ON THE ROLE OF CRYSTAL LATTICE ANHARMONISM IN SPIN-LATTICE RELAXATION AND ON THE PHONON WIDTH OF THE EPR LINE

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The relation between the phonon width of the EPR line in a crystal and the spin-lattice relaxation probabilities, and the "elastic" phonon width of the EPR line are considered on the basis of the spin-phonon kinetic equation. The relaxation coefficients of the spin-phonon kinetic equation are expressed in terms of the Fourier transforms of the lattice correlators. The contribution of anharmonism to the relaxation coefficients is considered. For both the acoustic and optical branches, the contribution of the single-phonon anharmonic correlator may be greater than that of the Raman harmonic correlator. Formulas are obtained which take into account the effect of the anharmonism of the lattice on the spin-lattice transition probabilities and on the line width. The temperature dependence of the relaxation coefficients with account of anharmonism differs from the temperature dependence in the harmonic case for the acoustic branches in the temperature range $(1/10)\Theta < T < \Theta$ (Θ is the Debye temperature). The inverse correlation time in the lattice is considered for various temperature ranges.

1. INTRODUCTION

THE study of spin-lattice relaxations has as its aim the explanation of experimental data, or the prediction of the latter, for objects of interest for EPR and applied problems of quantum electronics. At the same time, experimental study of spin-phonon interactions in a wide temperature range, including the high temperatures $T \sim \Theta$ (Θ is the Debye temperature of the crystal), can be a source of information on the spectrum of lattice oscillations, the role of quasi-local and local oscillations, and so on. For such purposes, those samples are of interest which have sufficiently strong dilution, small disorders of axes of local symmetry of impurity centers, and sufficiently strong temperature dependence of the EPR linewidth. However, specimens which are of interest in applied problems as a rule satisfy the requirements at which the spin-phonon EPR line-width is negligible. The number of experiments in which the temperature broadening of lines has been studied is unfortunately small (see, for example,[1]).

One of the important characteristics of the phonon system is the magnitude of the anharmonic forces. Account of lattice anharmonism in the EPR line shape is important not only for the purpose of studying the phonon system, but also for the ordinary problems of explaining the spin-lattice relaxation times observed in the experiment.

The role of anharmonism in EPR spin-lattice relaxation was considered by Aleksandrov,[2] who concluded that the account of anharmonism is important. In[2] anharmonism was taken into account by the phenomenological introduction of damping in the correlation functions of the particle displacements in the lattice. In the present paper, we consider the effect of anharmonism on the relaxation coefficients of the spin-phonon kinetic equation,[1)] and the anharmonic terms are explicitly taken into account in the phonon part of the Hamiltonian of the system. Consideration of the relaxation coefficients makes it possible to take into account the effect of anharmonism both on the spin-lattice relaxation probabilities and on the EPR line width and shape. Our results confirm the conclusions of Van Kranendonk and Walker[4] that the anharmonic single phonon relaxation mechanism can dominate the ordinary two-phonon Raman process. We also take into account the optical branches, the contribution of which to the relaxation coefficients becomes significant at sufficiently high temperatures. Moreover, some problems connected with the application of kinetic spin-phonon equations for the description of EPR lines and, in particular, the calculation of phonon widths are also considered in the work.

2. THE SPIN-PHONON KINETIC EQUATION. DEPENDENCE OF THE RELAXATION COEFFICIENTS ON LATTICE CORRELATORS

Consideration of spin-phonon kinetic equations[5-8] is convenient in that the description of the shape of EPR lines and the relaxation times of different macroscopic spin quantities is possible from a single point of view. Both the parameters of the line shape (say, the quantities T_1 and T_2 in the simplest case of a two-level system) and the different relaxation times are expressed in terms of the relaxation coefficients of the kinetic equation.

Equations, which are actually useful in the UHF range and in the radio-frequency range, can be written

[1)] Some of the results of this work were reported at the All-union Jubilee Conference on Paramagnetic Resonance (Kazan', 1969). [3]

down for a non-equidistant spectrum $\omega_{mn} \neq \omega_{m'n'}$ in the form (see, for example,[8])[2)]

$$\frac{d\sigma_{mn}}{dt} = i[\sigma, \mathcal{H}(t)]_{mn} - \frac{\sigma_{mn}}{T_{mn}}, \qquad m \neq n,$$
$$\frac{d\sigma_{mm}}{dt} = i[\sigma, \mathcal{H}(t)]_{mm} + \sum_{l} (w_{lm}\sigma_{ll} - w_{ml}\sigma_{mm}). \tag{1}$$

Here σ_{mn} are the density matrix elements of the dynamic spin subsystem, in our case—a single paramagnetic center with Hamiltonian

$$\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_1(t), \tag{2}$$

where $\mathcal{H}_0$ describes the interaction with the static fields and $\mathcal{H}_1(t)$ with the variable external fields, while the conditions of sufficient smallness of the variable field enter as the criterion of the validity of (1).[5-8] The indices m and n enumerate the states of $\mathcal{H}_0$, while ω_{mn} are the frequencies of the dynamic subsystem (the Hamiltonian $\mathcal{H}$ is assumed to be expressed in frequency units).

The relaxation transition probabilities w_{ml} and the transverse relaxation times T_{mn} are expressed in terms of the relaxation coefficients of the spin-phonon kinetic equation Γ_{mkln}. As is shown in[8],

$$w_{ml} = 2\Gamma_{lmml}, \tag{3}$$

$$T_{mn}^{-1} = \frac{1}{2}\sum_{k\neq m,n}(w_{mk} + w_{nk}) - 2\Gamma_{mmnn} + \Gamma_{nnnn} + \Gamma_{mmmm}. \tag{4}$$

It is understood that the spin-phonon interaction can be represented in the form

$$\mathcal{H}_{\text{sph}} = \sum_{\mu} U_{\mu} V_{\mu}, \tag{5}$$

where V_μ are the spin operators, U_μ the lattice operators. If we introduce the Fourier transforms of the lattice correlators (FC) $\langle U_\mu; U\rangle_\omega$ such that

$$G_{\mu\nu}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\langle U_\mu(t); U_\nu\rangle\, dt \equiv \langle U_\mu; U_\nu\rangle_\omega, \tag{6}$$

then the relaxation coefficients can be put in the form

$$\Gamma_{mkln} = \pi\sum_{\mu\nu} G_{\mu\nu}(\omega_{ln}) V_{\mu ln} V_{\nu mk} \Delta(\omega_{mk} + \omega_{ln}), \tag{7}$$

where

$$\Delta(\omega_{mk} + \omega_{ln}) = \begin{cases} 1, & |\omega_{mk} + \omega_{ln}| \leqslant \omega^*, \\ 0, & |\omega_{mk} + \omega_{ln}| \gtrsim \omega^*, \end{cases} \tag{8}$$

$\omega^* = \tau_c^{-1}$, where τ_c is the correlation time of the lattice correlators. In Eq. (1), as is seen from (3) and (4), only such Γ_{mkln} appear for which $\omega_{mk} + \omega_{ln} = 0$.

Equations (1) are identical with those obtained by Bloch.[6] On the other hand, Eqs. (1) were obtained in the book of Faĭn and Khanin[8] from more general equations[3)] in which all the $\Gamma_{mkln} \neq 0$ enter, deleting the Γ_{mkln} with $\omega_{mk} + \omega_{ln} \neq 0$ under the assumption that $|\omega_{mk} + \omega_{ln}| \gtrsim \omega^*$ is satisfied for these m, k, l, n. The conditions $\Gamma_{mkln} = 0$ and $\omega_{mk} + \omega_{ln} \neq 0$ are identical, as is seen from (7) and (8), only for the case $|\omega_{mk} + \omega_{ln}| \gtrsim \omega^*$. However, in crystals for UHF, and even more, for the radio frequencies we have $\omega_{mk} \ll \omega^*$ if $\hbar\omega_{mk} \ll k_B T$, $T > T_0$ (see Sec. 4 on the parameter ω^*), so that the condition $|\omega_{mk} + \omega_{ln}| \gtrsim \omega^*$ is not satisfied in solids for $T > T_0$. Therefore, it is important to note that the conditions $|\omega_{mk} + \omega_{ln}| \gtrsim \omega^*$ are sufficient but not necessary for the validity of Eqs. (1) for a dynamic system with an unequally spaced spectrum. In other words, if $|\omega_{mk} + \omega_{ln}| \ll \omega^*$, then all the terms in the spin-phonon kinetic equation containing Γ_{mkln} with $\omega_{mk} + \omega_{ln} \neq 0$ are inessential for the stationary solutions of Eqs. (1).[10]

For practical purposes of the interpretation of the experimental results, it is important to explain the relation between the phonon EPR line width, which is determined by the transverse relaxation times T_{mn}, and the time T_1, which enters into the saturation factor of the EPR line and the ω_{ln} determined from (3). The time T_{mn} from (4) consists of a relativistic "inelastic" contribution, given by the sum w in (4), and of an "elastic" contribution, the value of which, according to (7), is determined by the FC at zero frequency. If the "elastic" contribution dominates, then the EPR phonon line width will not be determined by the relaxation transition probabilities, as is sometimes assumed when attempts are made to characterize the relaxation transition probabilities of the EPR phonon line width.

Let us define the operator (5) concretely. Let u^p_{sj} be the displacement of the ion with equilibrium position R_{sj} in the direction of the x_p axis (s is the number of the elementary cell, j the number of the site in the cell). For brevity, we introduce the index σ in place of sj. Then (see, for example,[2])

$$\mathcal{H}_{\text{sph}} = O_L^M[a^p_{LM\sigma}u_{\sigma}{}^p + b^{pp'}_{LM\sigma\sigma'}u^p_{\sigma}u^{p'}_{\sigma'} + c^p_{LM\sigma}\dot{u}_{\sigma}{}^p + d^{pp'}_{LM\sigma\sigma'}\dot{u}_{\sigma}{}^p\dot{u}_{\sigma'}{}^{p'} + e^{pp'}_{LM\sigma\sigma'}u_{\sigma}{}^p\dot{u}_{\sigma'}{}^{p'} + \ldots], \tag{9}$$

where O_L^M are the well-known Hermitian spin operators, which are described in terms of the spherical tensor operators. The allowed values of L and M are determined by the value of the spin ($L \leq 2S$), the point symmetry of the problem, and the invariance of (9) relative to the time inversion; the coupling constants a, b, c, d, and e can in principle be calculated for each specific case[2,11] or expressed in terms of the parameters permitted by symmetry theory. The components c and d describe the rate (nonadiabatic) mechanisms, and the component e the mixed mechanism. Summation is assumed for repeated indices in (9).

From the invariance relative to an arbitrary displacement and the Galileo principle we obtain the well-known relations:

$$\sum_{\sigma} a^p_{LM\sigma} = 0, \qquad \sum_{\sigma} b^{pp'}_{LM\sigma\sigma'} = 0, \qquad \sum_{\sigma} c^p_{LM\sigma} = 0, \ldots, \tag{10}$$

so that actually (9) is an expansion in terms of the differences of the displacements of the atoms and their velocities. If we denote the impurity ion by the indices s = 0 and γ = 0, then in place of u^p_σ and $\dot{u}^p_\sigma$ in (9) we have $u^p_{\sigma_0} \equiv u^p_\sigma - u^p_0$ and $\dot{u}^p_{\sigma_0} \equiv \dot{u}^p_\sigma - \dot{u}^p_0$. Everywhere below, by u_σ, $\dot{u}_\sigma$, we mean u_{σ_0}, $\dot{u}_{\sigma_0}$.

[2)] Degeneracy of the levels of the dynamic system is assumed to be absent. For the equations in the degenerate case, see [9].

[3)] See Eq. (8.3) in the book [8]. These latter essentially are identical with and differ only in form from the equations in the review [7].

Using the expansion (9), with the help of (6), (7), (10), we find

$$\Gamma_{mkln}=\pi(O_{L'}^{M})_{ln}(O_{L'}^{M'})_{mk}[a_{LM\sigma}^{p}a_{L'M'\sigma'}^{p'}\langle u_\sigma^p;u_{\sigma'}^{p'}\rangle_{\omega_{ln}}$$
$$+b_{LM\sigma\sigma'}^{pp'}b_{L'M'\sigma''\sigma'''}^{p''p'''}\langle u_\sigma^p u_{\sigma'}^{p'};u_{\sigma''}^{p''}u_{\sigma'''}^{p'''}\rangle_{\omega_{ln}}$$
$$+c_{LM\sigma}^{p}c_{L'M'\sigma'}^{p'}\langle\dot u_\sigma^p;\dot u_{\sigma'}^{p'}\rangle_{\omega_{ln}}+d_{LM\sigma\sigma'}^{pp'}d_{L'M'\sigma''\sigma'''}^{p''p'''}\langle\dot u_\sigma^p\dot u_{\sigma'}^{p'};\dot u_{\sigma''}^{p''}\dot u_{\sigma'''}^{p'''}\rangle_{\omega_{ln}}$$
$$+e_{LM\sigma\sigma'}^{pp'}e_{L'M'\sigma''\sigma'''}^{p''p'''}\langle u_\sigma^p\dot u_{\sigma'}^{p'};u_{\sigma''}^{p''}\dot u_{\sigma'''}^{p'''}\rangle_{\omega_{ln}}+\text{interference terms}]. \quad (11)$$

If the temperatures are not very low and the basic contribution to Γ_{mkln} is made by the two-phonon FC of the displacements, calculated in the harmonic approximation, or the single phonon FC of the displacements, calculated with account of anharmonism (see Sec. 3), then the FC at zero frequency and the FC at UHF will not differ (since $|\omega_{ln}| \ll \omega^*$). Consequently, the phonon parts of w_{mn} and Γ_{mmmm} and Γ_{nnnn} are identical, and the difference of the "elastic" and "inelastic" parts of T_{mn}^{-1} can be caused only by the coupling constants. Actually, it follows from (11) that Γ_{nnnn} and Γ_{mmmm} are determined by the diagonal spin matrix elements, i.e., by the operators O_L^M with $M = 0$, while the Γ_{nmnm} are determined by the nondiagonal matrix elements. If, say, $|b_{L,M=0}| \ll |b_{L,M\neq 0}|$, then the "elastic" part will dominate and $T_{mn}^{-1} \gg w_{mn}$ ($T_2 \ll T_1$).

As an example, let us consider the Kramers doublet in a cubic field. For simplicity, let

$$\mathcal{H}_{\text{sph}}=\sum_{ijkl}\beta c_{ijkl}S_kH_l\varepsilon_{ij},$$

where, in the macroscopic approximation, we introduce the deformation tensor ϵ_{ij} (i, j = x, y, z) in place of the particle displacements. Here $O_1^{\pm 1} = S_{xy}$, $O_1^0 = S_z$) and the coupling constant a from (9) is represented by the tensor $\beta c_{ijkl}H_l$. It follows from (3), (4) and (9) that

$$\frac{w_{12}}{\Gamma_{1111}+\Gamma_{2222}-2\Gamma_{1122}}\sim\frac{c_{xzxz}^2}{c_{zzzz}^2}.$$

For Ho^{2+} in CaF_2, this ratio is equal to 1.6×10^{-3}; for Yb^{3+} in ThO_2, it is equal to 2.25.[12]

The velocity FC $\langle \dot u;\dot u\rangle_{\omega\to 0}\to 0$ so that, if the constant c dominates in (9) the "elastic" part is negligible and the phonon linewidth is determined only the relaxation part. For sufficiently low temperatures, when the basic role is played by direct processes, the FC at zero frequency become small in comparison with the FC at the frequency ω_{ln}, so that the phonon width is completely determined by the relaxation part. We note that the account of anharmonism leads to the result that the components with coupling constant a give a contribution to the "elastic" part of T_{mn} (see Sec. 3).

3. THE EFFECT OF ANHARMONISM OF THE LATTICE ON THE RELAXATION COEFFICIENTS OF THE SPIN-PHONON EQUATION

As follows from (11), the effect of the lattice on the relaxation coefficients is completely determined by the FC of the differences of the displacements and velocities of the particles. Computation of the latter is not a part of EPR problems. There are many researches in which the lattice FC is considered for one problem or another of the physics of crystals, with account of anharmonism,[13-15] lattice defects,[15,16], local and quasilocal oscillations.[17,18] However, for clarity, we shall dwell on a number of initial premises, all the more since in the calculation of the lattice FC at UHF and radio frequencies there are certain features that are not important in the region of higher frequencies. We shall not take into account the local and quasilocal oscillations, the center of which can be a paramagnetic impurity. We shall assume that the centers considered do not appreciably distort the normal oscillations (see Sec. 5):

$$\mathbf{u}=\sum_{\substack{\mathbf{k}>0\\ j}}\left(\frac{\hbar}{2mN\omega_{\mathbf{k}j}}\right)^{1/2}[\mathbf{e}_{\mathbf{k}j\gamma}e^{i\mathbf{k}\mathbf{R}_\sigma}-\mathbf{e}_{\mathbf{k}j0}](a_{\mathbf{k}j}-a_{-\mathbf{k}j}^{+}), \quad (12)$$

where $a_{\mathbf{k}j}^{+}$ and $a_{\mathbf{k}j}$ are the Bose creation and annihilation operators of phonons of the j-th branch and of the wave vector k; $\mathbf{e}_{\mathbf{k}j}$ are polarization vectors, and

$$\mathbf{e}_{-\mathbf{k}j\gamma}=-\mathbf{e}_{\mathbf{k}j\gamma}^{*}, \qquad \sum_\sigma \mathbf{e}_{\mathbf{k}j\gamma}\mathbf{e}_{\mathbf{k}'j'\gamma}m_\gamma\exp\{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_\sigma\}=Nm\delta_{\mathbf{k}\mathbf{k}'}\delta_{jj'}, \quad (13)$$

$m=\sum_\gamma m_\gamma$ is the mass of the elementary cell, and Nm the mass of the crystal. Thus, the calculation of the FC of displacements and velocities reduces to the calculation of the FC of the operators $a_{\mathbf{k}j}$ and $a_{\mathbf{k}j}^{+}$. We denote

$$\varphi_{\mathbf{k}j\mathbf{k}'j'}(\omega)\equiv\langle(a_{\mathbf{k}j}-a_{-\mathbf{k}j}^{+}),\ (a_{\mathbf{k}'j'}-a_{-\mathbf{k}'j'}^{+})\rangle_\omega, \quad (14)$$

$$\Delta_{\mathbf{k}j\sigma}^{p}\equiv[e_{\mathbf{k}j\gamma}^{p}e^{i\mathbf{k}\mathbf{R}_\sigma}-e_{\mathbf{k}j0}^{p}], \qquad \Delta_{-\mathbf{k}j\sigma}^{p}=-\Delta_{\mathbf{k}j\sigma}^{p*}. \quad (15)$$

Then, for example,[4)]

$$\langle u_\sigma^p;u_{\sigma'}^{p'}\rangle_\omega=\frac{\hbar}{2mN}\sum_{\mathbf{k}jj'}(\omega_{\mathbf{k}j}\omega_{\mathbf{k}j'})^{-1/2}\Delta_{\mathbf{k}j\sigma}\Delta_{-\mathbf{k}j'\sigma'}'\varphi_{\mathbf{k}j,-\mathbf{k}j'}, \quad (16)$$

$$\langle\dot u_\sigma^p;\dot u_{\sigma'}^{p'}\rangle_\omega=\omega^2\langle u_\sigma^p;u_{\sigma'}'\rangle_\omega. \quad (17)$$

Calculation of (14) in the harmonic approximation is quite simple. In the anharmonic approximation, the Hamiltonian of the lattice has the form

$$\mathcal{H}_{\text{ph}}=\sum_{\mathbf{k}j}\hbar\omega_{\mathbf{k}j}a_{\mathbf{k}j}^{+}a_{\mathbf{k}j}+\frac{1}{6}\sum_{1,2,3}V_{1,2,3}(a_1-a_{-1}^{+})(a_2-a_{-2}^{+})(a_3-a_{-3}^{+})+$$
$$V_{1,2,3}=\left(\frac{\hbar}{2mN}\right)^{\frac{3}{2}}\sum_{\sigma,\sigma',\sigma''}\sum_{pp'p''}V_{\sigma\sigma'\sigma''}^{pp'p''}\frac{e_{1\gamma}^{p}e_{2\gamma'}^{p'}e_{3\gamma''}^{p''}}{\sqrt{\omega_1\omega_2\omega_3}}\cdot\exp[i(\mathbf{k}_1\mathbf{R}_\sigma+\mathbf{k}_2\mathbf{R}_{\sigma'}+\mathbf{k}_3\mathbf{R}_{\sigma''})]. \quad (18)$$

The anharmonic terms of fourth order are similar. Here $1\equiv(\mathbf{k}_1j_1)$, $-1\equiv(-\mathbf{k}_1j_1)$ and so on. The force constants $V_{\sigma\sigma'\sigma''}$ are the coefficients of the expansion of the lattice potential energy in powers of the displacements of the atoms from the equilibrium positions, and satisfy a number of symmetry properties (see, for example,[19]).

Formulas are given in the Appendix for the various FC of the creation and annihilation operators of phonons. Formulas (A.1)–(A.4) were obtained by us by calculation of the corresponding two-time Green's functions by means of uncoupling the chain of equations for the Green's functions,[20] so that anharmonism of third order is taken into account in the polarization operator with accuracy up to quadratic terms, and the anharmonism of fourth order is taken into account with

[4)] The absence of terms with $\mathbf{k}' \neq -\mathbf{k}$ in (16) follows from the invariance of the correlator of the difference of the displacements relative to the choice of the origin of the coordinates.

accuracy up to linear terms (the anharmonism of fourth order in this approximation makes no contribution to phonon damping). Most of the results given in the Appendix are contained in[4,13,14]. The feature noted above is that as $\omega \to 0$[5] the contribution of the FC of the type $\langle a_{kj}; a^+_{k'j'}\rangle$ and $\langle a_{kj}; a^+_{k'j'}\rangle$ to the FC of the displacements is equal to the contribution of the FC of type $\langle a_{kj}; a^+_{kj}\rangle$, which are ordinarily taken into account. From (A.1) and (16) we get

$$\langle u_\sigma^p; u_{\sigma'}^{p'}\rangle_\omega = \frac{\hbar}{2mN}\sum_{kj}\omega_{kj}^{-1}\Delta^p_{kj\sigma}\Delta^{p'}_{-kj\sigma'}\left\{[n(\omega)+1]\times\frac{1}{\pi}\frac{-\Gamma_{kj}(\omega)}{[(\omega^2-\omega^2_{kj})/2\omega_{kj}-P_{kj}(\omega)]^2+\Gamma^2_{kj}(\omega)}\right\} \quad (19)$$

$$+\frac{\hbar}{2mN}\sum_{kj,j'\neq j}\frac{\Delta^p_{kj\sigma}\Delta^{p'}_{-kj'\sigma'}}{\sqrt{\omega_{kj}\omega_{kj'}}}\varphi_{kj,-kj'}(\omega).$$

The second sum takes into account the polarization mixing and we shall not take it into consideration (in the Debye approximation, the polarization mixing of longitudinal and transverse waves yields zero).

In (19), $n(\omega) = (e^{\hbar\omega/k_BT} - 1)^{-1}$ is the Planck factor;

$$\Gamma_{kj}(\omega) = \frac{\pi}{2\hbar^2}\sum_{1,2}|V_{-kj,1,2}|^2\{(1+n_1+n_2)[\delta(\omega-\omega_1-\omega_2) - \delta(\omega+\omega_1+\omega_2)] + 2(n_1-n_2)\delta(\omega+\omega_1-\omega_2)\}. \quad (20)$$

For $\omega = \omega_{kj}$, $\Gamma^{-1}_{kj}(\omega)$ is the phonon lifetime; $n_i \equiv n(\omega_i)$.

In what follows, we shall be interested in ω in the UHF range, i.e., $\hbar\omega \ll k_B\Theta$ and, if $T \gg 1°K$, then $\hbar\omega \ll k_BT$. Therefore, the first two terms in (20) are really unimportant. The quantity $P_{kj}(\omega)$ is the frequency shift, the expression for which is found, for example, in[15] (Eq. (37.4)). In the following, we shall neglect $P_{kj}(\omega)$.

In (19), we separate the contribution of the resonance phonons $\omega_{kj} \sim \omega$ in the summation over k, j. In the harmonic approximation, one need consider only this contribution, since, the "quasilorentzian" in the curly brackets of (19) will be replaced by $\delta(\omega - \omega_{ky}) - \delta(\omega + \omega_{ky})$. Anharmonism leads to the replacement of the δ-functions by bell-shaped curves of width $\Gamma_{kj}(\omega)$ and a shift of the center of the bell that is small in comparison with ω_{kj}. This shift changes the contribution of the resonant phonons by an insignificant amount. The sum with $\omega_{ky} > \omega$ remaining after separation of the resonant phonons (the sum with $\omega_{ky} < \omega$ is generally insignificant) gives the fundamental anharmonic contribution, since this part contains summation over the entire spectrum. For the nonresonance region, the function in the curly brackets of (19) is proportional to $4(n(\omega)+1)\Gamma_{kj}(\omega)/\pi\omega^2_{kj}$. Moreover, $[n(\omega)+1]\Gamma_{kj}(\omega) \approx \lim[n(\omega)+1]\Gamma_{kj}(\omega)$. From (19), (20), we get

$$\langle u_\sigma^p; u_{\sigma'}^{p'}\rangle_\omega \approx \langle u_\sigma^p; u_{\sigma'}^{p'}\rangle_\omega^{harm} + \langle u_\sigma^p; u_{\sigma'}^{p'}\rangle_0^{anharm}, \quad (21)$$

$$\langle u_\sigma^p; u_{\sigma'}^{p'}\rangle_0^{anharm} = \frac{2}{\hbar mN}\sum_{1,2,3}|V_{-1,2,3}|^2\omega_1^{-3}n_2\cdot \times(n_2+1)\Delta_{1\sigma}{}^p\Delta^{p'*}_{1\sigma'}\delta(\omega_2-\omega_3). \quad (22)$$

For comparison, we write down the FC in the harmonic approximation

$$\langle u_\sigma^p; u_{\sigma'}^{p'}\rangle_\omega^{harm} = \frac{\hbar}{2mN}\sum_1\frac{n_1+1}{\omega_1}\Delta_{1\sigma}{}^p\Delta^{p'*}_{1\sigma'}[\delta(\omega-\omega_1)-\delta(\omega+\omega_1)]. \quad (23)$$

$$\langle u_\sigma{}^p u_{\sigma'}{}^{p'}; u_{\sigma''}^{p''}u_{\sigma'''}^{p'''}\rangle_\omega^{harm} \approx \langle u_\sigma{}^p u_{\sigma'}{}^{p'}; u_{\sigma''}^{p''}u_{\sigma'''}^{p'''}\rangle_0^{harm} = \frac{\hbar^2}{m^2N^2}\sum_{1,2}\frac{n_1(n_2+1)}{\omega_1\omega_2}\frac{1}{2}[\Delta_{1\sigma}{}^p\Delta^{p'}_{2\sigma'}(\Delta^{p''}_{1\sigma''}\Delta^{p'''}_{2\sigma'''}+\Delta^{p'''}_{1\sigma'''}\Delta^{p''}_{2\sigma''})^*]\delta(\omega_1-\omega_2). \quad (24)$$

The temperature regions in which the single-phonon FC in (21) are important are different. Upon decrease in temperature, the occupation numbers of the high-frequency phonons decrease, and the number of phonons that make a contribution to the anharmonic part of the FC falls off rapidly, so that, at some temperature (see Sec. 4), the anharmonic part ceases to be significant. Similarly, summation over the spectrum contains the FC of (24). Comparison in the long wavelength approximation for the acoustic branches, when

$$\Delta^p_{kj\sigma} \approx e^p_{kj\gamma}ik\mathbf{R}_\sigma, \quad V_{1,2,3} \sim \sqrt{\omega_1\omega_2\omega_3}, \quad (25)$$

shows that the FC in (22) and (24) have the same temperature dependence when $T \ll \Theta$.[4]

We note that the contribution to the "elastic" part T_{mn} from (4) can give the anharmonic part of the single-phonon FC of the displacements and the harmonic two-phonon FC of the displacements, as follows from (22), (23), (24), (17). The velocity mechanisms $\langle \dot u_\sigma; \dot u_{\sigma'}\rangle_0$ and $\langle \dot u_\sigma u_{\sigma'}; \dot u_{\sigma''}u_{\sigma''}\rangle_0$ make no contribution to the "elastic" part of T_{mn}. The anharmonic contribution to (17) at $\omega \neq 0$ is equal to $\omega^2\langle u^p_\sigma; u^{p'}_{\sigma'}\rangle_0^{anharm}$.

Account of anharmonism in the two-phonon FC of the displacements and velocities is inadvisable, for even in the harmonic approximation these FC are expressed in terms of a sum over all the phonons of the spectrum.

4. TEMPERATURE DEPENDENCES OF THE RELAXATION COEFFICIENTS. THE VALUE OF ω^* IN A CRYSTAL

Let us consider the contributions of the various branches of oscillations to the anharmonic FC (22), separate the temperature dependences of this FC, and compare the anharmonic (AFC) FC [Eq. (22)] with the two-phonon harmonic FC (H2FC) [Eq. (24)]. At high temperatures, $k_BT > \hbar\omega_m$, the planck factors in (22) is $\sim (k_BT/\hbar\omega_2)^2$, so that, independent of the dispersion law for the different branches, AFC and H2FC $\sim T^2$. At low temperatures $T \ll \Theta$, when long wavelength phonons are fundamental in the lattice, the temperature dependences of AFC and H2FC are identical (AFC of the displacements $\sim T^7$). The region $T \sim \Theta$ for the acoustic branches and the region $k_BT \sim \hbar\omega_{opt}$ for the optical ones require special consideration. The exact calculation of (22) for each crystal requires the knowledge of the dispersion law and the use of computers.

Acoustical branches. We assume the long wavelength approximation (25) and the linear dispersion law $\omega_{kj} = c_jk$, $j = 1, 2, 3$. Moreover, we write

$$V_{1,2,3} = \frac{k_1k_2k_3}{\sqrt{\omega_1\omega_2\omega_3}}\sqrt{\frac{\rho}{mN}}A_{1,2,3}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3). \quad (26)$$

[5] Calculation of the correlators for local oscillations as $\omega \to 0$ is given in [17].

The quantity $A_{1,2,3}$ in (26) does not depend on the lengths K when $\mathbf{k}\cdot\mathbf{R} \ll 1$, but only on their directions $\mathbf{f} \equiv \mathbf{k}/k$; $\Delta(\mathbf{k}) \equiv \delta_{\mathbf{k},2\pi\mathbf{K}_n}$; ρ is the density of the crystal; $\mathbf{K}_n$ is the reciprocal lattice vector. Substituting (25) and (26) in (22), we obtain the AFC for the acoustic oscillations. The summation in (22), as in the other sums, goes over the first Brillouin zone, and $\Delta(\mathbf{k})$ and $\delta(\omega_1 - \omega_2)$ guarantee satisfaction of the laws of conservation of quasimomentum and energy. For the estimate of the AFC in this case, one can neglect the polarization mixing and take out $|A|^2$ and the polarization vectors at the mean value. In the long wavelength approximation, we use the estimate[21]

$$\langle |A_{t_1;\,t_1,t_2,t_3}|^2\rangle_{av} \approx {}^{16}/_{3}\gamma^2\hbar^3 c_j^4/\rho, \qquad (27)$$

where γ is the Grüneisen constant ($\gamma = 1-2$). Taking transport processes into account in (22), we obtain $\sum_{\mathbf{k}}\Delta(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}) = 1$. Transforming from summation over $\mathbf{k}_1$ and $\mathbf{k}_2$ to integration over the frequencies, we get, in the usual way,

$$\langle u_\sigma^p;\, u_{\sigma'}^{p'}\rangle_0^{anh} = \frac{24\hbar^2}{\pi^4\rho^2}\gamma^2 R_\sigma R_{\sigma'}\sum_{j=1}^{3}\left\langle\frac{(e\lambda f)_{j\sigma\sigma'}^{pp'}}{c_j^{10}}\right\rangle_{av}\left(\frac{k_B T}{\hbar}\right)^7 I_6\left(\frac{\Theta_j}{T}\right)$$

$$\approx \frac{24\hbar^2}{\pi^4\rho^2 c^{10}}\gamma^2 R_\sigma R_{\sigma'}\left(\frac{k_B T}{\hbar}\right)^7 I_6\left(\frac{\Theta}{T}\right)\sum_{j=1}^{3}\langle(e\lambda f)_{j\sigma\sigma'}^{pp'}\rangle_{av}. \qquad (28)$$

Here Θ_j is the Debye temperature, determined for the j-th acoustic branch,

$$\Theta_j = \frac{\hbar}{k_B}\left(\frac{6\pi^2\rho}{m}\right)^{1/3}\langle c_j^{-3}\rangle_{av}^{-1/3};\quad (e\lambda f)_{j\sigma\sigma'}^{pp'} \equiv e_{ij\gamma}^{p} e_{ij\gamma'}^{p'*}(f\lambda_\sigma)(f\lambda_{\sigma'});$$

$$\lambda_\sigma \equiv \frac{R_\sigma}{R_\sigma}.$$

$\langle\ldots\rangle_{av}$ denotes averaging over the propagation directions. The second equality in (28) is the result obtained in the ordinary Debye approximation, where c is the velocity averaged over all the branches and is determined by the Debye temperature $\Theta = (1/3)\sum_{j=1}^{3}\Theta_j$. Finally,

$$I_n\left(\frac{\Theta}{T}\right) \equiv \int_0^{\Theta/T} x^n \frac{e^x}{(e^x-1)^2}dx. \qquad (29)$$

In the long wavelength approximation, the H2FC (24) have such a temperature dependence, as is well known.

It is interesting to note that a temperature dependence different from (28) is obtained in the continuum model, in view of the absence of transport processes, i.e., $\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k} = 0$. In this case, the simultaneous satisfaction of the laws of conservation of the momentum and energy imposes additional restrictions on the region of change of the vectors $\mathbf{k}_1$, $\mathbf{k}_2$, $\mathbf{k}$. Calculations show that, without account of transport processes, $I_6(\Theta/T)$ in (28) will be replaced by ($z \equiv \Theta/T$)

$$= \frac{1}{2}\int_0^z x\,dx\int_{x/2}^{z}\frac{y^4 e^y}{(e^y-1)^2}dy = I_6\left(\frac{\Theta}{T}\right) \qquad (30)$$

$$+ \frac{1}{2}\int_{z/2}^{z}\left(\frac{1}{2}z^2x^4 - 2x^6\right)\frac{e^x}{(e^x-1)^2}dx,$$

I_6' does not differ from I_6 when $T \ll \Theta$. The drawing shows the difference between I_6' and I_6: $(I_6' - I_6)/I_6$ ~ 60% for $T = \Theta/2$ and 42% for $T = \Theta/8$. Thus the contribution of transport processes at $T \sim \Theta$ is not small and the long wavelength approximation is unsuitable. If we retain in (22) the exact $\Delta_{1\sigma}\Delta_{1\sigma'}^{*}$,[6] and if we take into account the dependence of $|A_{1,2,3}|$ on the k_i and the fact that the long wavelength approximation distorts the contribution of the transport processes more strongly than the contribution of the normal processes, then, for $T \lesssim \Theta$, the temperature dependences of the AFC and the H2FC will be different.

In the region $T \ll \Theta$, the AFC and the H2FC differ only numerically. Let us consider, for example, a process that is quadratic in the spin ($L = 2$) in (11). Then

$$\frac{\Gamma_{mkln}^{anharm}}{\Gamma_{mkln}^{harm}} \sim \frac{a^2\langle u_\sigma^p;\, u_{\sigma'}^{p'}\rangle_0^{anh}}{b^2\langle u_\sigma^p u_{\sigma'}^{p'};\, u_{\sigma''}^{p''}u_{\sigma'''}^{p'''}\rangle_0^{harm}} \sim \frac{a^2R^2}{b^2R^4}\frac{32\gamma^2}{\langle(e\lambda f)\rangle_{av}}. \qquad (31)$$

Assuming $a^2R^2 \sim b^2R^4$, $\gamma \approx 1-2$, and $\langle(e\lambda f)\rangle_{av} < 1$, see that the contribution of the single-phonon anharmonic mechanism can exceed, by two orders of magnitude, the usual Raman process.[4] Their ratio depends on the coupling constants a and b and a more exact calculation of the AFC, but in each case, even for $T \ll \Theta$, it is necessary to take this mechanism into account. It also follows from (31) that in (21) the anharmonic correlator lowers the temperature T_0 at which the Raman processes become important, in comparison with direct processes.[7]

The relation between $\langle \dot{u}_\sigma^p;\, \dot{u}_{\sigma'}^{p'}\rangle_\omega^{anharm}$ and $\langle u_\sigma^p \dot{u}_{\sigma'}^{p'};\, u_{\sigma''}^{p''}\dot{u}_{\sigma'''}^{p'''}\rangle_\omega^{harm}$ is the same as between the AFC and the H2FC of the displacements.

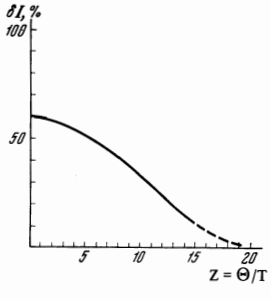
We note that independent estimates of $|A|^2$ in the point-charges model for ionic crystals[14] and from the contribution of anharmonism to the heat capacity[19] lead to quantities of the same order as in (27).

Optical branches. The optical branches at temperatures $T \sim \Theta$ can give a contribution comparable with the acoustic branches to the spin-lattice relaxation.[23,24] If there is a comparatively narrow optical branch in the crystal, separated by sufficient space from the other optical branches, then this can lead to an exponential growth of the EPR linewidth when $k_BT \lesssim \hbar\omega_{opt}$.

Let us consider the contribution of anharmonic effects in (22). We approximate the dispersion law

$$\omega_{kj} = \omega_{0j} + {}^1/_2 a_j k^2, \qquad (32)$$

and assume $|\omega_{kj} - \omega_{0j}| \ll \omega_{0j}$. If $k_BT \ll \hbar\omega_{0j}$, then the Planck factor in (22) leads to the temperature de-



Temperature dependence of $(I_6 - I_6')/I_6 \equiv \delta I$.

[6] Averaging of $\Delta_{1\sigma}^{\rho}\Delta_{1\sigma}^{\rho'*}$ over the directions of propagation is itself not complicated, [22] but, if $\mathbf{k}\cdot\mathbf{R} \sim 1$, it is also necessary to take into account the dependence of $|A|^2$ on the lengths of the wave vectors.

[7] Comparison of (28) with (23) gives $T_0 = 2 - 15°K$ for $\Theta = 10^2 - 10^3$ °K.

pendence AFC ~ $\exp(-\hbar\omega_0/k_BT)$. Using (32) and the narrowness of the band, and writing

$$V_{1,2,3}=\sqrt{\frac{\rho}{mN}}Q_{1,2,3}\Delta(k_1+k_2+k_3), \tag{33}$$

we obtain from (22) the AFC for the optical branches. We estimate this AFC by neglecting the polarization mixing, for atoms belonging to an other sublattice than the paramagnetic impurity. We have

$$\Delta^{p}_{kj\sigma}\approx e^{p}_{kj\gamma}-e^{p}_{kj0}\sim(m_1-m_0)/\sqrt{m_1m_0}. \tag{34}$$

The proportionality indicated in (34) occurs for the two-atom lattice (γ = 1.0). We take the constant $|Q|^2$ in the average outside the sign of summation over the wave vectors and estimate it in the long wavelength approximation, using (33) and (26),

$$\langle|Q_{t_1j_1\,t_2j_2\,t_3j_3}|^2\rangle_{av}\sim k_m^{6}\langle|A|^2\rangle_{av}/\omega_{0j}^{3}, \tag{35}$$

where k_m is the maximum value of the wave vector, $k\sim k_B\Theta/\hbar c$, and the estimate of $\langle|A|^2\rangle_{av}$ is given in (27). Thus,

$$\langle u^{p}_{\sigma};u^{p'}_{\sigma'}\rangle_0^{anharm}\approx\frac{2\hbar^2c^4k_m^{10}}{3\pi^4\rho^2}\gamma^2\sum_j\frac{n(\omega_{0j})[n(\omega_{0j})+1]}{a_j\omega_{0j}^{6}}\langle\Delta^{p}_{kj\sigma}\Delta^{p'*}_{kj\sigma'}\rangle_{av}. \tag{36}$$

The optical H2FC has in the approximation (34) the form

$$\langle u^{p}_{\sigma}u^{p'}_{\sigma'};u^{p''}_{\sigma''}u^{p'''}_{\sigma'''}\rangle_0^{harm}\approx\frac{\hbar^2k_m^{4}}{32\pi^4\rho^2}\sum_j\frac{n(\omega_{0j})[n(\omega_{0j})+1]}{a_j\omega_{0j}^{2}} \tag{37}$$

$$\times{}^1/_2[\langle\Delta^{p}_{kj\sigma}\Delta^{p''*}_{kj\sigma''}\rangle_{av}\langle\Delta^{p'}_{kj\sigma}\Delta^{p'''*}_{kj\sigma'''}\rangle_{av}+\langle\Delta^{p}_{kj\sigma}\Delta^{p'''*}_{kj\sigma'''}\rangle_{av}\langle\Delta^{p'}_{kj\sigma}\Delta^{p''*}_{kj\sigma''}\rangle_{av}].$$

Equation (37) agrees with the formula obtained by Kochelaev[23] for w_{km}. The ratio (31) has the form

$$\frac{\Gamma^{anharm}_{mkln}}{\Gamma^{harm}_{mkln}}\sim\frac{a^2k_m^{2}}{b^2}20\gamma^2\frac{c^4k_m^{4}}{\omega_{0j}^{4}}\frac{1}{\langle\Delta^{p}_{kj\sigma}\Delta^{p*}_{kj\sigma}\rangle_{av}}, \tag{38}$$

$\hbar ck_m\approx k_B\Theta$, $a^2k_m^2\sim b^2$, so that the ratio (38) is $\sim20\gamma^2$ for $\omega_{0\gamma}\approx k_B\Theta/\hbar$ and ~1 for $\omega_{0j}\approx3k_B\Theta/\hbar$. Thus, our estimates indicate that, even for the optical branches, the contribution of the anharmonism to the relaxation coefficients can be substantial.

We note that the transport processes, which are important here, were taken into account in (36). Without them, the value of (36) is reduced to one half.

Interference terms. Interference terms appear in Eq. (11). Their role can be important if the contribution to (11) of two different autocorrelators are of the same order. We consider the correlator $\langle u_\sigma;u_{\sigma'}u_{\sigma''}\rangle$. It differs from zero only with account of anharmonism, and can give a contribution comparable with $\langle u_\sigma;u_{\sigma'}\rangle$ and $\langle u_\sigma u_{\sigma'};u_{\sigma''}u_{\sigma'''}\rangle$ in first order in the cubic anharmonism.

With the help of (12) and (A.4), one can show that

$$\langle u^{p}_{\sigma};u^{p'}_{\sigma'}u^{p''}_{\sigma''}\rangle_\omega\approx\left(\frac{\hbar^{1/3}}{2mN}\right)^{3/2}\sum_{1,2,3}\frac{\Delta^{p}_{1\sigma}\Delta^{p'}_{2\sigma'}\Delta^{p''}_{3\sigma''}}{\sqrt{\omega_1^{3}\omega_2\omega_3}}2V_{-1,-2,-3}n_2(n_2+1)\delta(\omega_2-\omega_3). \tag{39}$$

It follows from (39) that the interference component $\langle u_\sigma;u_{\sigma'}u_{\sigma''}\rangle$ gives the same temperature dependence for $T\ll\Theta$ and $T>\Theta$ as the H2FC or the AFC. It is not difficult to obtain a numerical estimate of (39) on the basis of the approximation (27) for the acoustic branches and (33) and (35) for the optical branches is similar to what was done for the correlator (22).

The parameter ω^*. The parameter ω^* in the theory of spin-phonon kinetic equations determines one width of the frequency distribution of the FC. If $\omega\ll\omega^*$, then the FC at the frequency and at zero can be assumed to be the same. Thus, in (24), although $\omega\ll k_BT/\hbar(T<\Theta)$ or $k_B\Theta$ $(T>\Theta)$, one can replace $\delta(\omega_1-\omega_2+\omega)$ by $\delta(\omega_1-\omega_2)$, which also leads to H2FC independent of ω. The value of the H2FC begins to fall off sharply only for $\hbar\omega\sim k_BT$ $(T<\Theta)$, or $\omega\sim k_B\Theta/\hbar$ $(T>\Theta)$ because of the Planck factor $n_1(n_2+1)\delta(\omega+\omega_1-\omega_2)$. The completely analogous dependence on ω for the AFC follows from (22). Consequently, $\omega^*\sim k_BT/\hbar$ $(T<\Theta)$ or $\omega^*\sim k_B\Theta/\hbar$ $(T>\Theta)$, which agrees with the conclusion of Bloch and Wangsness,[5] while account of the anharmonism does not change the estimate of ω^*. The ω^* are of the same order for the velocity correlators.

Similar considerations show that the correlator determined by the optical branch with the narrow band begins to fall off sharply when ω becomes comparable with the width of the optical band. In other words, for the optical branches, $\omega^*\sim a_jk_m^2$ (which also occurs for the H2FC).

If $T\sim T_0$, then the AFC and the H2FC do not play roles and then $\omega^*\sim\Gamma_{kj}(\omega_{kj})$, where $\omega_{kj}=\omega$UHF, i.e., $\omega^*<\omega$, and is actually determined by the lifetime of the resonance phonons. This conclusion follows from (23), if we replace $\delta(\omega-\omega_1)$ in the latter by a bell curve with width $\Gamma_{kj}(\omega_{ky})$.

Thus, for $T\sim T_0$ we have $\omega^*\sim\Gamma_{kj}(\omega_{kj})$ for $T_0<T<\Theta$ we have $\omega^*\sim k_BT/\hbar$, and for $T\gtrsim\Theta$ we have $\omega^*\sim k_B\Theta/\hbar$ for the acoustic phonons and $\omega^*\sim a_jk_m^2$ for the optical phonons.

5. CONCLUSION

Actually, any mechanism can be dominant in (11). A typical situation, without account of anharmonism, is the following: the single-phonon mechanism with constant a plays a role for $T\sim T_0$ and the two-phonon mechanism with constant b for $T>T_0$. Account of anharmonism leads to the result that the contribution of the single-phonon anharmonic correlator with constant a, for $T>T_0$, can be the same, as or in the most favorable case, two orders larger, than the contribution of the ordinary harmonic correlator. This is true both for the acoustic branches and for the narrow optical branches.

Qualitatively, the anharmonic contribution could be observed in the temperature dependence of the phonon width of the EPR line only in simple lattices, where there are no optical branches, or in a lattice in which the optical branches are sufficiently far removed from the acoustic one, so that the contribution of the optical branches could be neglected in the range $\Theta/10<T<\Theta$. One could then expect a departure of the temperature dependence of the phonon width of the EPR line in the specified range from the harmonism dictated by the two phonon correlator.

We also note that our calculations of the single-phonon FC with account of the scattering of phonons by static displacements (see Sec. 36, of[15]) have shown that the scattering from defects leads, at small defect concentrations or small static distortions, to an inconsequential change in the relaxation coefficients in comparison with an ideal lattice (here, the local and quasilocal oscillations were not taken into account).

These changes are proportional to $c(1-c)\epsilon^2$, where c is the defect concentration and ϵ is a parameter characterizing the relative change of mass or force constants.

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APPENDIX

For $\omega \neq 0$, we have

$$\langle (a_{kj}-a_{-kj}); (a_{-kj}-a_{kj}^+)\rangle_\omega = -\frac{1}{\pi}\frac{[n(\omega)+1]\Gamma_{kj}(\omega)}{[(\omega^2-\omega_{kj}^2)/2\omega_{kj}-P_{kj}(\omega)]^2+\Gamma_{kj}^2(\omega)} \tag{A.1}$$

As $\omega \to 0$,

$$\langle (a_{kj}-a_{-kj}^{\pm}); (a_{-kj}-a_{kj}^+)\rangle_0 = -\frac{1}{\pi}\frac{4}{\omega_{kj}^2}\lim_{\omega\to 0}[n(\omega)+1]\Gamma_{kj}(\omega). \tag{A.2}$$

The role of real correlators in the limit as $\omega \to 0$ is seen from (A.3):

$$\begin{aligned}
\langle a_{kj}; a_{kj}^+\rangle_{\omega\to 0} &= \frac{1}{\pi\omega_{kj}^2}\lim_{\omega\to 0}[n(\omega)+1]\Gamma_{kj}(\omega),\\
\langle a_{kj}; a_{kj'}^+\rangle_{\omega\to 0} &= \frac{1}{\pi\omega_{kj}\omega_{kj'}}\lim_{\omega\to 0}[n(\omega)+1]\Gamma_{kjkj'}(\omega),\\
\langle a_{kj}; a_{kj}\rangle_{\omega\to 0} &= \frac{-1}{\pi\omega_{kj}^2}\lim_{\omega\to 0}[n(\omega)+1]\Gamma_{kj}(\omega),
\end{aligned} \tag{A.3}$$

the quantity $\Gamma_{kjkj'}$ is defined in[15].

The interference terms are represented in (A.4):

$$\begin{aligned}
&\langle (a_{kj}-a_{-kj}^+); (a_{k_1j_1}-a_{-k_1j_1}^+)(a_{k_2j_2}-a_{-k_2j_2}^+)\rangle_0\\
&\quad = 2V_{-kj;\,-k_1j_1;\,-k_2j_2}\frac{n_1(n_1+1)}{\hbar\omega_{kj}}\delta(\omega_1-\omega_2).
\end{aligned} \tag{A.4}$$

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