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INERTIAL QUADRUPOLE SPIN-LATTICE RELAXATION AND ACOUSTIC MAGNETIC RESONANCE

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Resonance absorption of energy of external sound generators caused by interaction between the inertial quadrupole moments of the impurities and the field gradient of the accelerations produced by the sound wave (AQ interaction) is considered. It is shown that the contribution of AQ interactions in a one-quantum excitation regime can be detected against the absorption background due to ordinary spin-phonon (SL) interaction. Under two-quantum excitation conditions and when hypersound generators are used, the AQ interaction contribution may be comparable with or even exceed absorption due to SL interaction.

A theory of direct and Raman relaxation processes is developed, with both SL and Aq interactions are taken into account. In the direct processes, relaxation of AQ interaction (inertial relaxation) contributes appreciably only at high frequencies ω ($\omega \gg 10^{11}$ rad/sec). On the other hand in Raman relaxation processes of the electron and nuclear magnetic systems the AQ interaction contribution is comparable with and in many cases greater than the contribution made to the relaxation rate by the ordinary SL interactions. It is shown that if AQ interactions are taken into account the inverse relaxation time for the Raman processes in many cases is a polynomial of the (13–15)-th power of the absolute temperature (the first nonvanishing terms are proportional to the (5–7)-th power, depending on the temperature range investigated and on the parameters of the system).

IN a coordinate system moving with an accelerated particle, the latter is acted upon by inertial forces capable of changing the state of this particle (nucleus, atom, molecule, etc.). Assume that such a particle does not have a spherically symmetrical distribution of the inertial mass m_i, and has a number of discrete or continuous energy levels. Then the interaction of the inertial-mass quadrupole moment of this particle with the gradient of the acceleration field (the AQ interaction) can lead to absorption or emission of the energy of this field by the particle. If the particle levels are discrete, and the acceleration varies harmonically, then effects of resonant absorption at emission of the acceleration-field energy quanta are possible.

Such a situation arises when a harmonic sound wave propagates in a medium containing atomic nuclei and magnetic ions with spin $S > 1/2$, or ions with electric dipole moments, etc. When the sound wave propagates, these particles experience alternating accelerations that vary with the circular speed of sound ω. If the inertial mass quadrupole moment of such a particle differs from zero and the energy of the acoustic quantum $h\omega$ coincides with the splitting energy between any two levels 1 and 2 of this particle in external and internal fields, then the interaction between the inertial quadrupole moment of the particle and the gradient of the acceleration field, due to the elastic wave, will cause them to absorb energy from the sound generator. Such a phenomenon can be called acoustic inertial quadrupole resonance (AIQR). The transition of the particles from the excited state to the ground state by means of AQ interaction of impurities with the gradient of the acceleration field from the thermal vibrations of the crystal can naturally be called inertial quadrupole spin-lattice relaxation. As will be shown below, allowance for this relaxation is particularly important in the case of large splittings and in processes of relaxation in which two or more phonons take part. AIQR can in principle be observed in any quantum object where the AQ interaction is not too small. Thus, for example, it is possible to excite with the aid of AQ interaction resonances of the type of ferromagnetic, paraelectric, cyclotron, nuclear, magnetic, ferromagnetic, antiferromagnetic, ferroelectric, antiferroelectric, etc. On the basis of the theorem concerning the connection between the resonant and superradiant responses[1,2], superradiant analogs of all types of AIQR can be observed, including phenomena of the spin-echo type.

1. HAMILTONIAN OF AQ INTERACTION

To obtain the operator $\mathcal{H}^j_{AQ}$ of the AQ interaction between the gradient of the acceleration field and an inertial massive quadrupole moment of a particle j, we can follow the derivation of the operator $\mathcal{H}^j_{EQ}$ of the interaction between the gradient of an electric field and the electric quadrupole moment[3] (Sec. 74). Assuming that the laws governing the distribution of the charge in a particle having electric quadrupole moment and a mass having a carrier of this charge are identical, we obtain immediately the form of the operator of the inertial mass quadrupole operator by replacing the charge by the inertial mass in the operator of the electric quadrupole moment of the atoms and ions. We shall apply this reasoning to obtain the operator $\mathcal{H}^j_{AQ}$.

Let us examine a system of N identical particles (j, k = 1, 2, ..., N) having a spin $S > 1/2$, an electric quadrupole moment eQ_e (see (74.1) of[3]) an inertial-mass quadrupole moment m_iQ_i, where e is the electron charge. Let for simplicity these particles occupy in the substance positions (sites) at which the point symmetry of the internal field is axial (the axis is along the unit vector z_0) or spherical in the absence of a static magnetic field H_0z_0. The unperturbed Hamiltonian of this system is

$$\mathscr{H}_0 = \sum \mathscr{H}_{0j}, \quad \mathscr{H}_{0j} = g_z\beta H_0 S_z{}^j + D[S_z{}^2 - {}^1/_3 S_j(S_j+1)], \tag{1}$$

where β is the Bohr magneton or the nuclear magneton, g_Z is the factor of spectroscopic splitting along the direction z_0, S_α (α = x, y, z) are the components of the effective spin of the particle j, and D is the constant of the axial crystal field. In the case of nuclei with $eQ_e \neq 0$, the constant D describes the interaction of the gradient of the electric field with eQ_e[4].

Assume that a traveling acoustic wave with wave vector k and circular frequency ω produces periodic displacements of the particles at the point r^j, of the quantity

$$x(t) = \frac{e_{\gamma\zeta}v}{\omega}\cos(\omega t - kr^j) = \frac{v}{\omega}u_{\gamma\zeta}, \tag{2}$$

where $\epsilon_{\gamma\zeta}$ is the amplitude of the component of the relative deformation tensor, and v is the speed of sound. According to the foregoing, the AQ interaction is given by

$$\mathscr{H}^j_{\mathrm{AQ}} = \sum_{m=2}^{-2} A^m_{2j}B^{m*}_2, \quad A^0_{2j} = \frac{1}{2}\alpha_i\,[3S^{j2}_Z - S_j(S_j+1)], \tag{3}$$

$$A_{2j}{}^{\pm1} = \alpha_i\frac{\sqrt{6}}{4}[S_z{}^jS_\pm{}^j + S_\pm{}^jS_z{}^j], \quad A_{2j}{}^{\pm2} = \alpha_i\frac{\sqrt{6}}{4}S_\pm{}^{j2},$$

$$B_2{}^0 = \frac{1}{2}a_{zz}, \quad B_2{}^{\pm1} = \frac{1}{\sqrt{6}}(a_{xz} \pm ia_{yz}), \tag{4}$$

$$B_2{}^{\pm2} = \frac{1}{2\sqrt{6}}(a_{xx} - a_{yy} \pm 2ia_{xy}),$$

$$a_{\gamma\zeta} = \varepsilon_{\gamma\zeta}\omega^2\cos(\omega t - kr^j).$$

$$\alpha_i = m_iQ_i[S_j(2S_j-1)]^{-1}, \quad S_\pm{}^j = S_x{}^j \pm iS_y{}^j.$$

It is curious that the Hamiltonian $\mathcal{H}^j_{\mathrm{AQ}}$ can be obtained from the operator of the interaction between the gradient of the gravitational field and the gravitational mass quadrupole moment[5] by using the Einstein equivalence principle[6]. According to this principle, we can replace the gradient of the gravitational field by the gradient of the acceleration field, and the gravitational quadrupole moment by the inertial one.

Besides the acceleration field, an impurity in a solid or a liquid is acted upon also by the usual spin-phonon (SL) interaction, due to the presence of internal local magnetic and electric fields and their gradients. The Hamiltonian of the SL interaction for a spin $S > 1/2$ is usually written in the form[4,7]

$$\mathscr{H}_{SL} = \sum_{\substack{\alpha\beta\\ \gamma\xi}}[G_{\alpha\beta\gamma\xi}S_\alpha S_\beta + F_{\alpha\beta\gamma\xi}H_{0\alpha}S_\beta]\,u_{\gamma\xi}; \quad \alpha, \beta, \gamma, \xi = x, y, z; \tag{5}$$

where $G_{\alpha\beta\gamma\xi}$ and $F_{\alpha\beta\gamma\xi}$ are the components of the tensors of the SL interaction, which do not depend on the frequency of the phonons ω or on the components of the constant external magnetic field $H_{0\alpha}$. As follows from (4), the AQ interaction can also be treated as a unique spin-phonon interaction proportional to the square of the frequency ω^2 and containing terms both linear and quadratic in the spin components.

The SL and the AQ interactions act on the impurities simultaneously. Both are proportional to $u_{\gamma\xi}$. Therefore the total Hamiltonian of the interaction between the impurities and the phonon field can be written in the form (the z axis is taken to be the quantization axis)

$$\mathscr{H}_{\mathrm{sph}} = \sum_{\alpha\beta\gamma\xi}[Q_{\alpha\beta\gamma\xi}S_\alpha S_\beta + F_{\alpha\beta\gamma\xi}H_{0\alpha}S_\beta]\,u_{\gamma\xi}, \tag{6}$$

where, according to (4) and (5), Q is the tensor of the spin-phonon interaction and is expressed in the following manner in terms of the G-tensor and the parameters of the AQ interaction (G_i tensor):

$$Q_{\alpha\beta\gamma\xi} = G_{\alpha\beta\gamma\xi} + \omega^2(G_i)_{\alpha\beta\gamma\xi}, \tag{7}$$

where the components of the G_i tensor in the Voigt notation are given by

$$(G_i)_{33} = -2(G_i)_{13} = -2(G_i)_{23} = \frac{\alpha_i}{2},$$

$$(G_i)_{66} = -2(G_i)_{22} = -2(G_i)_{11} = 2(G_i)_{12} = -\frac{\alpha_i}{2}$$

$$(G_i)_{55} = -(G_i)_{44} = \frac{\alpha_i}{2}.$$

The remaining components of the G_i tensor are equal to zero.

According to (6) and (7), the most general form of $\mathcal{H}_{\mathrm{sph}}$ is

$$\mathscr{H}_{\mathrm{sph}} = \sum[\mathscr{H}^{(\gamma\zeta)}_{SL} + \omega^2\mathscr{H}^{(\gamma\zeta)}_{\mathrm{AQ}}] = \mathscr{H}_{SL} + \omega^2\mathscr{H}^{(1)}_{\mathrm{AQ}}. \tag{8}$$

At the present time, three methods are used in the measurements of the tensors of the spin-phonon interaction: a) the method of static deformation[8,9]; b) the method of acoustic nuclear and electron magnetic resonances[8-11]; c) measurement of the spin-lattice relaxation time.

In method a), as follows from (7), only the components of the G tensor of the SL interaction are measured ($\omega = 0$). On the other hand, when method b) is used, one measures the components of the Q tensor to which contributions are made both by the SL and the AQ interactions. Depending on the signs of the G and G_i tensors, the components of the spin-phonon interaction tensor, measured in accordance with a), can be either larger or smaller in absolute magnitude than the components measured by method b).

Thus, by measuring the components of the spin-phonon interaction tensor by methods a) and b) and determining their difference, we are able to determine by the same token the components of the tensor of the inertial quadrupole moment. Obviously, the values of the G and G_i tensors can be measured by using only method c), by measuring the values of Q at two different frequencies $\omega = \omega_1$ and $\omega = \omega_2$ and solving the corresponding system of the equations from (7). An analysis of the available experimental results[8-11] shows that, as a rule, the constants of the spin-phonon interaction obtained by methods a) and b) differ little from each other. For example, for Mn^{2+} and MgO the components of the G tensor (in the Voigt notation) obtained under static deformations are $G_{11} = 1.3\ \mathrm{cm}^{-1}$/deformation unit and

$|G_{44}| = 0.28\ \text{cm}^{-1}$/deformation unit, whereas those obtained at $\omega = 6.28 \times 10^{10}$ rad/sec are $G_{11} = 1.4\ \text{cm}^{-1}$/deformation unit and $G_{44} = 0.28\ \text{cm}^{-1}$/deformation unit. If these differences are attributed to G_i, then we get $m_iQ_i \lesssim (10^{-39}-10^{-40})$ g-cm². This value is close in order of magnitude to the possible value of the inertial quadrupole moment of the Mn^{2+} ion. There is no doubt that the presented estimate is only tentative and indicates more readily that the inertial quadrupole moments of the impurities can be measured at the contemporary level of the experimental technique, rather than yield its numerical value. Since an increase of the acoustic-generator frequency by one order of magnitude increases the fraction of the absorption due to the AQ interaction by four orders, the progress in experiments with respect to the measurements of m_iQ_i is directly dependent on the progress in the development of hyper- and terasonic spectroscopy.

In the case of nuclei, where the measured spin-phonon interaction constants G lie in the interval $(10^{-19}-10^{-25})$ erg/deformation unit, and $\omega^2 m_iQ_i \sim \omega^2(10^{-44}-10^{-47})$ erg/deformation unit, measurement of m_iQ_i by methods a) and b) is possible if very strong magnetic fields and substances with small internal local fields (such as molecular crystals) are used.

2. ACOUSTIC INERTIAL QUADRUPOLE RESONANCE

A. Single-quantum Resonance

The sound attenuation $\sigma^{(1)}(\omega)$ due to resonant absorption of energy by impurity centers from an external acoustic generator of frequency $\omega = \hbar^{-1}(E_2 - E_1)$, due to the SL and AQ interactions, is described according to (8) by the formula

$$\begin{gathered}\sigma^{(1)}(\omega) = \sigma_{SL}(\omega) + \sigma_{AQ}(\omega),\\ \sigma_{SL}(\omega) = (\rho v^2\hbar)^{-1}\pi\Delta n\omega g(\omega)\,|\langle 2|\mathscr{H}_{SL}^{\gamma_0\xi_0}|1\rangle|^2 = A(\omega)\,|\langle 2|\mathscr{H}_{SL}^{\gamma_0\xi_0}|1\rangle|^2,\\ \sigma_{AQ}(\omega) = \omega^4 A(\omega)\,|\langle 2|\mathscr{H}_{AQ}^{\gamma_0\xi_0}|1\rangle|^2 = \omega^9 A(\omega)\,\sigma_{AQ}^{(1)}(\omega),\end{gathered} \tag{9}$$

where Δn is the population difference between the levels $|1\rangle$ and $|2\rangle$ is a unit volume, ρ is the crystal density, and $g(\omega)$ is the form factor of the line. According to (9), measurement of the absorption coefficient $\sigma^1(\omega)$ at two different frequencies of the external acoustic generator makes it possible to determine the values of m_iQ_i directly from $\sigma^{(1)}$. The higher the frequencies of the acoustic generators ω_1 and ω_2, the more effective this method. Since $\sigma_{AQ}^{(1)}(\omega) \ll \sigma_{SL}^{(1)}(\omega)$, we get

$$\frac{\sigma^{(1)}(\omega_1)}{\sigma^{(1)}(\omega_2)} = 1 + \omega_1{}^4\frac{\sigma_{AQ}^{(1)}(\omega_1)}{\sigma_{SL}^{(1)}(\omega_1)} - \omega_2{}^4\frac{\sigma_{AQ}^{(1)}(\omega_2)}{\sigma_{SL}^{(1)}(\omega_2)} = 1 + \omega_1{}^4\frac{|\langle 2|\mathscr{H}_{AQ}^{\gamma_1\xi_1}|1\rangle|^2}{|\langle 2|\mathscr{H}_{SL}^{\gamma_1\xi_1}|1\rangle|^2} - \omega_2{}^4\frac{|\langle 2|\mathscr{H}_{AQ}^{\gamma_2\xi_2}|1\rangle|^2}{|\langle 2|\mathscr{H}_{SL}^{\gamma_2\xi_2}|1\rangle|^2}.$$

If the substance is excited in such a way that only one of the components of the G or G_i tensors differs from zero each time, then, since

$$|\langle 2|\mathscr{H}_{SL}^{\gamma_i\xi_i}|1\rangle| \sim \mathscr{G}_i, \quad |\langle 2|\mathscr{H}_{AQ}^{\gamma_i\xi_i}|1\rangle| \sim \mathscr{G}_{ii}, \tag{10a}$$

it follows that

$$\sigma^{(1)}(\omega_1)\,/\,\sigma^{(1)}(\omega_2) = 1 + \omega_1{}^4 C_{i1}{}^2 - \omega_2{}^4 C_{i2}{}^4,\ C_{ii} = \mathscr{G}_{ii}\,/\,\mathscr{G}_i.$$

B. Two-quantum Resonance

The specific dependence of the AQ interaction on the frequency suggests the use of two-quantum resonances in order to enhance the effective absorption, due to this interaction, of the energy of the elastic oscillations by the nuclei and the ions. It is easy to see that in this respect, a promising process is one in which an acoustic quantum $\hbar\omega_1$ is absorbed, and a quantum $h\omega_2$ is emitted ($\hbar\omega_1 - \hbar\omega_2 = E_2 - E_1$).

The total Hamiltonian of the spin-phonon interaction is written in this case, in accordance with (8), in the form

$$\begin{aligned}\mathscr{H}' = {}&\mathscr{H}_{SL}^{\gamma_1\zeta_1} u^0_{\gamma_1\zeta_1}\cos(\omega_1 t - k_1 r^j) + \mathscr{H}_{SL}^{\gamma_2\zeta_2} u^0_{\gamma_2\zeta_2}\cos(\omega_2 t - k_2 r^j)\\ &+ \omega_1{}^2\mathscr{H}_{AQ}^{\gamma_1\zeta_1} u^0_{\gamma_1\zeta_1}\cos(\omega_1 t - k_1 r^j) + \omega_2{}^2\mathscr{H}_{AQ}^{\gamma_2\zeta_2}\cos(\omega_2 t - k_2 r^j),\end{aligned} \tag{11}$$

The probability per unit time of the transition induced by $\mathcal{H}'$ in the impurity particle from the state $|1\rangle$ into the state $|2\rangle$ is given by

$$\begin{aligned}W_{12}^{(2)} &= \frac{2\pi}{\hbar^2}|Y_{12}|^2 g'(\omega),\\ Y_{12} = \sum_p u^0_{\gamma_1\zeta_1}u^0_{\gamma_2\zeta_2}\cdot\Bigg[&\frac{\langle 2|\mathscr{H}_{SL}^{\gamma_1\zeta_1}|p\rangle\langle p|\mathscr{H}_{SL}^{\gamma_2\zeta_2}|1\rangle}{E_p + \hbar\omega_2 + i\Gamma_p/2} + \frac{\langle 2|\mathscr{H}_{SL}^{\gamma_2\zeta_2}|p\rangle\langle p|\mathscr{H}_{SL}^{\gamma_1\zeta_1}|1\rangle}{E_p - \hbar\omega_1 + i\,\Gamma_p/2}\\ &+ \omega_1{}^2\left[\frac{\langle 2|\mathscr{H}_{SL}^{\gamma_2\zeta_2}|p\rangle\langle p|\mathscr{H}_{AQ}^{\gamma_1\zeta_1}|1\rangle}{E_p - \hbar\omega_1 + i\Gamma_p/2} + \frac{\langle 2|\mathscr{H}_{AQ}^{\gamma_1\zeta_1}|p\rangle\langle p|\mathscr{H}_{SL}^{\gamma_2\zeta_2}|1\rangle}{E_p + \hbar\omega_2 + i\Gamma_p/2}\right]\\ &+ \omega_2{}^2\left[\frac{\langle 2|\mathscr{H}_{AQ}^{\gamma_2\zeta_2}|p\rangle\langle p|\mathscr{H}_{SL}^{\gamma_1\zeta_1}|1\rangle}{E_p - \hbar\omega_1 + i\Gamma_p/2} + \frac{\langle 2|\mathscr{H}_{SL}^{\gamma_1\zeta_1}|p\rangle\langle p|\mathscr{H}_{AQ}^{\gamma_2\zeta_2}|1\rangle}{E_p + \hbar\omega_2 + i\Gamma_p/2}\right]\\ &+ \omega_1{}^2\omega_2{}^2\left[\frac{\langle 2|\mathscr{H}_{AQ}^{\gamma_2\zeta_2}|p\rangle\langle p|\mathscr{H}_{AQ}^{\gamma_1\zeta_1}|1\rangle}{E_p - \hbar\omega_1 + i\Gamma_p/2} + \frac{\langle 2|\mathscr{H}_{AQ}^{\gamma_1\zeta_1}|p\rangle\langle p|\mathscr{H}_{AQ}^{\gamma_2\zeta_2}|1\rangle}{E_p + \hbar\omega_2 + i\Gamma_p/2}\right]\Bigg],\end{aligned} \tag{12}$$

where $g'(\omega)$ is the form factor of the line of the transition $|1\rangle \to |2\rangle$. E_p is the energy of the intermediate state and Γ_p is the width of the level E_p. For the analysis of (12), we assume that

$$\mathscr{G} \sim \langle 2|\mathscr{H}_{SL}^{\gamma_i\zeta_i}|p\rangle \sim \langle p|\mathscr{H}_{SL}^{\gamma_i\zeta_i}|1\rangle,\ \langle 2|\mathscr{H}_{AQ}^{\gamma_i\zeta_i}|p\rangle \sim \langle p|\mathscr{H}_{AQ}^{\gamma_i\zeta_i}|1\rangle \sim \mathscr{G}_i,$$
$$\omega \sim \omega_1 \sim \omega_2,$$

G and G_i will henceforth be called respectively the constants of the SL and AQ interactions. The terms in the square brackets will be denoted for convenience by G_{12}^S ($s = 1, 2, 3, 4$):

$$\begin{gathered}Y_{12}{}^1 \sim qG^2, \quad Y_{12}{}^2 \sim q\omega_1{}^2 GG_i, \quad Y_{12}{}^3 \sim q\omega_2{}^2 GG_i,\\ Y_{12} \sim qG_i{}^2\omega_1{}^2\omega_2{}^2,\ \ q = \left[\left(E_p - h\omega_1 + \frac{i}{2}\Gamma_p\right)^{-1} + \left(E_p + h\omega_2 + \frac{i}{2}\Gamma_p\right)^{-1}\right],\\ (Y_{12}{}^2/Y_{12}{}^1) \sim (Y_{12}{}^3/Y_{12}{}^1) \sim (G_i/G)\omega = C_i\omega^2,\\ (Y_{12}{}^4/Y_{12}{}^1) \sim (G_i/G)^2\omega_1{}^2\omega_2{}^2 \sim C_i{}^2\omega^4.\end{gathered} \tag{13}$$

Since the coefficient $\sigma^{(2)}$ for the attenuation of the sound at the frequency ω_1 (and for the growth of the sound at the frequency ω_2) is proportional to the square of the modulus of Y_{12}, we get

$$\begin{gathered}\sigma^{(2)} = \sigma_{11}^{(2)} + \sigma_{22}^{(2)} + \sigma_{33}^{(2)} + \sigma_{44}^{(2)} + 2\sigma_{12}^{(2)} + 2\sigma_{13}^{(2)} + 2\sigma_{14}^{(2)} + \sigma_{23}^{(2)} + \sigma_{24}^{(2)} + \sigma_{34}^{(2)},\\ \sigma_{ij}^{(2)} \sim \mathrm{Re}(Y_{12}{}^i)(Y_{12}{}^j)^*\end{gathered} \tag{14}$$

Let us examine the ratios

$$\begin{gathered}q_{22} \sim q_{33} \sim C_i{}^2\omega^4, \quad q_{44} \sim C_i{}^4\omega^8, \quad q_{12} \approx C_i\omega^2 \sim q_{13},\\ q_{14} \sim C_i{}^2\omega^4, \quad q_{23} \sim C_i{}^2\omega^4, \quad q_{24} \sim C_i{}^3\omega^6 \sim q_{34}.\end{gathered} \tag{15}$$

For paramagnetic ions in ionic crystals $G \sim (10^{-13}-10^{-18})$ erg/deformation unit, $G_i \sim 10^{-43}$ g-cm²/deformation unit, and $C_i = (G_i/G) \sim (10^{-30}-10^{-25})$ g-cm²-erg⁻¹. Consequently, to obtain q_{ij} on the order of unity it is necessary to have values $\omega \sim \omega_1 \sim \omega_2 \geq 10^{12}-10^{13}\ \text{sec}^{-1}$. At the present time hypersound with circular frequency $\omega = 2\pi \times 10^{10}\ \text{sec}^{-1}$ has already been generated[12], i.e., the measurement of the inertial quadrupole moments of a number of impurity centers becomes experimentally feasible. An increase of ω and the use of samples with small values of SL interaction constants (for example, molecular crystals), will greatly extend the range of investigated ions. As already mentioned, for nuclear particles $G_i \sim (10^{-47}-10^{-44})$ g-cm^2/deformation unit, $G \sim (10^{-19}-10^{-24})$ erg/deformation unit, and $C_i \sim 10^{-28}-10^{-20}$ g-cm^2-erg^{-1}.

Thus, in the case of nuclear quadrupoles, $q_{ij} \geq 1$ can be reached already at $\omega = 10^{10}-10^{11}$ sec^{-1}, i.e., in the well accessible range of hypersonic frequencies[11,12]. For the vibrational levels of the molecules $G_i \sim (10^{-40}-10^{-40})$ g-cm^2/deformation unit, i.e., they are likewise presently promising objects with respect to the measurement of G_i. However, in practically all cases, at reasonable values of ω and C_i, we can neglect in (14), as follows from (15), all terms with the exception of $\sigma_{12}^{(2)}$, $\sigma_{11}^{(2)}$, and $\sigma_{13}^{(2)}$.

Consequently

$$\sigma^{(2)} \approx \sigma_{11}^{(2)}(1 + 2q_{12} + 2q_{13}). \tag{16}$$

Since we can always assume that $\Gamma_p \ll h\omega_2$, $E_p - h\omega_1$, it follows that ($E_p = \hbar\omega_p$):

$$\begin{aligned} q_{12} = \omega_1^2 \operatorname{Re} [(\omega_p + \omega_2) \langle 2 | \mathcal{H}_{SL}^{\gamma_2\zeta_2} | p\rangle\langle p | \mathcal{H}_{AQ}^{\gamma_1\zeta} | 1\rangle \\ + (\omega_p - \omega_1) \langle 2 | \mathcal{H}_{AQ}^{\gamma_1\zeta_1} | p\rangle\langle p | \mathcal{H}_{SL}^{\gamma_2\zeta_2} | 1\rangle] \, p_0^{-1}, \\ p_0 = [(\omega_p - \omega_1) \langle 2 | \mathcal{H}_{SL}^{\gamma_1\zeta_1} | p\rangle\langle p | \mathcal{H}_{SL}^{\gamma_2\zeta_2} | 1\rangle \\ + (\omega_p + \omega_2) \langle 2 | \mathcal{H}_{SL}^{\gamma_2\zeta_2} | p\rangle\langle p | \mathcal{H}_{SL}^{\gamma_1\zeta_1} | 1\rangle], \\ q_{13} = \omega_2^2 \operatorname{Re} [(\omega_p + \omega_2) \langle 2 | \mathcal{H}_{AQ}^{\gamma\zeta} | p\rangle\langle p | \mathcal{H}_{SL}^{\gamma_1\zeta_1} | 1\rangle \\ + (\omega_p - \omega_1) \langle 2 | \mathcal{H}_{SL}^{\gamma_1\zeta_1} | p\rangle\langle p | \mathcal{H}_{AQ}^{\gamma_2\zeta_2} | 1\rangle] \, p_0^{-1}. \end{aligned} \tag{17}$$

3. INERTIAL SPIN-LATTICE RELAXATION

A. Direct Processes

It is obvious that interaction of the gradient of the field of accelerations produced by thermal vibrations of particles in solids and in liquids with the quadrupole moment of the inertial mass of the impurities should lead to processes of spin-lattice relaxation and to nonradiative transitions in optics. To calculate the probabilities of these processes, the Hamiltonian $H_{\text{sph}}^{(T)}$ of the interaction of the impurity with the thermal reservoir is conveniently written in the form (8), where $u_{\gamma\xi}$ should be taken to mean the deformations produced by the thermal vibrations of the crystal $u_{\gamma\xi}^{(T)}$:

$$u_{j\xi}^{(T)} = \frac{i}{2} \sum_{R_s} \left(\frac{h\omega_{k_s}}{2Mv_s^2} \right)^{1/2} \cdot (a_{k_s} \exp\{ik_s r^j\} + a_{k_s}^{+} \exp\{-ik_s r^j\}) d_{s\gamma\xi}, \tag{18}$$

where

$$d_{s\gamma\xi} = \Phi_{s\gamma} k_{s\xi}^0 + k_{s\gamma}^0 \Phi_{s\xi}, \quad k^0 = k / |k|,$$

$\Phi_{s\gamma}$ is the γ-th component of the unit vector of the polarization of the s-th mode of the lattice vibrations, ω_{k_s} is the frequency corresponding to the wave vector k_s, v_s is the speed of sound of the s-th mode, M is the crystal mass, and a_{ks}^{+} and a_{ks} are the operators of phonon creation and annihilation. Taking this into account, we get

$$\mathcal{H}_{\text{sph}}^{(T)} = \sum_{\gamma\xi} (\mathcal{H}_{SL}^{\gamma\xi} + \omega_{k_s}^2 \mathcal{H}_{AQ}^{\gamma\xi}) u_{\gamma\xi}^{(T)}, \tag{19}$$

In direct spin-lattice relaxation processes, when the transition from the excited state to the ground state results in one quantum of acoustic oscillations, both mechanisms act independently. Therefore we deduce the same conclusions concerning their relative effectiveness as in the case of resonant absorption of hypersound. When the Debye model of a crystal is used, we find, according to (15), that the probability of the direct relaxation transition due to the SL interaction ($W_{SL}^{(1)}$) and the corresponding probability for the AQ interaction ($W_{AQ}^{(1)}$) are proportional to the quantities

$$W_{SL}^{(1)} \sim \omega^3 (\bar{n}_\omega + 1), \quad W_{AQ}^{(1)} \sim \omega^7 (\bar{n}_\omega + 1), \tag{20}$$

$\bar{n}_\omega$ is the average number of thermal phonons of frequency ω, $\bar{n}_\omega = [\exp(\hbar\omega/k_B T) - 1]^{-1}$, k_B is Boltzmann's constant, and T is the temperature. In direct relaxation processes, $W_{AQ}^{(1)}$ can play an important role in splittings on the order of the Debye frequencies, i.e., in the infrared region. Indeed, in this region of frequencies $(W_{SL}^{(1)}/W_{AQ}^{(2)}) \sim C_i^2 \omega^4$; when $C_i \sim 10^{-26}-10^{-25}$ g-cm^2-erg^{-1} and $\omega \gtrsim 10^{13}$ sec^{-1}, this ratio is of the order of unity or higher. It is probable that an appreciable role is played by AQ interactions in direct processes of relaxation between the vibrational levels of the molecules, in view of the fact that $m_i Q_i$ for molecules is larger by 5–6 orders of magnitude than the analogous quantity for the electron shell of the impurity.

B. Raman Processes of Inertial Spin-lattice Relaxation

When $k_B T \gg \hbar\omega_{21}$, more effective processes are not the direct ones, but the combination relaxation processes (ion, nucleus, paraelectric impurity, etc.), going from the excited state $|2\rangle$ into one of the lower states $|1\rangle$, with simultaneous creation of a quantum of lattice oscillations $\hbar\omega_1$ and annihilation of a quantum $\hbar\omega_2$, $\hbar(\omega_1 - \omega_2) = \hbar\omega_{21}$, $\hbar\omega_{21} = E_2 - E_1$.

In Raman processes of relaxation of electronic and nuclear magnetic systems, the contribution of the AQ interaction is comparable, and in many cases it exceeds the contribution to the rate of relaxation of the ordinary SL interactions. As shown below, when account is taken of the AQ interactions, the reciprocal relaxation time in Raman processes is in many cases a polynomial in T of (13–15)-th power (the first zero-order terms are proportional to the (5–7)-th power, depending on the interval of the investigated temperature and parameters of the system).

The probability of such a process per unit time will be denoted by $W_{21}^{(2)}$. Using the Debye model of the crystal we obtain

$$\begin{aligned} W_{21}^{(2)} = \frac{9}{2^7\pi^3\hbar^2\rho^2 v^{10}} \int_0^{\omega_D} (\omega_{21} + \omega)^3 \omega^3 \bar{n}_\omega (\bar{n}_{(\omega+\omega_{21})} + 1) \cdot \\ \times \Big| \sum_p N_p(\omega, \omega_p, \omega_{21}) [1 + \omega^2 Q_{12}{}^{\Sigma} + (\omega_{21} + \omega)^2 Q_{21}{}^{\Sigma} \\ + (\omega_{21} + \omega)^2 \omega^2 Q_{22}{}^{\Sigma}] \Big|^2 d\omega, \end{aligned} \tag{21}$$

where ρ is the density of the crystal, ω_D is the circular Debye frequency,

$$N_p(\omega, \omega_p, \omega_{21})$$

$$= \frac{\langle 1 | \mathcal{H}_{SL}^{\gamma_1\zeta_1} | p\rangle \langle p | \mathcal{H}_{SL}^{\gamma_2\zeta_2} | 2\rangle}{\omega_{21} + \omega - \omega_p - i\Delta\omega_p/2} + \frac{\langle 1 | \mathcal{H}_{SL}^{\gamma_2\zeta_2} | p\rangle \langle p | \mathcal{H}_{SL}^{\gamma_1\zeta_1} | 2\rangle}{-\omega - \omega_p - i\Delta\omega_p/2},$$

Q_{ij}^{Σ} is obtained from the corresponding expressions (17) by making the substitutions $\omega_1 \to \omega_{21} + \omega$, $\omega_2 \to \omega$.

The analytic dependence of $W_{21}^{(2)}$ on T can be analyzed only in a number of particular cases, but these cases cover a rather wide range of experiments. For the frequencies of nuclear and electron paramagnetic resonances ($\omega_{21} \ll \omega_D$) and $k_BT \gg \hbar\omega_D$ we have with sufficient accuracy $\bar{n}_\omega(\bar{n}_\omega + 1) \sim (k_BT/\hbar\omega)^2$, and consequently $W_{21}^{(2)} \sim T^2$. A different situation arises in the other limiting case, $k_BT \ll \hbar\omega_D$. Assume that $\omega_p \gg \omega_{12}, \omega_D$. Then

$$W_{21}^{(2)} \sim \int\limits_0^{\omega_D} \omega^6\bar{n}_\omega(\bar{n}_\omega + 1)\left|\sum_p N_p(\omega, \omega_p, \omega_{21})\right|^2 |1 + \omega^2 Q_{12}{}^\Sigma + \omega^2 Q_{21}{}^\Sigma + \omega^4 Q_{22}^\Sigma|^2\, d\omega. \tag{22}$$

Therefore, making the substitution $\hbar\omega/k_BT = x$, we obtain

$$W_{21}^{(2)a} = B^a \sum_i \left(\frac{k_\text{Б} T}{\hbar}\right)^i f_i{}^a \int\limits_0^{\theta/T} \frac{x^{i-1}\exp x}{(e^x - 1)^2}\,dx, \tag{23}$$

$$B^a = \frac{9}{2^7\pi^3\hbar^2\rho^2 v^{10}}\left|\sum_p N_p{}^a(\omega, \omega_p, \omega_{21})\right|^2, \quad \theta = \hbar\omega_D/k_\text{B},$$

$$f_7 = 1, \quad f_9 = 2\,\text{Re}\,[Q_{12}{}^a + Q_{21}{}^a], \tag{24}$$
$$f_{11} = 2\,\text{Re}\,(Q_{22}{}^a) + 2|Q_{12}{}^a + Q_{21}{}^a|^2,$$
$$f_{13} = 2\text{Re}\,(Q_{12}{}^a + Q_{21}{}^a)\,Q_{22}{}^{a*}, \; f_{15} = |Q_{22}|^2.$$

The quantities Q_{ik}^a are obtained from the corresponding expression for Q_{ij}^Σ at $\omega = \omega_{12} = \Delta\omega_p = 0$, in accordance with the approximation $\omega_p \gg \omega_D$ assumed by us. The quantity $N_p^a(\omega, \omega_p, \omega_{21})$ is obtained from $N_p(\omega, \omega_p, \omega_{21})$ by neglecting ω in comparison with ω_p. In the case when $\omega_p \ll \omega$ and $k_BT \ll \hbar\omega_D$ we get

$$W_{21}^{(2)\bar{a}} = B^{\bar{a}} \sum_i \left(\frac{k_\text{Б} T}{\hbar}\right)^{i-2} f_i^{\bar{a}} \int\limits_0^{\Theta/T} \frac{x^{i-3}\,e^x}{(e^x - 1)^2}\,dx, \tag{25}$$

The quantity $B^{\bar{a}}$ is obtained from B^a (see (24)) by replacing N_p^a by $N_p^{\bar{a}}$. The quantity $N_p^{\bar{a}}(\omega, \omega_p, \omega_{12})$ is obtained from $N_p(\omega, \omega_p, \omega_{21})$ by neglecting in the latter ω_p compared with ω, and the $f_i^{\bar{a}}$ are described by formulas (20). In the latter we replace Q_{ij}^a by $Q_{ij}^{\bar{a}}$; $Q_{ij}^{\bar{a}}$ are obtained from the corresponding expressions for Q_{ij}^Σ by putting in the latter $\omega_p = 0$ and $\omega = \omega_D$. An analysis of the expressions shows that they change very little with changing ω. Therefore, putting $\omega = \omega_D$ and taking $Q_{ij}^{\bar{a}}$ outside the integral sign, we make by the same token a much smaller error in the calculation than when we approximate the spectrum by the Debye function. In the case when $\omega_p \lesssim \omega_D$, the main contribution to $W_{21}^{(2)}$ is made by the phonons in the vicinity of the point $\omega = \omega_p$ (the so-called Ohrbach mechanism). The temperature dependence of $W_{21}^{(2)}$ is in this case analogous to the temperature dependence of the probability of relaxation by this mechanism, i.e., it is linear when $k_BT \gg \hbar\omega_p$ and

$$W_{21}^{(2)} \sim \exp\left(-\frac{\hbar\omega_p}{k_BT}\right)$$

when $k_BT \ll h\omega_p$. The relative contribution made to $W_{21}^{(2)}$ by terms with different Q_{ij}^Σ can be readily estimated from (21), where ω must be replaced everywhere by $\omega = \omega_p$. As noted above, the contribution made to the relaxation by the AQ interaction can in this case be of the same order as the contribution from the SL interaction, and may even exceed it.

Particularly interesting, from the point of view of determining the inertial quadrupole moments from the relaxation parameters, are the cases (20) and (21). In these cases the terms $W_{21}^{(2)}$ at different powers of T are proportional to the Q_{ij}^Σ or to their products, making it possible to determine m_iQ_i directly from the relaxation measurements.

Thus, the interaction of the inertial quadrupole moment of the impurity with the gradient of the acceleration field plays a very important role in the absorption of sound and in relaxation processes occurring in solids and liquids. We have stopped to discuss only processes of resonant absorption of sound and spin-lattice (longitudinal) relaxation. However, the AQ interactions should influence strongly processes of harmonic and Raman cross relaxation via the field of the acceleration gradient both in the microwave and in the optical regions of the spectrum, just as the SL interactions cause analogous phenomena via the deformation field (phonon field) (see, for example,[12]). In addition, the AQ interactions should be taken into account together with the SL interactions in the investigation of the dynamic Jahn-Teller effect, in the calculation of multiquantum nonradiative transitions in optics, relaxation and cross-relaxation transitions, in collisions of atoms and molecules, in the investigation of effects of ordering in solids, of the interaction between excitons in semiconductors, etc.

The AQ interactions should influence also various types of scattering of elementary particles and scattering of light by acoustic and optical phonons, including the possible effects of stimulator scattering. As follows from the foregoing, they should come into play particularly strongly when the scattering gives rise to acceleration-field quanta of high frequency.

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[1] U. Kh. Kopvillem, Zh. Eksp. Teor. Fiz. 42, 1333 (1962) [Sov. Phys.-JETP 15, 924 (1962)].

[2] U. Kh. Kopvillem, Fiz. Tverd. Tela 11, 129 (1969) [Sov. Phys.-Solid State 11, 93 (1969)].

[3] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika, OGIZ, 1948 [Quantum Mechanics, Addison-Wesley, 1958].

[4] A. Abragam, Principles of Nuclear Magnetism, Oxford, 1961.

[5] U. Kh. Kopvillem and V. R. Nagibarov, ZhETF Pis. Red. 2, 529 (1965) and 5, 445 (1967) [JETP Lett. 2, 329 (1965) and 5, 360 (1967)]. Izv. vuzov Fizika 9, 66 (1967). Zh. Eksp. Teor. Fiz. 56, 201 (1969) [Sov. Phys.-JETP 29, 112 (1969)].

[6] A. Einstein, Jahrb. Radioakt. u. Elektronik 4, 411 (1967).

[7] S. A. Al'tshuler and B. M. Kozyrev, Elektronnyĭ paramagnitnyĭ resonans (Electron Paramagnetic Resonance), Fizmatgiz, 1961.

[8] E. B. Tucker, in: Physical Acoustics, Acad. Press, London, 1966.

[9] D. I. Bolef, in: Physical Acoustics, Acad. Press, London, 1966.

[10] U. Kh. Kopvillem and V. P. Smolyakov, Zh. Eksp. Teor. Fiz. 55, 2188 (1968) [Sov. Phys.-JETP 28, 1160 (1969)].

[11] Yu. V. Vladimirtsev, V. A. Golenishchev-Kutuzov, U. Kh. Kopvillem, and N. A. Shamukov, Fiz. Tverd. Tela 10, 2839 (1968) [Sov. Phys.-Solid State 10, 2239 (1969)].

[12] I. A. Nagibarova and V. R. Nagibarov, Zh. Eksp. Teor. Fiz. 55, 1277 (1968) [Sov. Phys.-JETP 28, 669 (1969)].

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