
It has been shown (Titman 1973) that, for dipole–dipole relaxation due to translational atomic motion in liquids, the three-particle term in the relaxation rate expressions is much smaller than the two-particle term provided that the distribution of the spins amongst the spin states is not correlated with the atomic positions and the temperature is sufficiently high to give small differences in the populations of the spin states. In solids one would expect that the three-particle function also has a negligible effect on dipolar relaxation if the above conditions are satisfied.

Unlike the dipolar field at a given nucleus, the electric field gradient does not depend on the spin states of the surrounding nuclei. The quadrupolar interaction depends on the resultant field gradient at the relaxing nucleus which is determined by the angular as well as the radial positions of the surrounding particles. The three-particle function represents the effect of the angular distribution of particles around the relaxing nucleus and therefore produces a term in the relaxation rate expressions which tends to cancel the two-particle term. In the extreme cases of spherical or cubic symmetry, the field gradient is always zero and there is no quadrupolar relaxation.

It is believed that the three-particle function does have an important effect on
quadrupolar relaxation due to atomic diffusion in liquids (Sholl 1974, Titman 1977), but the three-particle term appears to have been neglected in the corresponding treatments for crystalline solids. The following section is concerned with the evaluation of the three-particle term in the expressions for quadrupolar relaxation rates arising from diffusion on cubic lattices.

3. Evaluation of the three-particle function

In order to evaluate the probability function \( P(q, q', \omega) \) given by equation (2.25), one must choose an appropriate jumping model to describe the movement of particles on the lattice. The different models which have been employed in the case of dipole–dipole relaxation (Fedders and Sankey 1978, Barton and Sholl 1980) can also be applied to the calculation of \( P(q, q', \omega) \) for quadrupolar relaxation. In this paper the mean field theory for nearest-neighbour jumps on cubic lattices will be considered in detail. Physically, this approximation assumes that the probability of any site being vacant is \( \bar{c} = 1 - c \), but with the additional restriction that more than one of the specific particles being considered may not simultaneously occupy the same site. Other possible interactions between particles which may affect their motion on the lattice will be ignored. As well as including, in an average way, the effects of spatial correlations between the motions of particles, the mean field theory has the mathematical advantage of being the best approximation which allows the equations for the probability functions to be linearised (Sankey and Fedders 1977).

The procedure adopted in this section for the evaluation of the three-particle function in equation (2.25) involves the establishment of a rate equation which is converted to an integral equation by Fourier transforming with respect to time. After taking the spatial Fourier transform of all quantities, a formal solution for the required three-particle function within the mean field theory is obtained.

Let \( P_d(r_i, r_k; r_i, r_j; t) \) be the probability that in a time \( t \) two particles move from \( r_i \) to \( r_i \) and from \( r_k \) to \( r_j \) respectively relative to a third particle whose position always defines the origin (see figure 1(b)). If \( \Delta t \) denotes a sufficiently small increment in time, then

\[
P_d(r_i, r_k; r_i, r_j; t + \Delta t) = 3\Gamma \sum_{\delta \gamma} P_d(r_i, r_k; r_{\delta}, r_{\gamma}; t) W(r_{\delta}, r_{\gamma}; r_i, r_j) \Delta t
\]

\[+ (1 - 3\Gamma \Delta t) P_d(r_i, r_k; r_i, r_j; t)\]  

(3.1)

where \( \Gamma \) is the mean frequency of attempted jumps† by a single particle and \( W(r_{\delta}, r_{\gamma}; r_i, r_j) \) is the probability that the two particles move from \( r_{\delta} \) to \( r_i \) and from \( r_{\gamma} \) to \( r_j \) respectively, relative to the third particle at the origin, as a result of a total of one attempted jump among the three particles. In the limit as \( \Delta t \to 0 \), equation (3.1) may be written as a rate equation, i.e.

\[
\frac{d}{dr} P_d(r_i, r_k; r_i, r_j; t) = 3\Gamma \sum_{\delta \gamma} P_d(r_i, r_k; r_{\delta}, r_{\gamma}; t) W'(r_{\delta}, r_{\gamma}; r_i, r_j)
\]  

(3.2)

where

\[
W'(r_{\delta}, r_{\gamma}; r_i, r_j) = W(r_{\delta}, r_{\gamma}; r_i, r_j) - \delta_{r_{\delta}r_i} \delta_{r_{\gamma}r_j} (1 - \delta_{r_i0}) (1 - \delta_{r_j0}) (1 - \delta_{r_{\delta}r_{\gamma}}).
\]

(3.3)

† An attempted jump by a particle is successful if and only if the site to which it attempts the jump is vacant.
Defining $P_4(r_i, r_k; r_l, r_j; \omega)$ in an analogous way to equation (2.22), the temporal Fourier transform of equation (3.2) is

$$-i\omega P_4(r_i, r_k; r_l, r_j; \omega) = 2\delta_{r_i, r_l} \delta_{r_k, r_j} (1 - \delta_{r_i, 0}) (1 - \delta_{r_k, 0}) (1 - \delta_{r_i, r_j})$$

$$+ 3\Gamma \sum_{\xi, \gamma} P_4(r_i, r_k; r_\xi, r_\gamma; \omega) W' (r_\xi, r_\gamma; r_l, r_j)$$

(3.4)

which is an integral equation for $P_4(r_i, r_k; r_l, r_j; \omega)$. Since the particle which moves to $r_j$ can be initially at any site $r_k$ of the lattice except $r_l$ or the origin and $P_4(r_i, r_k; r_l, r_j; \omega)$ is zero when $r_k = r_l$ or $0$, both sides of equation (3.4) may be summed over all $r_k$. This yields

$$-i\omega P_3(r_i; r_l, r_j; \omega) = 2\delta_{r_i, r_l} (1 - \delta_{r_i, 0}) (1 - \delta_{r_l, 0}) (1 - \delta_{r_i, r_j})$$

$$+ 3\Gamma \sum_{\xi, \gamma} P_3(r_i; r_\xi, r_\gamma; \omega) W' (r_\xi, r_\gamma; r_l, r_j)$$

(3.5)

where

$$P_3(r_i; r_l, r_j; \omega) = \sum_k P_4(r_i, r_k; r_l, r_j; \omega).$$

(3.6)

Moreover, because the particle initially at $r_i$ can move to any site $r_l$ of the lattice apart from $r_j$ or the origin and $P_3(r_i; r_l, r_j; \omega)$ is zero when $r_l = r_j$ or $0$, equation (3.5) may be summed over all $r_l$. The resultant equation is

$$-i\omega P_2(r_i, r_j; \omega) = 2(1 - \delta_{r_i, 0}) (1 - \delta_{r_j, 0}) (1 - \delta_{r_i, r_j})$$

$$+ 3\Gamma \sum_{\xi, \gamma} P_3(r_i; r_\xi, r_\gamma; \omega) W'' (r_\xi, r_\gamma; r_j)$$

(3.7)

where

$$P_2(r_i, r_j; \omega) = \sum_l P_3(r_i; r_l, r_j; \omega)$$

(3.8)

and

$$W'' (r_\xi, r_\gamma; r_j) = \sum_l W' (r_\xi, r_\gamma; r_l, r_j).$$

(3.9)

The probability function $P_2(r_i, r_j; \omega)$ is equivalent to the temporal Fourier transform of the three-particle function $\sum_k \tilde{P}_2(r_k; r_l, r_j; t)$ in equation (2.23).

As in the case of the two-particle function $P_2(r_j, r_j; t)$ (Fedders and Sankey 1978), it is convenient, particularly when using models which include the effects of spatial correlations, to Fourier transform all functions in space as well as time. Therefore, by employing the multiple spatial transforms defined in the Appendix, equations (3.5) and (3.7) respectively become

$$-i\omega P_3(q; q'', q'; \omega) = F(q; q'', q')$$

$$+ 3\Gamma N^{-2} \sum_{q_1, q_2} P_3(q; q_1, q_2; \omega) W'(q_1, q_2; q'', q')$$

(3.10)

and

$$-i\omega P_2(q, q'; \omega) = F_0(q, q')$$

$$+ 3\Gamma N^{-2} \sum_{q_1, q_2} P_3(q; q_1, q_2; \omega) W''(q_1, q_2; q', q')$$

(3.11)
where

\[
F(q; q'', q') = 2[N^2 \delta(q - q'') \delta(q') - N \delta(q - q'')] - N \delta(q - q'') \]

\[
- N \delta(q - q'') + 2 \] (3.12)

\[
F_0(q, q') = F(q; 0, q') = 2[N^2 \delta(q) \delta(q') - N \delta(q) - N \delta(q') - N \delta(q - q') + 2] \] (3.13)

and the various \(q_s\) are all wavevectors in the first Brillouin zone of the crystal lattice. Equation (3.10) is needed for the evaluation of the function \(P_3\) which occurs in the solution of equation (3.11) for the required three-particle function \(P_2(q, q', \omega)\). As explained in the Appendix, equation (3.11) may be obtained from equation (3.10) by setting \(q'' = 0\) and thus is a special case of equation (3.10).

The theory developed so far in this section is quite general in that it is independent of jumping model. However, in order to investigate in more detail the form of equations (3.10) and (3.11), it is necessary to determine the function \(W'(q_1, q_2; q'', q')\) which depends on the particular jumping model adopted. In the remainder of this section the mean field theory is employed.

To obtain an expression for \(W'(q_1, q_2; q'', q')\), the corresponding function \(W'(r_1, r_2; r_3, r)\) in real space is determined by considering in turn the probabilities that one of the three particles initially at \(r_1, r_2\) and the origin respectively attempts a successful or an unsuccessful jump such that the final positions of the three particles are \(r_1, r_2, r\) and the origin respectively. (The final position of the origin may be different from its initial position in the lattice.) A single expression for \(W'(r_1, r_2; r_3, r)\), which is valid for all initial configurations of the three particles and which takes into account spatial correlations according to the mean field theory, may be written as

\[
W'(r_1, r_2; r_3, r) = \frac{1}{2} \delta(1 - \delta_{r_1, 0}) (1 - \delta_{r_2, 0}) (1 - \delta_{r_3, 0}) (1 - \delta_{r, 0})
\]

\[
\times \left\{ \delta_{r_1, r_2} \delta_{r_2, r_3} (1 - \delta_{r_1, r_2}) \left[ (2/Z) \sum_{n=1}^{Z} (\delta_{r_1, r_n} + \delta_{r_2, r_n} + \delta_{r_3, r_n} + r_n) - 3 \right] \right.
\]

\[
+ (1 - \delta_{r_1, r_2}) \left[ (1/Z) \delta_{r_1, r_1} \sum_{n=1}^{Z} \delta_{r_1, r_n + r} \right.
\]

\[
+ (1/Z) \delta_{r_2, r_2} \sum_{n=1}^{Z} \delta_{r_2, r_n + r} \right] \right.
\]

\[
+ (1/Z) (1 - \delta_{r_1, r_3}) (1 - \delta_{r_2, r_3}) \sum_{n=1}^{Z} \delta_{r_3, r_n + r} \delta_{r_1, r_n + r} \right\} \] (3.14)

where \(Z\) is the number of jump paths \(r_n\) available for a single jump of a particle. Since the factors \((1 - \delta_{r_1, 0}), (1 - \delta_{r_2, 0}), (1 - \delta_{r_3, 0})\) and \((1 - \delta_{r, 0})\) explicitly preclude the origin from being simultaneously occupied by more than one particle, the sums \(\Sigma_{n=1}^{Z}\) may be taken over all \(Z\) nearest-neighbour sites even when one of them is the origin.

After a considerable amount of straightforward algebra involving repeated use of equation (A1), the spatial Fourier transform of equation (3.14) is found to be

\[
W'(q_1, q_2; q'', q') = \frac{1}{3} \delta(1 - q_1 - q'') (1 - q_2 - q') f(q'', q')
\]

\[
+ N \delta(q_1 - q'' + q_2 - q') [2A(q_1 - q'') - A(q_1) - A(q_2) - f(q'', q')]
\]

\[
+ N \delta(q_1 - q'') [2A(q_2 - q') - A(q_1 - q'') - A(q_2) - f(q'', q')]
\]
and the structure factor $A(q)$ is

$$A(q) = \frac{1}{Z} \sum_{n=1}^{Z} \exp(iq \cdot r_n).$$

Substitution of equation (3.15) into equation (3.10) yields the result

$$P_3(q; q'', q'; \omega) = h(q'', q'; \omega) \left\{ F(q; q'', q') + Na \left[ \sum_{q_1} s(q_1, q'', q') P_3(q; q_1, q'; \omega) \right. \right.$$  

$$+ \sum_{q_2} s(q_2, q', q'') P_3(q; q'', q_2; \omega)$$  

$$+ \left. \sum_{q_1} s(q_1, q''', -(q'' + q')) P_3(q; q_1, q''' + q' - q_1; \omega) \right]$$  

$$- \alpha \sum_{q_1, q_2} t(q_1 + q_2, q''', q' + q', -q') P_3(q; q_1, q_2; \omega) \right\}$$

(3.18)

where terms which vanish for the reason given in the Appendix have been omitted. In the above equation

$$h(q'', q'; \omega) = -\tau [i\omega + f(q'', q')]^{-1}$$

(3.19)

$$s(q_a, q_b, q_c) = 2A(q_a - q_b) - A(q_a + q_c) - A(q_a)$$

(3.20)

$$t(q_a, q_b, q_c) = 4A(q_a - q_b) - A(q_a - q_b + q_c) - A(q_a + q_c) - 2A(q_a)$$

(3.21)

$$\alpha = (\tau N) -1$$

(3.22)

and $\tau = (\epsilon \Gamma) -1$ is the mean time between jumps of a single particle.

Because of the various delta functions in expression (3.15) for $W'(q_1, q_2; q''', q')$, the resulting equation (3.18) for $P_3(q; q''', q'; \omega)$ contains both single and double summations over the Brillouin zone and the single summations involve $P_3$ as a function of $q'''$ and/or $q'$. Therefore, it does not appear to be possible to obtain a complete analytical solution for $P_3(q; q''', q'; \omega)$ from equation (3.18). However, as described in II, an exact solution for $P_3(q; q''', q'; \omega)$ can be obtained in the low-temperature limit ($\omega \tau \gg 1$).

Let us now investigate equation (3.11) in more detail and examine the way in which $P_3$ occurs in the resulting expression for $P_2(q, q', \omega)$. Because of the relationship between
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equations (3.10) and (3.11), an equation for \( P_2(q, q', \omega) \) may also be obtained from equation (3.18) by setting \( q'' = 0 \). Thus

\[
P_2(q, q', \omega) = -2N\alpha h_0(q', \omega) \sum_{\mathbf{q}_1} s_0(q_2, -q') P_2(q, q_2, \omega)
\]

\[
+ h_0(q', \omega) \left[ F_0(q, q') + N\alpha \sum_{\mathbf{q}_1} s_0(q_1, q') P_3(q; q_1, q'; \omega)
\right.
\]

\[
+ s_0(q_1, -q') P_3(q; q_1, q' - q_1; \omega)]
\]

\[
- \alpha \sum_{\mathbf{q}_1, \mathbf{q}_2} t(q_1 + q_2, q', -q') P_3(q; q_1, q_2; \omega)
\]\n
(3.23)

where

\[
h_0(q', \omega) = h(0, q'; \omega) = \frac{1}{\tau}(-\frac{i}{2} \omega \tau + [1 - A(q')]^{-1}
\]

(3.24)

and

\[
s_0(q_2, q_b) = s(q_2, 0, q_b) = A(q_a) - A(q_2 + q_b).
\]

(3.25)

For nearest-neighbour jumps on cubic lattices, the integral equation (3.23) may be solved analytically for \( P_2(q, q', \omega) \) in terms of the function \( P_3 \). In order to fully exploit the properties of cubic symmetry, the solution of equation (3.23) is carried out separately for the simple cubic (sc), FCC and BCC lattices. The resultant expressions are all of the form

\[
P_2(q, q', \omega) = -P_1(q, q', \omega) + \Delta P_2(q, q', \omega)
\]

(3.26)

where

\[
\Delta P_2(q, q', \omega) = \frac{h_0(q', \omega)}{\tau} \left[ b(q, q', \omega) + 2 \sum_i D_i(q, \omega) D'_i(q') B_i(\omega) \right]
\]

(3.27)

and

\[
b(q, q', \omega) = N^{-1} \sum_{\mathbf{q}_1} [s_0(q_1, q') P_3(q; q_1, q'; \omega) + s_0(q_1, -q') P_3(q; q_1, q' - q_1; \omega)]
\]

\[
- N^{-2} \sum_{\mathbf{q}_1, \mathbf{q}_2} t(q_1 + q_2, q', -q') P_3(q; q_1, q_2; \omega).
\]

(3.28)

Terms for which the lattice sums \( T_\rho(q) \) and/or \( T'_\rho(q') \) or the summations over the Brillouin zone in equation (2.21) vanish because of symmetry have been omitted from equation (3.26). Some of the functions \( D_i(q, \omega) \) and \( D'_i(q') \), for example, those which are odd functions of \( q \) or \( q' \) or which are invariant under the 48 symmetry operations of the cubic point group, do not contribute to the relaxation rates because the corresponding summations over the Brillouin zone vanish. The expressions for those \( D_i(q, \omega) \) and \( D'_i(q') \) which do contribute to relaxation and for the corresponding \( B_i(\omega) \) are given in table 1 for sc, FCC and BCC lattices.

Mean field expressions for \( P_1(q, q', \omega) \) have already been given for cubic lattices by Barton and Sholl (1980) and will not be repeated here. However, it should be noted that, in the case of the BCC lattice, the term for which \( i = 1 \) in equation (3.20) of Barton and Sholl (1980) does not contribute to relaxation because of symmetry.

As may be seen from table 1, the expressions for the \( D_i(q, \omega) \) (but not the \( D'_i(q') \) and \( B_i(\omega) \)) involve the function \( b \). Therefore, in equations (3.26) and (3.27) for \( P_2(q, q', \omega) \), the function \( P_3 \) occurs only through \( b \) which, according to equation (3.28),
Table 1. Expressions for the functions $D_i(q, \omega), D_i(q')$ and $B_i(\omega)$ which occur in equation (3.27) for $\Delta P_2(q, q', \omega)$ for cubic lattices. In each case $a$ is the lattice parameter of the appropriate sc lattice as discussed in § 3.2 of Barton and Sholl (1980) ($a$ is half the conventional parameter of the FCC and BCC lattices).

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>$D_i(q, \omega) = (1/\tau N) \sum \limits_\rho h_\rho(q, \omega) \cos \rho_i a b(q, \rho, \omega)$</td>
</tr>
<tr>
<td></td>
<td>$D'_i(q') = \frac{1}{2} \cos q' a$</td>
</tr>
<tr>
<td></td>
<td>$B_i(\omega) = 1 - (2/3\tau N) \sum \limits_\rho h_\rho(q, \omega) [\cos^2 q_i a - \cos q_i a \cos q_{i+1} a]$</td>
</tr>
<tr>
<td></td>
<td>$(i = 1, 2, 3)$</td>
</tr>
<tr>
<td>FCC</td>
<td>$D_i(q, \omega) = (1/\tau N) \sum \limits_\rho h_\rho(q, \omega) \cos \rho_i a \cos \rho_j a b(q, \rho, \omega)$</td>
</tr>
<tr>
<td></td>
<td>$D'_i(q') = \frac{1}{2} \cos q_i a \cos q_j a$</td>
</tr>
<tr>
<td></td>
<td>$B_i(\omega) = 1 - (2/3\tau N) \sum \limits_\rho h_\rho(q, \omega) [\cos^2 q_i a \cos^2 q_j a - \cos^2 q_i a \cos q_{i+1} a \cos q_{i+2} a]$</td>
</tr>
<tr>
<td></td>
<td>$(i = 1, 2, 3; j = i + 1 - 3\delta_{i,3})$</td>
</tr>
<tr>
<td>BCC</td>
<td>$D_i(q, \omega) = (1/\tau N) \sum \limits_\rho h_\rho(q, \omega) \sin \rho_i a \sin \rho_j a b(q, \rho, \omega)$</td>
</tr>
<tr>
<td></td>
<td>$D'_i(q') = \frac{1}{2} \sin q_i a \sin q_j a$</td>
</tr>
<tr>
<td></td>
<td>$B_i(\omega) = 1 - (2/3\tau N) \sum \limits_\rho h_\rho(q, \omega) \sin^2 q_i a \sin^2 q_j a$</td>
</tr>
<tr>
<td></td>
<td>$(i = 4, 5, 6; k = i - 3; j = k + 1 - 3\delta_{i,3})$</td>
</tr>
</tbody>
</table>

essentially consists of summations over the Brillouin zone of products of a structure factor $A$ and $P_3$.

In order to evaluate numerically the effect of the function $\Delta P_2(q, q', \omega)$ in equation (3.26) on the relaxation rates at arbitrary temperatures, it is necessary to resort to approximation methods in the absence of an analytical solution for $P_3$. These methods, which are considered in II, are based on the fact that it is possible to obtain an analytical solution for $P_3$, and hence to evaluate the spectral density functions $J^{(3)}(\omega)$ exactly, in the low-temperature limit.

4. Behaviour in the low-temperature limit

It is physically instructive in the low-temperature limit ($\omega t \gg 1$) to consider the behaviour of the probability function $P(r_i, r_j, \omega)$ rather than its spatial Fourier transform $P(q, q', \omega)$. As in the case of the two-particle function $P_2(r_i, r_j, \omega)$ (Barton and Sholl 1980), analytical expressions for the three-particle function $P_3(r_i, r_j, \omega)$ and hence for $P(r_i, r_j, \omega)$ can be derived which incorporate exactly the effects of spatial correlations for any concentration of particles except the monovacancy limit $c \rightarrow 1$.

As described in § 2, $cP_2(r_i, r_j, t)$ is the probability, given that one particle defines the origin during a time $t$ and another particle was at $r_i$ initially, that a third particle moves
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to \( r_i \) in the time \( t \). Since, in the low-temperature limit, the probability of a total of more than one attempted jump among the three particles may be neglected, we can write

\[
cP_2(r_i, r_j, t) = w_0^3(t) R_{\text{000}}(r_i, r_j) + w_1^3(t) w_1(t) [R_{100}(r_i, r_j) + R_{010}(r_i, r_j) + R_{001}(r_i, r_j)]
\] (4.1)

where

\[
w_i(t) = (\Gamma t)^i e^{-\Gamma t}
\] (4.2)

is the Poisson distribution giving the probability of \( i \) jumps being attempted by a particle in a time \( t \). The function \( R_{\text{mmn}}(r_i, r_j) \) is the probability that, relative to a particle which attempts \( n \) jumps and whose position defines the origin, another particle moves to \( r_j \) after \( m \) attempted jumps given there was a third particle at \( r_i \) initially which makes \( m \) attempted jumps. In particular,

\[
R_{\text{000}}(r_i, r_j) = c(1 - \delta_{r_i, \theta})(1 - \delta_{r_i, \phi})(1 - \delta_{r_i, r_j})
\] (4.3)

since no jumps are attempted in this case and more than one of the three particles may not simultaneously occupy the same site. Using the results \( w_0(0) = 1 \) and \( w_1(0) = 0 \), equations (4.1) and (4.3) yield at \( t = 0 \) the condition

\[
P_2(r_i, r_j, 0) = (1 - \delta_{r_i, \theta})(1 - \delta_{r_i, \phi})(1 - \delta_{r_i, r_j})
\] (4.4)

which agrees with the three-particle term in equation (2.24).

Expressions for the functions \( R_{100}(r_i, r_j) \), \( R_{010}(r_i, r_j) \) and \( R_{001}(r_i, r_j) \) may be deduced by considering in turn the probabilities of whether or not a single attempted jump by one of the three particles will be successful. It will not be successful along one of the \( Z \) possible paths \( r_n \) if another of the three particles occupies the corresponding nearest-neighbour site. In addition, terms which imply that the particle initially at \( r_i \) is at \( r_j \) a time \( t \) later have to be excluded from the three-particle function and one must take into account the fact that the site vacated by one of the particles cannot be occupied by another of the three particles since only one jump among all three particles occurs. The resulting expressions are

\[
R_{100}(r_i, r_j) = c(1 - \delta_{r_i, \theta})(1 - \delta_{r_i, \phi}) \left[ 1 - \delta_{r_i, r_j} \left( c + \frac{2c}{Z} \sum_{n=1}^{Z} \delta_{r_i, r_n} \right) - \frac{c}{Z} \sum_{n=1}^{Z} \delta_{r_i, r_n} - \frac{c}{Z} \delta_{r_i, r_j} \sum_{n=1}^{Z} \delta_{r_i, r_n} \right]
\] (4.5)

and

\[
R_{010}(r_i, r_j) = R_{001}(r_i, r_j) = c(1 - \delta_{r_i, \theta})(1 - \delta_{r_i, \phi})(1 - \delta_{r_i, r_j}).
\] (4.6)

Comparison of equations (4.3) and (4.6) gives

\[
R_{010}(r_i, r_j) = R_{001}(r_i, r_j) = R_{000}(r_i, r_j).
\] (4.7)

It is not surprising that \( R_{010}(r_i, r_j) = R_{000}(r_i, r_j) \) because a successful jump by the particle initially at \( r_i \) does not alter the positions of the other two particles. The equality of \( R_{001}(r_i, r_j) \) and \( R_{000}(r_i, r_j) \) arises from the fact that, when the origin and/or \( r_i \) is a nearest-neighbour site of \( r_j \), the increase in probability of a particle at \( r_j \) attempting an unsuccessful jump is exactly cancelled by the decrease in probability of a particle (other
than the one at \( r_i \) initially) moving to \( r_j \) as a result of a successful attempted jump. The function \( R_{100}(r_i, r_j) \) is different from the functions in equation (4.7) because the origin is defined by the position of a particle and therefore moves when this particle makes a successful jump. One consequence of this definition is that, when \( r_i = r_j, R_{100}(r_i, r_j) \neq 0 \) because a particle other than the one initially at \( r_i \) may be located at \( r_j \) after the particle at the origin has jumped.

Using equations (4.2), (4.3), (4.5) and (4.6) in equation (4.1) produces an expression for \( P_2(r_i, r_j, t) \) which may be Fourier transformed in time to give

\[
P_2(r_i, r_j, \omega) = \frac{2\epsilon \tau}{(9 + \epsilon^2 y^2)^2} \left( 1 - \delta_{r_i, 0} \right) \left( 1 - \delta_{r_j, 0} \right) \left[ 54 - \frac{9(5 + c)}{\epsilon^2} \right] \delta_{r_i, r_j} \]

\[ - (9 - \epsilon^2 y^2) \frac{\delta}{Z} \left[ 2 \delta_{r_i, r_j} \sum_{n=1}^{Z} \delta_{r_i, r_n} - \delta_{r_i, \cdot} \sum_{n=1}^{Z} \delta_{r_i, r_n} + \sum_{n=1}^{Z} \delta_{r_i, r_n + r_n} \right] \]  

(4.8)

where \( y = \omega \tau \). Since contributions to the function \( P_2(r_i, r_j, t) \) which correspond to a total of more than one attempted jump among the three particles yield terms in the expression for \( P_2(r_i, r_j, \omega) \) which are of higher order than \( y^{-2} \) in the large-\( y \) limit, this low-temperature limit may be obtained from equation (4.8). When \( y^2 \gg 9(5 + c)/\epsilon^2 \), the result can be written in the form

\[
P_2(r_i, r_j, \omega) = -P_1(r_i, r_j, \omega) + \Delta P_2(r_i, r_j, \omega) \]

(4.9)

where

\[
\Delta P_2(r_i, r_j, \omega) = \frac{2\epsilon \tau}{y^2} (1 - \delta_{r_i, 0})(1 - \delta_{r_j, 0}) \left[ \delta_{r_i, r_j} - \frac{1}{Z} \delta_{r_i, \cdot} \sum_{n=1}^{Z} \delta_{r_i, r_n} - \frac{1}{Z} \sum_{n=1}^{Z} \delta_{r_i, r_n + r_n} \right] \]

(4.10)

and \( P_1(r_i, r_j, \omega) \) is the large-\( y \) limit of the two-particle function which has been determined analytically by Barton and Sholl (1980). As one would expect, equation (4.9) is analogous to the more general result for arbitrary \( y \) given in equation (3.26).

The term \( \epsilon^2 \) in the expression for the spectral density functions which arises from the three-particle function \( P_2(r_i, r_j, \omega) \) in the large-\( y \) limit may be obtained by substituting equations (4.9) and (4.10) into the temporal Fourier transform of equation (2.17). It is found that

\[
J_2^{(p)}(\omega) = -\frac{2\sigma^2 \tau}{a^6 y^2} \left[ S_0^{(p)}(H) - \frac{1}{Z} (S_1^{(p)}(H) + S_{20}^{(p)}(H)) \right], \quad y^2 \gg 9(5 + c)/\epsilon^2 \]

(4.11)

where

\[
S_0^{(p)}(H) = \Delta \pi a^6 \sum_i v_2(r_i) Y_{2p}(\Omega_i) \left( \sum_{\text{neighbours}} v_2(r_j) Y_{2p}(\Omega_j) \right) \]

(4.12)

\[
S_{20}^{(p)}(H) = \Delta \pi a^6 \sum_{n=1}^{Z} v_2(r_n) \left| Y_{2p}(\Omega_n) \right|^2 \]

(4.13)

\( a \) is the length of the side of a cubic unit cell and \( H \) denotes the direction of the applied magnetic field. The second sum in equation (4.12) is over the \( m \)th nearest neighbours of each \( r_i \).

From the way in which equation (4.8) depends on the concentration \( c \), the validity of the limiting forms (4.10) and (4.11) is restricted to \( y^2 \gg 9(5 + c)/\epsilon^2 \)—a more stringent
condition than \( y^2 \gg 4(1 + c)/\bar{c}^3 \) which applies to the large-\( y \) limit of the \( J_1^{(p)}(\omega) \) (the spectral density functions for quadrupolar relaxation arising from the two-particle function \( P_1(r_i, r_j, \omega) \)) (Barton and Sholl 1980). The above conditions arise from terms in the expressions for the probability functions which are non-zero only when \( r_i = r_j \). The factors of 4 and 9 are due to the fact that the motions of two and three specific particles, respectively, are being considered and the factors \( 1 + c \) and \( 5 + c \) arise more subtly for the same reason. As \( c \) increases, the asymptotic forms of all the spectral density functions are reached at larger values of \( y \) (lower temperatures). In the monovacancy limit \( c \rightarrow 1 \), expression (4.8) and the corresponding one for the two-particle function diverge, indicating that the mean field theory is no longer an appropriate model.

In the low-temperature limit, the \( J_1^{(p)}(\omega) \) and \( J_2^{(p)}(\omega) \) are both proportional to \( \omega^{-2} \bar{r}^{-1} \). Therefore, the spectral density functions for quadrupolar relaxation depend on \( \omega \) and \( \bar{r} \) in the same way as the corresponding functions for dipolar relaxation.

Since, in the large-\( y \) limit, \( \Delta P_2(r_i, r_j, \omega) \) produces a term in the expression for the \( J_2^{(p)}(\omega) \) which is exactly half of that arising from \( P_1(r_i, r_j, \omega) \), equation (4.11) may be written as

\[
J_2^{(p)}(\omega) = -\frac{1}{4} J_1^{(p)}(\omega), \quad y^2 \gg 9(5 + c)/\bar{c}^3. \tag{4.14}
\]

Taking into consideration the form of equation (2.23) for the probability function \( P(r_i, r_j, t) \), the spectral density functions \( J^{(p)}(\omega) \) are therefore given, in the low-temperature limit, by

\[
J^{(p)}(\omega) = c(1 - c/2) J_1^{(p)}(\omega), \quad y^2 \gg 9(5 + c)/\bar{c}^3. \tag{4.15}
\]

Thus the three-particle corrections to the \( J^{(p)}(\omega) \), i.e. \( -c^2 J_1^{(p)}(\omega) \), are of the opposite sign to the two-particle terms, \( c J_1^{(p)}(\omega) \), and become larger in relative magnitude as \( c \) increases. According to the mean field theory, the magnitudes of the three-particle corrections to the \( J^{(p)}(\omega) \) in the low-temperature limit never exceed half of those of the two-particle terms.

If it is assumed that the mean frequency of attempted jumps by a single particle is independent of \( c \), then the concentration dependence of the quadrupolar spectral density functions (and hence the spin–lattice relaxation rates) at a fixed temperature in the large-\( y \) regime is given by

\[
J^{(p)}(\omega) \propto c(1 - c)(1 - c/2) \tag{4.16}
\]

which has a maximum at \( c = 0.4226 \). The corresponding relation for dipolar relaxation, \( J_{\text{dip}}^{(p)}(\omega) \propto c(1 - c) \), has a maximum at \( c = 0.5 \).

The important effect of spatial correlations on quadrupolar relaxation may be demonstrated by tracing the origin of the various terms contributing to the three-particle functions in equation (4.9). If all spatial correlations between the motions of particles were ignored, then one would obtain the result

\[
J_{\text{RW}}^{(p)}(\omega) = c(1 - c) J_1^{(p)}(\omega) \tag{4.17}
\]

where the \( J_{\text{RW}}^{(p)}(\omega) \) are the two-particle spectral density functions for quadrupolar relaxation according to the random walk model (Barton and Sholl 1976). It may also be seen that the function \( \Delta P_2(r_i, r_j, \omega) \) in equation (4.9) is entirely due to the effect of the particle initially at \( r_i \) on the probability of some other particle diffusing to \( r_j \) in a time \( t \),

\[\text{\footnote{Although the } J^{(p)}(\omega) \text{ and the spectral density functions which occur in the theory of dipolar relaxation both involve the same probability function } P_1(r_i, r_j, \omega), \text{ they are not identical in general.}}\]
and omission of the resulting corrections to the $f^{(p)}(\omega)$ given by equation (4.15) leaves the expression

$$c(1 - c)f^{(p)}(\omega).$$  \hspace{1cm} (4.18)

It may be shown that the form of the expressions in (4.17) and (4.18) is retained at all temperatures. Therefore, if $\nu(r) \propto r^{-1}$, these results both imply that, for a given value of $c$, the quadrupolar relaxation rates are proportional to the corresponding dipolar rates over the entire temperature range. On the other hand, as discussed in II, both the inclusion of the term $\Delta P_2(r, r, \omega)$ and the use of a screened potential for $\nu(r)$ in a conductor remove this proportionality between the quadrupolar and dipolar relaxation rates and produce a shift in the position of the quadrupolar $T_1$ minimum, relative to the position of the corresponding dipolar minimum, which increases with concentration.

5. Concluding remarks

The evaluation of the spectral density functions for quadrupolar relaxation due to the interactions between particles undergoing translational diffusion on cubic lattices is complicated by the inclusion of three-particle probability functions in the theory, especially when the jumping model adopted incorporates the effects of spatial correlations between the motions of particles. One of the difficulties encountered is that it is not possible within the mean field theory to obtain a complete solution for the probability function $P(q, q', \omega)$ in terms of known functions except in the low-temperature limit or when $c \to 0$.

By substituting the results (2.25) and (3.26) into equation (2.21), it is found that

$$f^{(p)}(\omega) = c(1 - c)f_1^{(p)}(\omega) + c^3\Delta f_2^{(p)}(\omega)$$  \hspace{1cm} (5.1)

where the $\Delta f_2^{(p)}(\omega)$ are the terms in the spectral density functions arising from $\Delta P_2(q, q', \omega)$. Within the mean field theory the $f_1^{(p)}(\omega)$ and $\Delta f_2^{(p)}(\omega)$ are independent of $c$ and, therefore, the three-particle terms (which are proportional to $c^2$) are negligible compared with the two-particle terms $c f_1^{(p)}(\omega)$ in the dilute limit ($c \to 0$) and become relatively more important as $c$ increases. Moreover, because the factor $c(1 - c)$ in equation (5.1) decreases for $c > 0.5$, the terms $c^2\Delta f_2^{(p)}(\omega)$ are more dominant in this concentration range.

The final term in equation (5.1) and the effects of any conduction-electron screening of the potential $\nu(r)$ prevent the quadrupolar relaxation rates from being proportional to the corresponding dipolar rates at a particular value of $c$. Unfortunately, however, this is the term which cannot be evaluated exactly except in the low-temperature limit. In II, methods of obtaining approximate numerical results for this term at arbitrary temperatures are considered and the predictions of the mean field theory are applied to the interpretation of spin–lattice relaxation rates which have been measured for deuterons in several transition metal deuterides.

Acknowledgments

I am indebted to Professor E F W Seymour for drawing my attention to the possibility of three-particle effects on quadrupolar relaxation in solids and wish to thank him for many valuable discussions and comments. I am also grateful to Professor C A Sholl for
some useful suggestions. This work was supported by a fellowship from the Science and Engineering Research Council and a NATO research grant.

Appendix

The spatial Fourier transform of quantities $Q_4(r_a, r_β; r_γ, r_δ)$ which depend on four lattice position vectors may be defined as

$$Q_4(q_a, q_β; q_γ, q_δ) = \sum_{α, β, γ, δ} Q_4(r_α, r_β; r_γ, r_δ) \exp(-i q_α \cdot r_α - i q_β \cdot r_β + i q_γ \cdot r_γ + i q_δ \cdot r_δ)$$

(A1)

where $q_a, q_β, q_γ$ and $q_δ$ are all wavevectors in the first Brillouin zone of the crystal lattice. When $Q_4(r_α, r_β; r_γ, r_δ)$ is summed over one or more of the position vectors, the Fourier transform is obtained by setting the corresponding wavevector(s) to zero. Thus

$$Q_3(q_a; q_β, q_δ) = Q_4(q_a, 0; q_β, q_δ)$$

(A2)

and

$$Q_2(q_a, q_δ) = Q_4(q_a, 0; 0, q_δ)$$

(A3)

With

$$Q_2(r_α, r_δ) = \sum_{β, γ} Q_4(r_α, r_β; r_γ, r_δ),$$

(A4)

equation (A3) is equivalent to the double spatial Fourier transform given by equation (2.19).

The inverse of the Fourier transform in equation (A1) is

$$Q_4(r_α, r_β; r_γ, r_δ) = N^{-d} \sum_{q_a, q_β, q_γ, q_δ} Q_4(q_a, q_β; q_γ, q_δ) \times \exp(i q_α \cdot r_α + i q_β \cdot r_β + i q_γ \cdot r_γ - i q_δ \cdot r_δ)$$

(A5)

where $N$ is the number of lattice points in the crystal. Similar inverse transforms corresponding to equations (A2) and (A3) may be obtained by summing both sides of equation (A5) over the appropriate position vector(s).

It is not necessary to transform all of the position vectors or wavevectors. For example, one can have

$$Q_3(q_a; r_γ, q_δ) = N^{-1} \sum_{q_γ} Q_3(q_a; q_γ, q_δ) \exp(-i q_γ \cdot r_γ)$$

(A6)

or, more particularly,

$$Q_3(q_a; 0, q_δ) = N^{-1} \sum_{q_γ} Q_3(q_a; q_γ, q_δ)$$

(A7)

where the parameter $0$ here denotes the origin in real space. Therefore, if $Q_3$ is the probability function $P_3$ defined in § 3, then $Q_3(q_a; 0, q_δ) = 0$ because the origin is always occupied by a particle other than the one denoted by the wavevector $q_γ$. 


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