SPIN RELAXATION OF IMPURITY NUCLEI

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Low temperature anomalies of the spin relaxation time of impurity nuclei due to the presence of quasilocal oscillations are investigated. The two-phonon (Raman) mechanism of quadrupole relaxation in nonconducting crystals is analyzed in detail.

RECENTLY, much attention has been given to the dynamics of impurity atoms in a crystalline lattice. Following the famous series of articles of I. Lifshitz, [1] which were the first to consider the problem of the oscillation of an isotope impurity, many theoretical and experimental papers have appeared, in which a wide range of phenomena sensitive to the special properties of the vibrational spectrum of the crystal impurities have been studied (see the review by Kagan[2].

In the present paper, the question of the anomalous temperature dependence of the spin-lattice relaxation of impurity nuclei in nonconducting crystals is considered. As is well known, spin-lattice relaxation of nuclei having $I > 1/2$ results from quadrupole interaction in the absence of conduction electrons and paramagnetic impurities. We examine here quadrupole relaxation of impurity nuclei; however, the qualitative results will be true generally for spins (in particular, electron spins) "attached" to impurity atoms.

The effecacy of spin-lattice relaxation is determined by the amplitudes of the impurity atom displacements relative to the adjacent atoms of the lattice; these can differ greatly from the amplitudes of the mutual displacements of the atoms in the regular crystal. Further, the temperature dependence of the relaxation rate of the impurity spins should deviate from the usual behavior.

One can expect pronounced anomalies in the temperature dependence of the spin-lattice relaxation time at low temperatures for heavy impurity nuclei, the dynamics of which can differ significantly from the dynamics of the atoms of the regular lattice in the low-frequency region. It is just this case which is investigated in detail below.

In a static lattice the interaction of the quadrupole moment of a nucleus with the intracrystalline field has the form

$$\mathcal{H}_Q^{(0)} = {}^1/_6 \sum_{\mu\nu} Q_{\mu\nu} V_{\mu\nu}^{(0)}, \tag{1}$$

where $Q_{\mu\nu}$ is the quadrupole moment tensor, and $V_{\mu\nu}^{(0)} = \partial^2 V/\partial x_\mu \partial x_\nu|_0$ (V is the electric potential).

Taking into account the lattice vibrations, the Hamiltonian of the quadrupole interaction is $\mathcal{H}_Q = \mathcal{H}_Q^{(0)} + \mathcal{H}_Q'$, where

$$\mathcal{H}_Q' = \mathcal{H}_Q^{(1)} + \mathcal{H}_Q^{(2)} + \ldots, \tag{2}$$

in which

$$\mathcal{H}_Q^{(1)} = \sum_n C_n^\alpha v_n^\alpha, \quad \mathcal{H}_Q^{(2)} = \sum_{nn'} C_{nn'}^{\alpha\beta} v_n^\alpha v_{n'}^\beta. \tag{3}$$

In Eq. (3), $v_n^\alpha = u_n^\alpha - u_0^\alpha$ designates the components of the displacement of the n-th atom of the lattice relative to the impurity atom, the equilibrium position of which is taken as the origin of coordinates (n = 0) (summation over twice repeated Greek superscripts is understood). The coefficients C_n^α and $C_{nn'}^{\alpha\beta}$ are given by

$$C_n^\alpha = {}^1/_6 \sum_{\mu\nu} Q_{\mu\nu} \frac{\partial V_{\mu\nu}}{\partial x_n^\alpha}\Big|_0,$$

$$C_{nn'}^{\alpha\beta} = {}^1/_{12} \sum_{\mu\nu} Q_{\mu\nu} \frac{\partial^2 V_{\mu\nu}}{\partial x_n^\alpha \partial x_{n'}^\beta}\Big|_0.$$

We are interested in the temperature dependence of the transition probability of the nuclear spin of the impurity atom (the transition $m \to m'$) under the influence of the perturbation $\mathcal{H}_Q'$.

To first order in the interaction $\mathcal{H}_Q^{(1)}$, the probability of a one-phonon process is given by the expression

$$W^{(1)}(m \to m') = -\frac{2}{1 - e^{-\omega_0/kT}} \sum_{nn'} (m'|C_n^\alpha|m)^* (m'|C_{n'}^\beta|m) \times \operatorname{Im} \mathcal{D}_{nn'}^{\alpha\beta}(\omega_0 + i\delta), \tag{4}$$

where ω_0 is the Zeeman frequency (for $m - m' = \pm 1$), and $\mathcal{D}_{nn'}^{\alpha\beta}(\omega)$ is the Fourier component of the one-phonon retarded Green function

$$\mathcal{D}_{nn'}^{\alpha\beta}(t) = -i\theta(t) \langle [v_n^\alpha(t);\ v_{n'}^\beta(0)] \rangle,$$

which is constructed from the relative displacement vectors.

To first order in $\mathcal{H}_Q^{(2)}$ the probability of a two-phonon process is given by[1)]

$$W^{(2)}(m \to m') = -\frac{2}{1 - e^{-\omega_0/kT}} \sum_{nn'} \sum_{pp'} (m'|C_{nn'}^{\alpha\beta}|m)^* \times (m'|C_{pp'}^{\gamma\delta}|m) \operatorname{Im} \mathcal{D}_{nn'pp'}^{\alpha\beta\gamma\delta}(\omega_0 + i\delta), \tag{5}$$

where $\mathcal{D}_{nn'pp'}^{\alpha\beta\gamma\delta}(\omega)$ is the Fourier component of the two-phonon Green function

$$\mathcal{D}_{nn'pp'}^{\alpha\beta\gamma\delta}(t) = -i\theta(t) \langle [v_n^\alpha(t) v_{n'}^\beta(t);\ v_p^\gamma(0) v_{p'}^\delta(0)] \rangle.$$

It is not difficult to show that in the harmonic approximation, to which we limit our considerations in the following,

$$\mathcal{D}_{nn'pp'}^{\alpha\beta\gamma\delta}(\omega) = -\frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{d\omega'}{1 - e^{-\omega'/kT}} \{ \mathcal{D}_{np}^{\alpha\gamma}(\omega - \omega') \operatorname{Im} \mathcal{D}_{n'p'}^{\beta\delta}(\omega' + i\delta) + \mathcal{D}_{n'p}^{\beta\gamma}(\omega - \omega') \operatorname{Im} \mathcal{D}_{np'}^{\alpha\delta}(\omega' + i\delta) + \mathcal{D}_{np'}^{\alpha\delta}(\omega + \omega') \operatorname{Im} \mathcal{D}_{pn'}^{\gamma\beta}(\omega' + i\delta) + \mathcal{D}_{n'p'}^{\beta\delta}(\omega + \omega') \operatorname{Im} \mathcal{D}_{pn}^{\gamma\alpha}(\omega' + i\delta) \}. \tag{6}$$

[1)] It is well known that the spin-flip probability calculated in second order in $\mathcal{H}_Q(^1)$ is negligibly small compared with $W(^2)$ $(m \to m')$.

In addition, using the symmetry properties of the coefficients $C^{\alpha\beta}_{nn'}$ and the functions $\mathcal{D}^{\alpha\beta}_{nn'}$, we find that

$$W^{(2)}(m\to m')=\frac{4}{\pi}\frac{1}{1-e^{-\omega_0/kT}}\sum_{nn'}\sum_{pp'}(m'|C^{\alpha\beta}_{nn'}|m)^*(m'|C^{\delta\nu}_{pp'}|m)$$
$$\times\int_{-\infty}^{+\infty}\frac{d\omega}{1-e^{-\omega/kT}}\operatorname{Im}[\mathcal{D}^{\alpha\gamma}_{np}(\omega_0-\omega)+\mathcal{D}^{\alpha\gamma}_{np}(\omega_0+\omega)]\operatorname{Im}\mathcal{D}^{\beta\delta}_{n'p'}(\omega).$$

Since $\operatorname{Im}\mathcal{D}^{\alpha\beta}_{nn'}(\omega)=-\pi G^{\alpha\beta}_{nn'}(\omega^2)$ sign ω, one can obtain the following expression for the probability of a Raman transition in the limit $\omega_0\to 0$ (after integration by parts):

$$W^{(2)}(m\to m')=\int_0^\infty d\omega\, n(\omega)\,(n(\omega)+1)F(\omega^2), \tag{7}$$

where

$$F(\omega^2)=8\pi\sum_{nn'}\sum_{pp'}(m'|C^{\alpha\beta}_{nn'}|m)^*(m'|C^{\gamma\delta}_{pp'}|m)G^{\alpha\gamma}_{np}(\omega^2)G^{\beta\delta}_{n'p'}(\omega^2),$$

and $n(\omega)$ is the Bose distribution.

We remark that, as follows directly from Eq. (4), the probability of a direct (one-phonon) transition can be written

$$W^{(1)}(m\to m')=f(\omega_0^2)\,(n(\omega_0)+1)\ \operatorname{sign}\omega_0\approx kTf(\omega_0^2)/|\omega_0|, \tag{8}$$

in which

$$f(\omega^2)=2\pi\sum_{nn'}(m'|C_n{}^{\alpha}|m)^*(m'|C_{n'}{}^{\beta}|m)G^{\alpha\beta}_{nn'}(\omega^2).$$

For the calculation of the spin-lattice relaxation, we still have to find the explicit form of the function $G^{\alpha\beta}_{nn'}(\omega^2)$. First we introduce the quantity $D^{\alpha\beta}_{nn'}(\omega)$, which is the Fourier component of the retarded Green function

$$D^{\alpha\beta}_{nn'}(t)=-i\theta(t)\langle[u_n{}^{\alpha}(t);\,u_{n'}{}^{\beta}(0)]\rangle,$$

constructed from the vector displacements of the lattice atoms from their equilibrium positions. Since we shall consider effects connected with the replacement of a regular atom oscillating in an acoustic branch by a heavy impurity atom, it is sufficient to examine a simple dynamic crystal model which does not include the optical oscillations. In the approximation in which we consider only the difference in mass of the impurity atom M′ and the replaced atom M, the equation for $D^{\alpha\beta}_{nn'}(\omega)$ is

$$D^{\alpha\beta}_{nn'}(\omega)=D^{0\alpha\beta}_{nn'}(\omega)+\varepsilon M\omega^2D^{0\alpha\gamma}_{n0}(\omega)D^{\gamma\beta}_{0n'}(\omega), \tag{9}$$

where $D^{0\alpha\beta}_{nn'}(\omega)$ is the Green function for the regular lattice, and the parameter ϵ is defined as $\epsilon=1-M'/M$.

For a crystal with cubic symmetry, $D^{0\alpha\beta}_{nn'}(\omega)=D_0(\omega)\delta_{\alpha\beta}$, and the solution to Eq. (9) is

$$D^{\alpha\beta}_{nn'}(\omega)=D^{0\alpha\beta}_{nn'}(\omega)+\varepsilon M\omega^2\mu(\omega)D^{0\alpha\gamma}_{n0}(\omega)D^{0\gamma\beta}_{0n'}(\omega), \tag{10}$$

$$\mu(\omega)=[1-\varepsilon M\omega^2D_0(\omega)]^{-1}.$$

Recalling now the definition of the function $\mathcal{D}^{\alpha\beta}_{nn'}(\omega)$, we obtain with the aid of Eq. (10),

$$\mathcal{D}^{\alpha\beta}_{nn'}=D^{0\alpha\beta}_{nn'}+\mu(\omega)\,(D^{\alpha\beta}_{00}-D^{0\alpha\beta}_{n0}-D^{0\alpha\beta}_{0n'}+\varepsilon M\omega^2D^{0\alpha\gamma}_{n0}D^{0\gamma\beta}_{0n'}). \tag{11}$$

In the following, we use the isotropic (Debye) model for the description of the regular lattice oscillations, for which

$$D^{0\alpha\beta}_{nn'}(\omega)=D^{0}_{nn'}(\omega)\delta_{\alpha\beta},$$
$$D^{0}_{nn'}(\omega)=\frac{1}{M}\int_0^{\omega_D{}^2}\frac{d\omega_1{}^2g(\omega_1{}^2)}{\omega^2-\omega_1{}^2}\frac{\sin\omega_1R_{nn'}/c}{\omega_1R_{nn'}/c}. \tag{12}$$

Here $g(\omega^2)$ is the spectral density distribution of the squared frequency for the ideal crystal, c is the velocity of sound, and $R_{nn'}=|\mathbf{R}_n-\mathbf{R}_{n'}|$.

Using Eqs. (11) and (12), we find after some simple manipulations that

$$G^{\alpha\beta}_{nn'}(\omega^2)\equiv-\frac{1}{\pi}\operatorname{Im}\mathcal{D}^{\alpha\beta}_{nn'}(\omega>0)=G_{nn'}(\omega^2)\delta_{\alpha\beta}, \tag{13}$$

where

$$G_{nn'}(\omega^2)=\frac{g(\omega^2)}{M}\Big\{[f_{nn'}(\omega^2)-f_{n0}(\omega^2)f_{0n'}(\omega^2)]+$$
$$+\frac{[1-f_{n0}+\varepsilon\omega^2(J_{00}f_{n0}-J_{n0})][1-f_{0n'}+\varepsilon\omega^2(J_{00}f_{0n'}-J_{0n'})]}{[1-\varepsilon\omega^2J_{00}(\omega^2)]^2+[\pi\varepsilon\omega^2g(\omega^2)]^2}\Big\},$$

and

$$f_{nn'}(\omega^2)=\frac{\sin\omega R_{nn'}/c}{\omega R_{nn'}/c},\qquad J_{nn'}(\omega^2)=\int_0^{\omega_D{}^2}\frac{d\omega_1{}^2g(\omega_1{}^2)}{\omega^2-\omega_1{}^2}f_{nn'}(\omega_1{}^2).$$

To simplify the subsequent calculations, we limit our considerations to the point-ion model of Van Kranendonk,[3] which has been studied in detail for the case of quadrupole relaxation of nuclear spins in a regular lattice. In this model, $C^{\alpha\beta}_{nn'}=C^{\alpha\beta}_{nn}\delta_{nn'}$. Taking into account the nearest neighbors of the impurity ion, one can write the Raman transition probability as

$$W^{(2)}(m\to m')=\frac{18\pi}{M^2\omega_D{}^3}\sum_{nn'}(m'|C^{\alpha\beta}_{nn}|m)^*(m'|C^{\alpha\beta}_{n'n'}|m)L_{nn'}(T/\Theta,\varepsilon), \tag{14}$$

where Θ is the Debye temperature, and

$$L_{nn'}(\tau,\varepsilon)=\int_0^1\frac{dx\,x^2e^{x/\tau}}{(e^{x/\tau}-1)^2}\Big\{\Big[\varphi\Big(2x\sin\frac{\vartheta_{nn'}}{2}\Big)-\varphi^2(x)\Big]$$
$$+[1-\varphi(x)+3\varepsilon x^2\Phi(x)]^2\Big/\Big(\Big[1+3\varepsilon x^2\Big(1-\frac{x}{2}\ln\frac{1+x}{1-x}\Big)\Big]^2+\Big[\frac{3\pi}{2}\varepsilon x^3\Big]^2\Big)\Big\}^2,$$

where

$$\varphi(x)=\sin\alpha x/\alpha x,\qquad \alpha=\omega_Dl_1/c,$$
$$\Phi(x)=\int_0^1\frac{dy\,y^2}{x^2-y^2}\Big(\frac{\sin\alpha x}{\alpha x}-\frac{\sin\alpha y}{\alpha y}\Big).$$

For an ideal lattice ($\epsilon=0$)

$$L_{nn'}(\tau,0)=\int_0^1\frac{dx\,x^2e^{x/\tau}}{(e^{x/\tau}-1)^2}[\varphi(2x\sin\vartheta_{nn'}/2)-2\varphi(x)+1]^2 \tag{15}$$

at low temperature ($T\ll\Theta$) it is not difficult to see that $L_{nn'}(T/\Theta,0)\sim(T/\Theta)^7$. This gives the well known result that the spin-lattice relaxation time of the nuclei in a regular crystal is proportional to $(T/\Theta)^{-7}$ in the low temperature region (with the exception of very low temperatures, where the one-phonon mechanism is important).

For the relaxation of an impurity spin, this result can change significantly. As is well known,[2] for a sufficiently heavy impurity ($|\epsilon|\ll 1$), the equation

$$\varepsilon\omega^2J_{00}(\omega^2)=1$$

has the solution $\omega=\omega^*$ in the frequency range where the spectral density $g(\omega^2)$ of the regular crystal is small. For frequencies $\omega\sim\omega^*$, the character of the oscillations of the impurity atom and its neighbors is significantly different from the dynamics of the atoms of the ideal lattice.

For very low temperatures, this circumstance has little significance for the spin-lattice relaxation of impurity nuclei; however, with increase in temperature, the role of the quasi-localized oscillations will increase, and the temperature dependence of the spin-lattice re-

laxation time can be altered substantially (in comparison with the temperature dependence characteristic of the ideal lattice). We note in connection with this that the low temperature heat capacity and electric conductivity anomalies, resulting from quasi-localized oscillations in crystals having impurities, were discussed in papers of Kagan and his collaborators.[4,5] We investigate below the anomalies in the temperature dependence of the quadrupolar nuclear spin relaxation of heavy impurity atoms; as already remarked, the qualitative results apply as well to electron spin relaxation.

The distinctive features of the spin-lattice relaxation of impurity electron centers has been investigated in a recent paper by Mills.[6] In that paper, the peculiarities in the vibrational spectrum of an impurity atom were calculated; however, the amplitudes of the relative displacements of the neighboring atoms were considered in a macroscopic approximation, suitable for a description of the deformation of the regular lattice by long wavelength acoustic oscillations. We give below the results of a completely microscopic calculation of the nuclear spin-lattice relaxation time, which, within the framework of the isotopic model, reproduces all the characteristics of the local deformations of the lattice in the neighborhood of the impurity atom. One should keep in mind that for ionic crystals, the neglect of the change in force constants can in some cases be too crude an approximation, in which case the parameter ϵ, characterizing the impurity "defect," can be understood as some phenomenological parameter fixing the true value of the quasilocal frequency.

In the notation of[3] the coefficients $C_{nn'}^{\alpha\beta}$, are given by $C_{nn'}^{\alpha\beta} = \Sigma_\mu Q_\mu A_{\mu;nn'}^{\alpha\beta}$, ($\mu = 0, \pm 1, \pm 2$), and Eq. (14) for the transition probability $m \to m + \mu$ takes the form

$$W^{(2)}(m \to m+\mu) \equiv W_{\mu m}^{(2)} = \frac{18\pi}{M^2\omega_D{}^3} |Q_{\mu m}|^2 F_\mu(T/\Theta, \varepsilon), \tag{16}$$

where

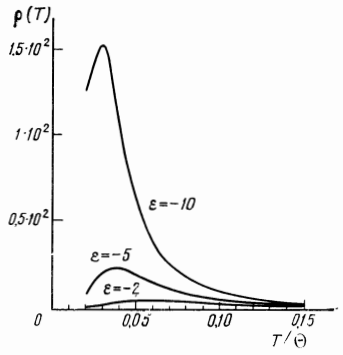
$$F_\mu(\tau, \varepsilon) = \sum_{nn'} N_{\mu;nn'} L_{nn'}(\tau, \varepsilon), \qquad N_{\mu;nn'} = \mathrm{Sp}\{A_{\mu;nn}^{+} A_{\mu;n'n}\}.$$

Following Hebel and Slichter,[7] one can introduce a single spin-lattice relaxation time T_1 by the formula

$$1/T_1 = {}^1/_2 \left[\sum_{\mu m} \mu^2 W_{\mu m}^{(2)}\right]\left[\sum_m m^2\right]^{-1} = C(I)[F_1(T/\Theta, \varepsilon) + 4F_2(T/\Theta, \varepsilon)], \tag{17}$$

where the function C(I), whose explicit form is not important in the following, describes the dependence of the relaxation upon the magnitude of the spin.

In the figure we show the calculated temperature dependence of the quantity $\rho(T) = (1/T_1)/(1/T_1)_0$, where $(1/T_1)_0$ corresponds to the value calculated assuming no impurities (i.e., $\epsilon = 0$). Curves are given for different values of ϵ. For a very heavy impurity ($\epsilon = -10$, $\omega^*/\omega_D \approx 0.18$) the quantity $\rho(T)$ has a sharp maximum in the low temperature region; here, at $T/\Theta \approx 0.03$, the spin-lattice relaxation rate is two orders of magnitude larger than the corresponding quantity calculated for $\epsilon = 0$. As $|\epsilon|$ decreases, the maximum decreases and is displaced toward higher temperatures. The calculations have not been carried out at very low temperatures; however, it is easy to show that $\rho \to 1$ as $T \to 0$.



These results are related to two-phonon (Raman) relaxation. The direct (one-phonon) process for nuclear spin-lattice relaxation, the probability of which is given by Eq. (8), is unimportant because ω_0 is in the radio-frequency region and is always much smaller than ω^*. However, in the electron spin relaxation of the impurity centers, it is possible to achieve the condition $\omega_0 \sim \omega^*$, and in this region one should observe an anomalous dependence of the spin-lattice relaxation rate upon the magnitude of an external magnetic field. This is entirely realizeable because in a number of cases, a very low-lying quasilocal impurity level is observed (apparently in consequence of a significant reduction in force constant).

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