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CONCERNING ONE MECHANISM FOR ABSORPTION OF LOW FREQUENCY ELECTROMAGNETIC OSCILLATIONS BY LOCALIZED STATES IN CRYSTALS

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It is shown that when anharmonicity is taken into account the local of quasi-local oscillations of impurity centers containing ions lead to the appearance of a peak in the low frequency electromagnetic absorption spectrum at frequencies $\omega \lesssim \Gamma_K$, where Γ_K is the local oscillation damping. The dielectric losses due to this mechanism possess a specific temperature dependence and may be comparable with (or even greater than) the losses calculated in the harmonic approximation. A similar type of damping connected with electron local states of impurity centers is considered and it is shown that it may be significant in the absence of a symmetry center.

LOCAL oscillations which occur in the vicinity of impurity atoms or defects in crystals[1] give rise to peaks in the infrared absorption spectrum at the frequencies ω_K of these oscillations. Allowance for anharmonicity leads, on the one hand, to a broadening Γ_K of these peaks, and on the other to the appearance of new peaks (overtones) at multiple or combination frequencies. This corresponds to the fact that, in the presence of local oscillations, peaks appear in the spectral distribution of the correlation function not only at the frequencies ω_K, but also at multiple and combination frequencies, and also at low frequencies $\omega \lesssim \Gamma_K$. As a result, owing to the finite width of the local levels, absorption of electromagnetic radiation with low (but not zero) frequency $\omega \lesssim \Gamma_K$ becomes possible, corresponding to processes at which a quantum of the same local oscillation is absorbed and emitted.

Physically this absorption mechanism is connected with the fact that allowance for the anharmonicity leads to a certain entanglement of the local states with the states of the continuous spectrum, and the exact and very complicated eigenfunctions correspond, strictly speaking, not to a discrete impurity level, but to a band of frequencies (energies) near ω_K, with width $\sim \Gamma_K$; owing to the smallness of Γ_K, the density of the states in this band can be quite high. Quantum transitions between different exact states inside this narrow band indeed ensure absorption of the electromagnetic radiation at frequencies $\omega \lesssim \Gamma_K$, which will be considered in Sec. 2 below.

No less intense an absorption of the low-frequency electromagnetic radiation should take place if not local, but quasi-local states are produced near the defect, within the continuous spectrum, corresponding to the peaks of the state density and to the spectral density of the square of the amplitude[2,3]. This question is discussed in Sec. 2.

Finally, in Sec. 3 we consider similar effects which arise in the case when the electromagnetic wave interacts with electronic localized states of the impurity centers.

All the discussed effects become much more pronounced if the impurity centers have no symmetry centers (the crystal itself, of course, can have a symmetry center in this case). We shall therefore consider below just such a case. The analysis will be made for the case of sufficiently low impurity-center concentrations when all the effects of the concentration broadening of local or quasi-local levels can be neglected.

1. ABSORPTION OF ELECTROMAGNETIC RADIATION BY LOCAL OSCILLATIONS

The imaginary part of the dielectric constant $\epsilon''_{xx}(\omega)$, which determines the coefficient of absorption of the electromagnetic radiation by the impurity centers, can be expressed in terms of the temporal correlation function for the dipole moment M of the center (see[4]):

$$\varepsilon_{xx}''(\omega) = 4\pi^2 N \,\mathrm{th}\,\frac{\omega}{2T} \langle M_x, M_x\rangle_\omega,$$

$$\langle M_x, M_x\rangle_\omega = \frac{1}{2\pi}\int_{-\infty}^{\infty} \langle\{M_x(t) M_x(0)\}\rangle e^{i\omega t}\,dt, \qquad (1)^*$$

where N is the number of centers per unit volume,

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*th ≡ tanh.

$\{AB\} = AB + BA$, $\langle \ldots \rangle$ denotes the quantum-statistical averaging, $\hbar = 1$, and $k = 1$.

If the dipole moment is connected with the vibrations of the atoms of the center (which contains charged ions), then M_x can be expanded in powers of the operators a_κ^+ and a_κ for the creation and annihilation of vibration quanta,

$$M_x = \sum_{\kappa} m_\kappa a_\kappa + \sum_{\kappa\kappa'} m_{\kappa\kappa'} a_\kappa^+ a_{\kappa'} + \sum_{\kappa\kappa'} m'_{\kappa\kappa'} a_\kappa a_{\kappa'} + \text{h.c.} \quad (2)$$

Here κ labels both the local oscillations and the oscillations of the continuous spectrum (which are distorted during the appearance of the defect). In our case of impurity centers without a symmetry center, the coefficients $m_{\kappa\kappa}$ (which take into account the nonlinear polarization of the electron shells by displacement of the ions), and also the coefficients V in (A.2), are generally speaking different from zero.

From (1) and (2) we see that the determination of $\epsilon''_{xx}(\omega)$ for small ω reduces to a calculation of correlation functions of the type

$$\langle a_\kappa, a_{\kappa'} \rangle_\omega, \quad \langle a_\kappa, a_{\kappa'}^+ \rangle_\omega, \ldots,$$
$$\langle a_\kappa^+ a_\kappa, a_{\kappa'}^+ \rangle_\omega, \ldots, \langle a_\kappa^+ a_\kappa, a_\kappa^+ a_\kappa \rangle_\omega.$$

This calculation can be carried out by the method of temperature Green's functions (see the appendix).

For example, if the decay of a local oscillation into another local oscillation and a crystal oscillation is much less probable than its decay into two crystal oscillations, then in the case of small ω ($\omega \lesssim \Gamma_\kappa \ll \omega_\kappa$, $\omega \ll T$, $\omega \neq 0$), as follows from formulas (A.5), (A.6), and (A.8) of the appendix, we have

$$\langle a_\kappa, a_{\kappa'}^+ \rangle_\omega = \frac{2}{\pi} \sum_{\kappa_1}{}' \frac{V_{\kappa_1\kappa_1\kappa} V^*_{\kappa_1\kappa_1\kappa'}}{\omega_\kappa \omega_{\kappa'}} \frac{2\Gamma_{\kappa_1}}{\omega^2 + 4\Gamma_{\kappa_1}^2} n_{\kappa_1}(n_{\kappa_1} + 1)$$
$$+ \sum_{\kappa_1\kappa_2}{}'' \frac{V_{\kappa_1\kappa_2\kappa} V^*_{\kappa_1\kappa_2\kappa'}}{\omega_\kappa \omega_{\kappa'}} (n_{\kappa_1} + n_{\kappa_2} + 2n_{\kappa_1} n_{\kappa_2})$$
$$\times \delta(\omega - \omega_{\kappa_1} + \omega_{\kappa_2}),$$
$$\langle a_\kappa^+ a_\kappa, a_{\kappa'}^+ \rangle_\omega = -\frac{2}{\pi} \frac{1}{\omega_\kappa} V^*_{\kappa\kappa\kappa'} \frac{2\Gamma_\kappa}{\omega^2 + 4\Gamma_\kappa^2} n_\kappa(n_\kappa + 1)$$
$$(\omega \ll \omega_\kappa, \omega_{\kappa'}),$$
$$\langle a_{\kappa_2}^+ a_{\kappa_1}, a_{\kappa'}^+ \rangle_\omega$$
$$= -\frac{1}{\omega_{\kappa'}} V^*_{\kappa_1\kappa_2\kappa'} (n_{\kappa_1} + n_{\kappa_2} + 2n_{\kappa_1} n_{\kappa_2}) \delta(\omega - \omega_{\kappa_1} + \omega_{\kappa_2}) \quad (3)$$
$$(\omega \ll \omega_{\kappa_1}, \omega_{\kappa_2}),$$

where Γ_{κ_1} is the damping of the local oscillation κ_1. In connection with the statements made in the appendix, the summation over κ_1 is carried out over only the local oscillations in the sum Σ' and over the oscillations of the continuous spectrum in the sum Σ''.

Using the same approach as in the appendix, we can readily show that the expressions for the correlation functions $\langle a_\kappa, a_{\kappa'} \rangle_\omega$ or $\langle a_\kappa^+, a_{\kappa'}^+ \rangle_\omega$ are obtained from formula (3) for $\langle a_\kappa, a_\kappa^+ \rangle_\omega$, by replacing in it $V_{\kappa_1\kappa_2\kappa_3} V^*_{\kappa_1\kappa_2\kappa_3}$ by $V_{\kappa_1\kappa_2\kappa} V_{\kappa_1\kappa_2\kappa'}$, or $V^*_{\kappa_1\kappa_2\kappa} V^*_{\kappa_1\kappa_2\kappa'}$, respectively. The correlation functions $\langle a_\kappa^+ a_\kappa, a_\kappa^+ a_{\kappa'} \rangle_\omega$ are determined by formula (A.6).

We consider first the contribution, connected only with the local oscillations, made by $\epsilon''_{1xx}(\omega)$ to the imaginary part of the dielectric constant. We therefore take into account, say in $\langle a_\kappa, a_{\kappa'}^+ \rangle$, only the first term for the time being. Substituting (2) in (1) and taking into consideration the presented expressions for the correlation functions, we find that in the region of low frequencies $\epsilon''_{1xx}(\omega)$ can be represented in the form

$$\varepsilon''_{1xx}(\omega) = \sum_{\kappa} \varepsilon''_{1xx}(\omega, \kappa)$$
$$= 16\pi^2 N \frac{\omega}{T} \sum_{\kappa}{}' A_\kappa^2 \frac{1}{\pi} \frac{2\Gamma_\kappa}{\omega^2 + 4\Gamma_\kappa^2} n_\kappa(n_\kappa + 1),$$
$$A_\kappa = \mathrm{Re} \sum_{\kappa'} \frac{m_{\kappa'}}{\omega_{\kappa'}} V_{\kappa\kappa\kappa'} + m_{\kappa\kappa}. \quad (4)$$

We see from this expression that the contribution made to $\epsilon''_{xx}(\omega)$ by the local oscillations is proportional to ω at low frequencies, when $\omega \ll \Gamma_\kappa$ for all such oscillations, and then the dependence of ϵ''_{1xx} on ω goes through a maximum, so that at high frequencies $\epsilon''_{1xx} \sim 1/\omega$. The coefficient A_κ contains a small third-order anharmonicity constant V_3 (or else a small coefficient $m_{\kappa\kappa}$ connected with the nonlinear polarization). However, Γ_κ is also proportional to V_3^2 (if decay of the local oscillation into two crystal oscillations is possible), and therefore for small ω the quantity $\epsilon''_{1xx}(\omega)$ does not contain the small anharmonicity parameter and can make an appreciable contribution to the dielectric loss. In the case of high-frequency local oscillations, when the local oscillations can decay only into three phonons, $\Gamma_\kappa \sim V_4^2$, where the fourth-order anharmonicity constant V_4 is much smaller than V_3, ϵ''_{1xx} is proportional to V_3^2/V_4^2 and is especially large.

For a rough estimate of $\epsilon''_{1xx}(\omega)$ let us consider, for example, the case when only one local oscillation arises near the impurity center of the charged ion, and we can neglect the nonlinear polarization $m_{\kappa\kappa}$. Then $m_\kappa \sim e u_{\kappa x}$ ($u_{\kappa x}(a_\kappa + a_\kappa^+)$ is the displacement of the impurity ion in the local oscillation) and $A_\kappa^2 \sim e^2 u_{\kappa x}^2 P_\kappa/\omega_\kappa$, where P_κ is of the same order as the frequency shift, due to the anharmonicity, of the local oscillation at $T = 0$. Since $u_{\kappa x}^2 \sim 1/M'\omega_\kappa$ ($\hbar = 1$), where M′ is the mass of the impurity ion, we have in this case for $\omega \ll \Gamma_\kappa$ and $T \gg \omega_\kappa$:

$$\varepsilon''_{1xx}(\omega) \sim 8\pi N\omega \frac{e^2}{M'} \frac{P_\varkappa T}{\omega_\varkappa{}^4 \Gamma_\varkappa}.$$

This value of ϵ''_{1xx} can be compared with the dielectric loss on charged defects, obtained in the harmonic approximation[7]. This loss makes a contribution $\epsilon''_{2xx}(\omega)$ to $\epsilon''_{xx}(\omega)$ (see formula (5)). According to the estimate given in[7], $\epsilon''_{2xx}(\omega)$ is of the order of $6\pi^2 N\omega e^2/M\omega_m^3$, where M is the average mass of the matrix atoms and ω_m is the maximum frequency of the continuous-spectrum oscillations. If decay of a local oscillation into two phonons is possible ($\omega_\kappa < 2\omega_m$), then $\omega_\kappa \Gamma_\kappa \sim TP_\kappa$ and $\epsilon''_{1xx}(\omega)$ has the same order of magnitude as $\epsilon''_{2xx}(\omega)$. On the other hand, in the case of high-frequency local oscillations ($\omega_\kappa > 2\omega_m$), when the local oscillation decays into three (or more) phonons, then $\Gamma_\kappa \ll P_\kappa$ and, as already indicated, $\epsilon''_{1xx}(\omega)$ is particularly large and can exceed $\epsilon''_{2xx}(\omega)$ when $T \gtrsim \omega_\kappa$.

When $T \to 0$ the damping Γ_κ tends to a constant limit, i.e., $\epsilon''_{1xx}(\omega)$ depends exponentially on the temperature (like $\exp(-\omega_{\kappa\,\min}/T)$, where $\omega_{\kappa\,\min}$ is the minimum frequency of the local oscillations). At high temperatures Γ_κ is proportional to T or T^2, depending on whether the local oscillation can decay into two or three phonons, and when $\omega \ll \Gamma_\kappa$ the value of $\epsilon''_{1xx}(\omega, \kappa)$ does not depend on the temperature or else is inversely proportional to T, respectively. Such a specific temperature dependence of $\epsilon''_{1xx}(\omega)$ can help separate the dielectric losses connected with the local oscillations.

The frequency dependence of $\epsilon''_{1xx}(\omega)$ has, in accord with (4), the form characteristic of the loss due to the relaxation processes and the corresponding characteristic relaxation times $\tau_\kappa = 1/2\Gamma_\kappa$. These processes are connected with the change in the occupation numbers of the local oscillations under the influence of the electric field of the wave E_x. Formula (4) can be easily obtained also with the aid of the usual approach of the phenomenological relaxation theory of oscillation damping, if account is taken of the fact that the quantity $-A_\kappa E_x$ determines, in accord with (4), (2), and (A.2), the change in the oscillation frequency κ when the field E_x is turned on. The microscopic approach used here makes it possible, however, to express $\epsilon''_{xx}(\omega)$ in terms of macroscopic characteristics of the dipole moment of the center and the anharmonicity, and makes it possible also to consider in unified fashion the losses connected with the oscillations of the continuous spectrum, particularly with quasi-local oscillations.

2. ABSORPTION OF ELECTROMAGNETIC RADIATION BY THE OSCILLATIONS OF THE CONTINUOUS SPECTRUM

In the harmonic approximation and neglecting nonlinear polarization ($m_{\kappa\kappa'} = 0$), as follows from (1) and (2), the dielectric loss is connected only with the low frequency oscillations of the crystal, for which $\omega_\kappa = \omega$. Recognizing that when anharmonicity is neglected we get

$$\begin{aligned}\langle a_\varkappa, \overset{+}{a}_{\varkappa'}\rangle_\omega &= (2n_\varkappa + 1)\,\delta(\omega - \omega_\varkappa)\,\delta_{\varkappa\varkappa'} \\ &\approx 2\frac{T}{\omega}\,\delta(\omega - \omega_\varkappa)\,\delta_{\varkappa\varkappa'} \quad (\omega \ll T)\end{aligned}$$

and substituting (2) in (1), we find that the corresponding contribution to $\epsilon''_{xx}(\omega)$ is

$$\varepsilon''_{2xx}(\omega) = 4\pi^2 N \sum_\varkappa |m_\varkappa|^2\,\delta(\omega - \omega_\varkappa) \qquad (\omega \ll T). \tag{5}$$

Loss of this type was considered by Vinogradov[7] and was compared above with $\epsilon''_{1xx}(\omega)$. We shall therefore no longer discuss this contribution to $\epsilon''_{1xx}(\omega)$.

Allowance for anharmonicity and nonlinear polarization leads to an additional contribution to the dielectric loss, connected with the oscillations of the continuous spectrum. This loss is determined by the entire spectrum of oscillations, with the frequency region $\omega_\kappa \sim \kappa$ corresponding to a very small volume in κ-space and making a negligibly small contribution. We can therefore assume that $\omega_\kappa, \omega_{\kappa'} \gg \omega$ and determine the correlation functions with account of anharmonicity by means of formulas (A.5) and (A.8). Taking these formulas into consideration, as well as the analogous formulas for $\langle a_\kappa, a_{\kappa'}\rangle_\omega$ and $\langle \overset{+}{a}_\kappa, \overset{+}{a}_{\kappa'}\rangle_\omega$ (see Sec. 1) and substituting (2) in (1), we find that the corresponding contribution to $\epsilon_{xx}(\omega)$ is

$$\begin{gathered}\varepsilon''_{3xx}(\omega) = 16\pi^2 N \frac{\omega}{T} \sum_{\varkappa\varkappa'}{}'' |A_{\varkappa\varkappa'}|^2 n_\varkappa (n_\varkappa + 1)\,\delta(\omega_\varkappa - \omega_{\varkappa'}), \\ A_{\varkappa\varkappa'} = \mathrm{Re} \sum_{\varkappa''} \frac{m_{\varkappa''}}{\omega_{\varkappa''}} V_{\varkappa\varkappa'\varkappa''} + m_{\varkappa\varkappa'} \qquad (\omega \ll \omega_m, \quad \omega \ll T).\end{gathered} \tag{6}$$

$\epsilon''_{3xx}(\omega)$ is proportional to ω, just like $\epsilon''_{2xx}(\omega)$, but since it contains as a factor the square of the small anharmonicity or nonlinear-polarization constant, it is usually appreciably smaller than $\epsilon''_{2xx}(\omega)$. Unlike ϵ''_{2xx}, the value of ϵ''_{3xx} is proportional to T when $T > \omega_m$ and at high temperatures it can amount to ~10% of ϵ''_{2xx}. However, as seen from (6), $\epsilon''_{3xx}(\omega)$ can become much larger if the distribution function of the oscillation frequencies has sharp maxima (for example, in the presence of a narrow branch of optical-oscillation frequencies).

The contribution of $\epsilon''_{3xx}(\omega)$ to the dielectric loss increases also in the case of centers near which quasi-local oscillations are produced[2,3]. In the investigation of this case it is more convenient not to make use of formula (6), in which summation is carried out over the exact normal oscillations of the harmonic crystal perturbed by the presence of the center, but go over to the usual displacements u_{sx} of the atoms about the center (s—number of atom). To this end we introduce the quantities

$$A_{ss'ij} = \sum_{\varkappa\varkappa'} A_{\varkappa\varkappa'}\beta_{\varkappa si}\beta_{\varkappa' s' j},$$

where $\beta_{\kappa si}$ are the coefficients in the expansion of the real normal coordinates in the displacements of the atoms:

$$a_\varkappa + a_\varkappa^+ = \sum_{si} \beta_{\varkappa si} u_{si} \qquad (i = x, y, z),$$

after which we can transform the quadratic form

$$\sum_{\varkappa\varkappa'} A_{\varkappa\varkappa'}(a_\varkappa + a_\varkappa^+)(a_{\varkappa'} + a_{\varkappa'}^+) \equiv A_{ss'ij}u_{si}u_{s'j}$$

(here and below, summation is implied over the repeated indices such as s or i). Neglecting anharmonicity, the quantities $A_{ss'ij}$ are the coefficients in the quadratic term of the expansion of the dipole moments of the center M_x in powers of the displacements, and have a simple physical meaning. With increasing distance from the center, these quantities decrease rapidly. Making the indicated transition from the normal coordinates to the displacements, and taking (A.8) into consideration, we can rewrite expression (6) in the form

$$\varepsilon''_{3xx}(\omega) = 2\pi^2 N\frac{\omega}{T}A_{s_1s_2ij}A_{s_3s_4lm}$$

$$\times\langle u_{s_1i}(t)u_{s_2j}(t),\ u_{s_3l}(t')u_{s_4m}(t')\rangle_\omega$$

$$= 4\pi^2 N\frac{\omega}{T}A_{s_1s_2ij}A_{s_3s_4lm}\int_{-\infty}^{\infty}\langle u_{s_1i}, u_{s_3l}\rangle_{\omega'}$$

$$\times\langle u_{s_2j}, u_{s_4m}\rangle_{\omega-\omega'}\left(1 + \operatorname{ch}\frac{\omega'}{T}\right)^{-1} d\omega' (\omega \ll \omega_m, \omega \ll T) \quad (7)^*$$

We used here Wick's temperature theorem and took into account the fact that $A_{ss'ij} = A_{s'sji}$. The appearance of the factor $(1 + \cosh\omega' T^{-1})^{-1}$ under the integral sign is connected with the fact that the correlation functions $\langle A, B\rangle_\omega$ correspond to the anti-commutator AB + BA.

Let us apply formula (7) to a center consisting of a heavy impurity ion that differs in mass M′ (but not in the force constants) from the atoms of the cubic lattice (which have a mass M). In this case the quasi-local oscillations are produced in the region of very low frequencies. The correlation function $\langle u_{si}, u_{s'j}\rangle_\omega$ was determined for this case by Eliott and Taylor[8], and it has a sharp peak near the frequency of the quasi-local oscillation ω_0. It is easy to verify that in the region of the peak $\langle u_{si}, u_{s'j}\rangle_\omega$ can be represented approximately in the form

$$\langle u_{si}, u_{s'j}\rangle_{|\omega'|}$$

$$= \frac{1}{2\pi}\delta_{ij}\frac{1}{M'\omega_0}\operatorname{cth}\frac{|\omega'|}{2T}\ \frac{d_{s0}d_{0s'}\Gamma_0/2}{(|\omega'| - \omega_0)^2 + \Gamma_0^2/4}, \quad (8)^*$$

where $|\omega'| \approx \omega_0 \ll \omega_m$,

$$\Gamma_0 = \frac{\pi}{2}\ \frac{M'}{M}\omega_0^2 g(\omega_0),$$

$$\omega_0^2 = \frac{M}{M'}\left(\int\frac{g(\omega)\,d\omega}{\omega^2}\right)^{-1};$$

$$d_{s0} = \sum_k\frac{\exp(-i\mathbf{k}\mathbf{R}_s)}{\omega_k^2}\left(\sum_k\frac{1}{\omega_k^2}\right)^{-1} \quad (M' \gg M); \qquad (9)$$

k denotes the wave vector **k** and the number of the oscillation branch of the ideal crystal, $g(\omega)$ is the distribution function of the oscillation frequencies, normalized to unity ($g(\omega) \sim \omega^2$ for small ω), and it is assumed here that the impurity atom is at the zero site. In the derivation of (8) we took account of the fact that for the quasi-local oscillations $\Gamma_0 \ll \omega_0$.

Substituting (8) in (7) and integrating over ω', we obtain

$$\varepsilon''_{3xx}(\omega) = 16\pi^2 N\frac{\omega}{T}|A_{0ij}|^2\frac{1}{\pi}\ \frac{\Gamma_0}{\omega^2 + \Gamma_0^2}n_0(n_0 + 1),$$

$$A_{0ij} = \frac{1}{2M'\omega_0}\sum_{ss'} A_{ss'ij}d_{s0}d_{s'0}, \qquad n_0 = \left(\exp\frac{\omega_0}{T} - 1\right)^{-1}$$

$$(\omega \lesssim \Gamma_0 \ll \omega_0, \quad \omega \ll T). \qquad (10)$$

The frequency dependence of ϵ''_{3xx} is the same as for ϵ''_{1xx}. At low temperatures ϵ''_{3xx}, just like ϵ''_{1xx}, depends exponentially on T, but in the case of quasi-local oscillations the temperature dependence of ϵ'' goes over much earlier to the high temperature limit corresponding to $\epsilon''_{3xx} \sim T$ (when $\omega \ll \Gamma_0$). Neglecting the nonlinear polarizability, the order of magnitude of A_{0ij}^2 is $A_{0ij}^2 \sim e^2P_0/\omega_m M'\omega_0$, where P_0 is the frequency shift of the short-wave oscillation of the ideal crystal ($\omega_k \sim \omega_m$) due to the anharmonicity at T = 0 (usually $P_0 \sim 10^{-2}\omega_m$). If we use for an estimate of ω_0

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*ch ≡ cosh.

*cth ≡ coth.

and Γ_0 the Debye approximation, in which $g(\omega) = 3\omega^2/\omega_m^3$, then, in accord with (9),

$$\omega_0^2 = \frac{M}{3M'}\omega_m^2, \quad \Gamma_0 = \frac{3\pi}{2}\frac{M'}{M}\frac{\omega_0^4}{\omega_m^3} = \frac{\pi}{2}\frac{\omega_0^2}{\omega_m}.$$

Substituting these estimates in (10), we find that when $\omega \ll \Gamma_0$ and $T \gg \omega_0$ $\epsilon''_{3xx}(\omega)$ is of the order

$$\varepsilon''_{3xx}(\omega) \sim 10^3 N\omega \frac{P_0}{\omega_m}\left(\frac{M'}{M}\right)^{3/2}\frac{e^2}{M\omega_m^3}\frac{T}{\omega_m},$$

From a comparison of these results with the estimate given above, $\epsilon''_{2xx}(\omega) \sim 10^2 N\omega e^2/M\omega_m^3$, we see that in the case of sufficiently heavy impurity atoms at high temperatures $\epsilon''_{3xx}(\omega)$ may exceed $\epsilon''_{2xx}(\omega)$, i.e., the interaction with the quasi-local oscillations will make the main contribution to the dielectric loss.

Similar results for a somewhat more general case of quasi-local oscillations (for example, corresponding to the intramolecular oscillations in impurity molecules or complexes), can be obtained by expanding the displacements in terms of the approximate normal oscillations κ, describing the long-lived quasi-local oscillations, and in terms of the remaining oscillations k. Then the harmonic part of the Hamiltonian of the oscillations is not completely diagonalized and contains, in particular, terms of the type

$$\sum_{\varkappa k} H_{\varkappa k} a_\varkappa^+ a_k + \text{h.c.}$$

(which upon successful separation of the quasi-local oscillations can be made sufficiently small). If the main contribution in the expansion (2) of the dipole moment is made by such quasi-local oscillations, then, obviously, we obtain, using the same reasoning as in the case of local oscillations in Sec. 1, expression (4) for $\epsilon''_{3xx}(\omega)$. All that changes is the meaning of the damping Γ_κ, which can now contain not only the term (A.7), connected with the anharmonicity (and playing in the case of quasi-local oscillations a much smaller role than in the case of local oscillations), but also the temperature-independent term

$$\Gamma_\varkappa = \pi \sum_k |H_{\varkappa k}|^2 \delta(\omega_\varkappa - \omega_k),$$

which takes into account the non-stationarity of the quasi-local oscillations and which determines the damping $\Gamma_0/2$ in the case considered above.

3. INFLUENCE OF LOCALIZED ELECTRONIC STATES ON THE ABSORPTION OF ELECTROMAGNETIC RADIATION

For simplicity we confine ourselves to the case of impurity centers containing one electron, and neglect the probability of the transitions of the electrons to the conduction band. In the second-quantization representation, the operator of the dipole moment can be represented in the form

$$M_x = \sum_{pp'} m_{pp'} b_p^+ b_{p'}, \tag{11}$$

where b_p^+ and b_p are the operators of creation and annihilation of the electrons in the p-th local state. In the case under consideration, when there is no symmetry center, the diagonal coefficients m_{pp} are in general different from zero. The correlation functions $\langle N_p, N_{p'}\rangle$ $(N_p = b_p^+ b_p)$, corresponding to just these diagonal terms in (11), are of importance for the investigation of the absorption of the low frequency oscillations.

As in the case of local oscillations, let us find $\langle N_p, N_{p'}\rangle$, defining the Green's function $\langle\langle N_p; N_{p'}\rangle\rangle$ (for the anticommutators). We consider, for example, the closely-lying electronic levels, when the Bohr frequencies are smaller than ω_m, and assume first for concreteness that the Hamiltonian of the system of electrons of the impurity centers and of the oscillations is

$$H = \sum_p \omega_p b_p^+ b_p + \sum_\varkappa \omega_\varkappa a_\varkappa^+ a_\varkappa + \sum_{pp'\varkappa} V_{pp'\varkappa} b_p^+ b_{p'} (a_\varkappa + a_\varkappa^+). \tag{12}$$

Assuming the constants $V_{pp'\kappa}$ small, we can go through the usual procedure of splitting up the chain of equations for the Green's function, neglecting, in particular, the functions $\langle\langle b_p^+ b_{p'}; N_{p''}\rangle\rangle$ $(p \neq p')$ that are small with $\langle\langle N_p; N_{p'}\rangle\rangle$. We shall also assume that the number of electrons is much smaller than the number of the centers at which they can be situated, and consequently the average electron occupation numbers are $n_p \ll 1$, and the quantities $n_p n_{p'}$ can be neglected compared with n_p. This assumption, obviously, does not limit the generality, since the centers unoccupied by the electrons do not lead to absorption of the type under consideration.

As a result of the indicated procedure, the system of equations for the Green's function $\langle\langle N_p; N_{p'}\rangle\rangle$ (constructed for the anticommutators) takes the form

$$\omega \langle\langle N_p; N_{p'}\rangle\rangle_\omega = \frac{1}{\pi} n_p \delta_{pp'} - \sum_{p_1} R_{pp_1}(\omega) \langle\langle N_{p_1}; N_{p'}\rangle\rangle_\omega,$$

$$R_{pp}(\omega) = - \sum_{p_1 (p_1 \neq p)} R_{p_1 p}(\omega), \tag{13}$$

where

$$R_{pp_1}(\omega) = R'_{pp_1}(\omega) - R'_{pp_1}(-\omega),$$

$$R'_{pp_1}(\omega) = \sum_{\varkappa} |V_{pp_1\varkappa}|^2 \left[\frac{n_\varkappa + 1}{\omega - \omega_{pp_1} - \omega_\varkappa} + \frac{n_\varkappa}{\omega - \omega_{pp_1} + \omega_\varkappa} \right],$$

$$p \neq p_1, \quad \omega_{pp_1} = \omega_p - \omega_{p_1}. \tag{14}$$

In the expressions for

$$R_{pp_1}(\omega \pm i\delta) = P_{pp_1}(\omega) \mp i\Gamma_{pp_1}(\omega)$$

at small values of ω we can neglect P_{pp_1} with ω or with Γ_{pp_1}, and we can assume that

$$\begin{aligned} \Gamma_{pp_1}(\omega) &= \Gamma_{pp_1}(0) \equiv \Gamma_{pp_1} \\ &= 2\pi \sum_{\varkappa} |V_{pp_1\varkappa}|^2 [(n_\varkappa + 1) \\ &\times \delta(\omega_{p_1p} - \omega_\varkappa) + n_\varkappa \delta(\omega_{pp_1} - \omega_\varkappa)]. \end{aligned} \tag{15}$$

Then the solution of (13) can be written in matrix form

$$\langle\langle N_p; N_{p'} \rangle\rangle_{\omega \pm i\delta} = \frac{1}{\pi} (\omega I \mp i\Gamma)^{-1}_{pp_1} n_{p_1} \delta_{p_1p'}, \tag{16}$$

where I is a unit matrix and Γ is the matrix with matrix elements Γ_{pp_1}.

Substituting (16) in (A.1), we can find the correlation functions N_p, $N_{p'}$ and then determine, using formulas (1) and (11), the dielectric loss $\epsilon''_{exx}(\omega)$ due to the impurity-center electrons. As a result we get

$$\begin{aligned} &\varepsilon''_{exx}(\omega) \\ &= 4\pi N \frac{\omega}{T} \sum_{pp'} m_{pp} m_{p'p'} \operatorname{Im} (\omega I + i\Gamma)^{-1}_{pp_1} n_{p_1} \delta_{p_1p'}. \end{aligned} \tag{17}$$

In particular, for centers with two discrete electronic levels (p, p′ = 1, 2) we obtain

$$\begin{aligned} \varepsilon'_{exx}(\omega) &= 2\pi^2 N_e \frac{\omega}{T} (m_{11} - m_{22})^2 \\ &\frac{e^{\omega_{21}/T}}{(e^{\omega_{21}/T} + 1)^2} \frac{1}{\pi} \frac{\Gamma_{12} + \Gamma_{21}}{\omega^2 + (\Gamma_{12} + \Gamma_{21})^2}. \end{aligned} \tag{18}$$

where $N_e = N(n_1 + n_2)$ is the total number of electrons in the centers and

$$\Gamma_{12} + \Gamma_{21} = 2\pi [2n(\omega_{21}) + 1] \sum_{\varkappa} |V_{pp_1\varkappa}|^2 \delta(\omega_{21} - \omega_\varkappa).$$

In the derivation of (18) we took into account the fact that $n_1/n_2 = \Gamma_{12}/\Gamma_{21} = \exp(\omega_{21}/T)$.

Since the radius of the electronic wave function is much larger than the amplitude of the oscillations even for light ions, in our case when there is no symmetry center m_{pp} can be appreciably larger than m_κ, i.e., the dielectric loss due to the electrons of the centers can be quite appreciable, especially for large $\Gamma_{12} + \Gamma_{21}$ (Γ, however, must not be too small, so as to be able to satisfy the condition $\omega \lesssim \Gamma_{12} + \Gamma_{21}$).

From (18) we see that ϵ''_{exx} is exponentially small at low temperatures ($T \ll \omega_{21}$), and then with increasing temperature ϵ''_{exx} reaches a maximum, after which it decreases like $1/T^2$ for $T \gg \omega_{21}$ and $\omega \ll \Gamma_{12} + \Gamma_{21}$.

It is easy to show that (7) and (8) remain valid in a case of a Hamiltonian of electron-phonon interaction which is more general than (12). The quantities $\Gamma_{pp'}$ determine in this case, too, the probability of non-radiative electronic transitions between the states p′ and p, and for each concrete form of the Hamiltonian they can be readily calculated in the usual manner. We see from (18) that for large distances between the electronic levels, when $\omega_{21} \gg T$ for arbitrary temperatures, the losses of the type under consideration become negligibly small.

We note in conclusion that an investigation of the frequency dependence of the described mechanism of electromagnetic-oscillation absorption could yield interesting information on the damping of local oscillations as well as on the probabilities of the transitions between electronic levels.

APPENDIX

The calculation of the Fourier components of the correlation functions for small values of ω is conveniently carried out by considering retarded Green's functions of the type

$$\langle\langle A; B \rangle\rangle = -i\theta(t) \langle \{A(t) B(t')\} \rangle,$$

corresponding to the anticommutators, and taking into account the obvious relations between the Fourier components of the Green's functions and of the correlation functions

$$\langle A, B \rangle_\omega = i[\langle\langle A; B \rangle\rangle_{\omega + i\delta} - \langle\langle A; B \rangle\rangle_{\omega - i\delta}], \quad \delta \to +0. \tag{A.1}$$

Let us consider, for example, the Green's function $\langle\langle a_\kappa; \overset{+}{a}_{\kappa'} \rangle\rangle$ for an oscillation Hamiltonian that takes into account third-order anharmonicity:

$$\begin{aligned} H &= \sum_{\varkappa} \omega_\varkappa a_\varkappa^+ a_\varkappa \\ &+ \frac{1}{6} \sum_{\varkappa\varkappa'\varkappa''} [V_{\varkappa\varkappa'\varkappa''} (a_\varkappa a_{\varkappa'}^+ a_{\varkappa''}^+ \\ &+ a_{\varkappa'}^+ a_\varkappa a_{\varkappa''}^+ + a_{\varkappa'}^+ a_{\varkappa''}^+ a_\varkappa) \\ &+ V'_{\varkappa\varkappa'\varkappa''} a_\varkappa a_{\varkappa'} a_{\varkappa''} + \text{h.c.}]. \end{aligned} \tag{A.2}$$

Setting up in the usual manner the equations of motion for the Green's function, going over to

Fourier components, and retaining in the right side only the Green's functions which are significant in the region of small ω, namely of the type $\langle\langle \overset{+}{a}_{\kappa_1} a_{\kappa_2};\ \overset{+}{a}_{\kappa'}\rangle\rangle$ (the anharmonicity constants, as usual, are assumed small), we obtain

$$(\omega-\omega_{\varkappa})\langle\langle a_{\varkappa};\ a_{\varkappa'}{}^{+}\rangle\rangle_{\omega}=\frac{1+2n_{\varkappa}}{2\pi}\,\delta_{\varkappa\varkappa'}$$

$$+\sum_{\varkappa_1\varkappa_2} V_{\varkappa_1\varkappa_2\varkappa}\left\langle\left\langle \left(a_{\varkappa_2}{}^{+}a_{\varkappa_1}+\frac{1}{2}\,\delta_{\varkappa_1\varkappa_2}\right);\quad a_{\varkappa'}{}^{+}\right\rangle\right\rangle_{\omega},$$

$$n_{\varkappa}=[\exp(\omega_{\varkappa}/T)-1]^{-1}. \tag{A.3}$$

It is convenient to differentiate the Green's function $\langle\langle \overset{+}{a}_{\kappa_2}(t)a_{\kappa_1}(t);\ \overset{+}{a}_{\kappa'}(t')\rangle\rangle$ in (A.3) with respect to t′ (and not with respect to t as usual), making it possible to express these functions for $\kappa_1=\kappa_2$ in terms of the functions $\langle\langle \overset{+}{a}_{\kappa_1}a_{\kappa_1};\ (\overset{+}{a}_{\kappa_1}a_{\kappa_1}-n_{\kappa_1})\rangle\rangle$, which were determined earlier[5], and express them for $\kappa_1\neq\kappa_2$ in terms of the functions $\langle\langle \overset{+}{a}_{\kappa_2}a_{\kappa_1};\ \overset{+}{a}_{\kappa_1}a_{\kappa_2}\rangle\rangle$, which can be easily determined in the harmonic approximation. Neglecting the small terms $\sim V/\omega_{\kappa}$, the corresponding equation for the Fourier components at small (but nonzero) ω takes the form

$$(\omega-\omega_{\varkappa'})\langle\langle \overset{+}{a}_{\varkappa_2}a_{\varkappa_1};\ \overset{+}{a}_{\varkappa'}\rangle\rangle_{\omega}$$

$$=V^{*}_{\varkappa_1\varkappa_2\varkappa'}\langle\langle \overset{+}{a}_{\varkappa_2}a_{\varkappa_1};\ (\overset{+}{a}_{\varkappa_1}a_{\varkappa_2}-\delta_{\varkappa_1\varkappa_2}n_{\varkappa_1})\rangle\rangle_{\omega}. \tag{A.4}$$

Taking (A.1) into account, we can express with the aid of Eqs. (A.3) and (A.4) the correlation functions $\langle a_{\kappa},\ \overset{+}{a}_{\kappa'}\rangle_{\omega}$ and $\langle \overset{+}{a}_{\kappa_2}a_{\kappa_1},\ \overset{+}{a}_{\kappa'}\rangle_{\omega}$ for small values of ω in terms of $\langle \overset{+}{a}_{\kappa_1}a_{\kappa_1},\ \overset{+}{a}_{\kappa_2}a_{\kappa_2}\rangle_{\omega}$ and $\langle \overset{+}{a}_{\kappa_2}a_{\kappa_1},\ \overset{+}{a}_{\kappa_1}a_{\kappa_2}\rangle_{\omega}$:

$$\langle a_{\varkappa},\ \overset{+}{a}_{\varkappa'}\rangle_{\omega}=\sum_{\varkappa_1\varkappa_2}{}'\frac{1}{\omega_{\varkappa}\,\omega_{\varkappa'}}V_{\varkappa_1\varkappa_1\varkappa}V^{*}_{\varkappa_2\varkappa_2\varkappa'}\langle \overset{+}{a}_{\varkappa_1}a_{\varkappa_1},\ (\overset{+}{a}_{\varkappa_2}a_{\varkappa_2}-n_{\varkappa_2})\rangle_{\omega}$$

$$+\sum_{\varkappa_1\varkappa_2}{}''\frac{1}{\omega_{\varkappa}\,\omega_{\varkappa'}}V_{\varkappa_1\varkappa_2\varkappa}V^{*}_{\varkappa_1\varkappa_2\varkappa'}\langle \overset{+}{a}_{\varkappa_2}a_{\varkappa_1},\ \overset{+}{a}_{\varkappa_1}a_{\varkappa_2}\rangle_{\omega}$$

$$+O\left(\frac{V^4}{\omega_{\varkappa}{}^4}\right)\ (\omega\ll\omega_{\varkappa},\ \omega_{\varkappa'}),\quad \langle a_{\varkappa_2}{}^{+}a_{\varkappa_1},\ \overset{+}{a}_{\varkappa'}\rangle_{\omega}$$

$$=-\delta_{\varkappa_1\varkappa_2}\frac{1}{\omega_{\varkappa'}}\sum_{\varkappa_3}{}'V^{*}_{\varkappa_3\varkappa_3\varkappa'}\langle \overset{+}{a}_{\varkappa_1}a_{\varkappa_1},\ (\overset{+}{a}_{\varkappa_3}a_{\varkappa_3}-n_{\varkappa_3})\rangle_{\omega}$$

$$-(1-\delta_{\varkappa_1\varkappa_2})\frac{1}{\omega_{\varkappa'}}V^{*}_{\varkappa_1\varkappa_2\varkappa'}\langle \overset{+}{a}_{\varkappa_2}a_{\varkappa_1},\ \overset{+}{a}_{\varkappa_1}a_{\varkappa_2}\rangle_{\omega}$$

$$+O\left(\frac{V^2}{\omega_{\varkappa}{}^2}\right)(\omega\ll\omega_{\varkappa_1},\quad \omega_{\varkappa_2},\quad \omega_{\varkappa'};\quad \omega\neq 0). \tag{A.5}$$

The summation over κ_1, κ_2, and Σ' is carried out here only over the local oscillations, since for the crystal oscillations (belonging to the continuous spectrum) we have $V_{\kappa_1\kappa_2\kappa_3}\sim N_0^{-1}$ (N_0 is the number of atoms in the crystal), and in the limit of an infinite crystal the corresponding part of the sum vanishes. To the contrary, in the sum Σ'' the summation is carried out only over the crystal oscillations, so that

$$\langle a_{\varkappa_2}{}^{+}a_{\varkappa_1},\ a_{\varkappa_1}{}^{+}a_{\varkappa_2}\rangle_{\omega}\sim\delta(\omega-\omega_{\varkappa_1}+\omega_{\varkappa_2})$$

and vanishes for small values of ω, for local oscillations for which the difference $\omega_{\kappa_1}-\omega_{\kappa_2}$ is finite (we exclude the case of very close frequencies of local oscillations). The operators a_{κ} and $\overset{+}{a}_{\kappa'}$ themselves in (A.5) can correspond to either local or crystal oscillations.

The correlation function $\langle \overset{+}{a}_{\kappa_1}a_{\kappa_1}(\overset{+}{a}_{\kappa_2}a_{\kappa_2}-n_{\kappa_2})\rangle_{\omega}$ has a simple form in the case when the decay (or "scattering") of the local oscillations by another local oscillation and the crystal oscillation is much less probable, than its decay into two crystal oscillations (in particular, in the case of a single local oscillation only). In the case of small ω ($\omega\lesssim\Gamma_{\kappa}\ll\omega_{\kappa};\ \omega\ll T$), the calculation of $\langle \overset{+}{a}_{\kappa_1}a_{\kappa_1},\ (\overset{+}{a}_{\kappa_1}a_{\kappa_1}-n_{\kappa_1})\rangle_{\omega}$ was carried out earlier for this case in[5], and as follows from formulas (A.11)–(A.15) of[5]:

$$\langle a_{\varkappa}{}^{+}a_{\varkappa},\ (\overset{+}{a}_{\varkappa'}a_{\varkappa'}-n_{\varkappa'})\rangle_{\omega}$$

$$=\frac{2}{\pi}\,\frac{2\Gamma_{\varkappa}\delta_{\varkappa\varkappa'}}{\omega^2+4\Gamma_{\varkappa}{}^2}\,n_{\varkappa}(n_{\varkappa}+1)$$

$$(\omega\lesssim\Gamma_{\varkappa}\ll\omega_{\varkappa};\ \omega\ll T); \tag{A.6}$$

$$\Gamma_{\varkappa}\equiv\Gamma_{\varkappa}(\omega_{\varkappa})$$

$$=\frac{\pi}{2}\sum_{\varkappa'\varkappa''}{}''[|V_{\varkappa\varkappa'\varkappa''}|^2(1+n_{\varkappa'}+n_{\varkappa''})\,\delta(\omega_{\varkappa}-\omega_{\varkappa'}-\omega_{\varkappa''})$$

$$+2|V_{\varkappa'\varkappa\varkappa''}|^2(n_{\varkappa''}-n_{\varkappa'})\,\delta(\omega_{\varkappa}-\omega_{\varkappa'}+\omega_{\varkappa''})], \tag{A.7}$$

where the summation in Σ'' is carried out only over the oscillations of the continuous spectrum, and the second term differs from zero only if the frequency of the local oscillation κ lies lower than some branch of the frequency spectrum.

The quantity Γ_{κ} describes the damping of the local oscillation κ, due to the anharmonicity of third order, and for high-frequency local oscillations it vanishes when $\omega_{\kappa}>2\omega_m$ (ω_m—maximum frequency of the continuous spectrum). It is easy to see, however, that in this case, too, formula (A.6) is valid, but now Γ_{κ} is determined by the decay (or "scattering") of the local oscillation into three (or more) oscillations of the continuous spectrum, and will be appreciably smaller. It is important that the terms in the fourth-order anharmonicity in the Hamiltonian, of the type $V_{\kappa\kappa\kappa'\kappa''}\overset{+}{a}_{\kappa}a_{\kappa}\overset{+}{a}_{\kappa'}a_{\kappa''}$, which determine the "modulation" broadening of the spectral distribution of the local oscillations (see[6]), make no contribution to the damping Γ_κ (which characterizes only the "decay" broadening connected with the finite lifetime of the excited state).

The correlation functions $\langle a^+_{\kappa_2} a_{\kappa_1}, a^+_{\kappa_1} a_{\kappa_2} \rangle_\omega$ in the harmonic approximation are obviously equal to $(\kappa_1 \neq \kappa_2)$

$$\langle a_{\varkappa_2}{}^+ a_{\varkappa_1}, a_{\varkappa_1}{}^+ a_{\varkappa_2} \rangle_\omega = (n_{\varkappa_1} + n_{\varkappa_2} + 2n_{\varkappa_1} n_{\varkappa_2}) \delta(\omega - \omega_{\varkappa_1} + \omega_{\varkappa_2}). \tag{A.8}$$

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