SOVIET PHYSICS JETP VOLUME 21, NUMBER 1 JULY, 1965

THEORY OF BROADENING OF SPECTRAL LINES AND NONRADIATIVE TRANSITIONS IN SYSTEMS WITH WEAK COUPLING

M. A. KRIVOGLAZ

Institute of the Physics of Metals, Academy of Sciences, Ukrainian S.S.R.

Submitted to JETP editor July 12, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) **48**, 310-326 (January, 1965)

The broadening of spectral lines which is caused by the interaction between impurity-center electrons and lattice vibrations is considered. The treatment is carried through for the case of a weak electron-phonon interaction. Electron-phonon interaction Hamiltonians which are linear and quadratic in the phonon operators are investigated. Detailed examination is given to effects associated with the presence of local vibrations and with anharmonicity, and it is shown that local vibrations can lead to much greater broadenings than vibrations of the crystal. An Appendix deals with a new mechanism of nonradiative transitions and with spin-phonon relaxation caused by interaction with local vibrations.

1. INTRODUCTION

THE interaction of impurity-atom electrons or of nuclei which absorb photons with the vibrations of a crystal leads to the appearance of a broad spectral distribution, corresponding to electronic-vibrational (or nuclear-vibrational) transitions, and to a broadening of the so-called "no-phonon" line (NPL). This broadening is primarily due to the existence of a finite probability of nonradiative thermal transitions in which the energy released in an electronic transition is transferred to vibrations. If the energy difference of the electronic levels is smaller than the maximum energy of the phonons, then in the first order of perturbation theory such transitions are caused by an electron-phonon interaction Hamiltonian linear in the phonon operators. The probability for these transitions calculated in [1,2] is sizable, and they can lead to a broadening which is considerably larger than the natural width.

Besides this mechanism of broadening of the NPL there is another which is particularly important if the difference of the electronic levels exceeds the energy of the phonons and the probability for "changing" the electronic energy into the energy of several phonons is small. This broadening is caused by terms in the electron-phonon interaction Hamiltonian which are quadratic, not linear, in the phonon operators, and is due to fluctuations of the phonon field near the absorbing centers. This mechanism of broadening has been treated by Silsbee[3] (see also [4]) by means of the method of moments. A previous paper by the present writer[5] gave a more rigorous treatment, which permitted the determination in explicit form of the shape of the broadened NPL in an impurity-absorption spectrum or in a Mössbauer spectrum, and also the width of the line. There is an independent detailed treatment of the temperature broadening of the Mössbauer line in a paper by Kagan.[6] The broadening of the NPL has been treated by a somewhat different method by McCumbar[7] (see also [8]). According to [5], the decisive contribution to the broadening can be due to the interaction of the electrons with local vibrations. The anharmonicity of the vibrations must be taken into account in calculating this broadening.

In the previous paper[5] the treatment was made for the case in which the difference between the electronic (or nuclear) levels is considerably larger than the phonon energy, and the adiabatic approximation was used (but the electron-phonon interaction did not have to be small). If the difference of the electronic levels becomes comparable with or smaller than the phonon energy, some new features of the broadening effect appear. In this case the adiabatic approximation can no longer be used, but the calculation can be made by assuming that the electron-phonon interaction is weak. The results of a calculation of this kind will be presented in the present paper. Here, as in [5], our main attention will be given to effects caused by the interaction of the electrons with local vibrations and with anharmonicity (which was not considered in [3,7,8]). It is obvious that the results obtained can be applied both to the absorption of light and to the resonance absorption of microwave radiation. It is required that the concentration of impurity centers in the ideal crystal be sufficiently small, and that the broadening from other causes, for example dipole-dipole interaction, must be smaller than the broadening considered here.

Interaction with local vibrations can also lead to a sharp increase of the probability of nonradiative transitions between closely adjacent electronic levels. This effect will be treated in the Appendix.

2. GENERAL FORMULAS FOR THE SPECTRAL DISTRIBUTION

Let us consider the impurity absorption of photons by a crystal which contains one electronic impurity center. In this case the Hamiltonian of the system is of the form

$$H = H_0 + H_i; \qquad H_0 = H^0(r) + \sum_{\varkappa} \omega_\varkappa a_\varkappa^+ a_\varkappa + H_a, \tag{1}$$

where r is the set of coordinates of the electrons of the center; $H^0(r)$ is the Hamiltonian of the electrons; ω_κ are the frequencies of phonons in the distorted crystal containing the impurity center, and a_κ^+ and a_κ are their creation and annihilation operators; $\hbar = 1$; H_a is the Hamiltonian of the anharmonicity, containing a small parameter ϵ; and H_i is the Hamiltonian of the electron-phonon interaction, whose explicit form is presented below.

The cross section $\sigma(\omega)$ for impurity absorption of light can be expressed in terms of correlation functions (cf. e.g., [9]):

$$\sigma(\omega) = C'N \operatorname{th}\frac{\hbar\omega}{2kT}\int_{-\infty}^{\infty} \langle\langle\{\mathbf{MM}(t) + \mathbf{M}(t)\mathbf{M}\}\rangle\rangle \cos \omega t dt;$$

$$C' = \frac{4\pi\omega}{3\hbar c n(\omega)} \tag{2}$$

Here ME is the operator for the interaction of the electrons of the center with the electric field **E** of the wave; $\langle\langle\ldots\rangle\rangle$ denotes statistical and quantum-mechanical averaging over both electronic and vibrational states; c is the speed of light; $n(\omega)$ is the index of refraction; and N is the concentration of centers.

We perform the calculation of the expression (2) by means of two simplifying assumptions. First, we shall assume that the electron-phonon interaction contains a small parameter ζ, and shall drop all terms of order ζ^2 in $\sigma(\omega)$, keeping only terms $\sim \zeta^0$. Then the only effects of the interaction are a broadening and a shift of the no-phonon spectral lines. The electronic-vibrational spectrum, whose intensity is proportional to ζ^2, will not be considered. While neglecting terms $\sim \zeta^2$, we naturally shall not treat as small the terms $\sim \zeta^2 t$ which determine the shape of the broadened line and will be included essentially in all orders of perturbation theory. On the other hand terms $\sim \zeta^4 t$, which determine the contribution $\sim \zeta^4$ to the broadening, will also be neglected. Second, for simplicity we shall confine ourselves to the nondegenerate case, in which the different Bohr frequencies ω_B of the electronic centers do not coincide and are not close to each other, so that their differences $\Delta\omega_B$ are much larger than the widths γ_T and the shifts of the spectral lines. This makes it possible to examine separately the shape of only one broadened NPL, associated, for example, with the electronic transition from state s (with energy ω_s) to s′ ($\omega \approx \omega_{s's} \equiv \omega_{s'} - \omega_s$).

It is convenient to calculate the traces in (2) with zeroth-approximation wave functions (in the absence of interaction). Furthermore, with accuracy up to terms $\sim \zeta^2$, in calculating the traces we can keep only matrix elements in the functions s and s′; in the matrix element of a product of the type

$$(s|\mathbf{MM}(t)|s) = \sum_{s_1} \mathbf{M}_{ss_1}\mathbf{M}(t)_{s_1 s}$$

we can keep only the term with $s_1 = s'$, and then in the matrix element

$$\mathbf{M}(t)_{s's} = \sum_{s_1 s_2} (\exp[iHt])_{s's_1}\mathbf{M}_{s_1 s_2}(\exp[-iHt])_{s_2 s}$$

we can keep only the term with $s_1 = s'$ and $s_2 = s$. At frequencies $\omega \approx \omega_{s's}$ all other terms give corrections $\sim \zeta^2$ or $\sim \zeta^2\omega_B/\Delta\omega_B$, which are not to be included in the approximation we have adopted.

We also use the relations

$$\exp(iHt) = U(t)\exp(iH_0 t); \qquad U(t) = T\exp\left[i\int_0 \overline{H}_i(t')dt'\right];$$

$$\overline{H}_i(t') = \exp(iH_0 t')H_i\exp(-iH_0 t') \qquad (\hbar = 1).$$

Here T is the symbol for chronological ordering, and indicates that for t > 0 the operators are arranged in the order of decreasing time from left to right. For t < 0 the untangled ordered expression is obtained from the corresponding expression for t > 0 by replacing t by |t| and changing the signs of all coefficients in the Hamiltonians and that of the temperature T. Then (2) can be rewritten in the form

$$\sigma(\omega) = C\operatorname{Re}\int_{-\infty}^{\infty} dt \exp\{i(\omega - \omega_{s's})t\} K(t);$$

$$K(t) = \langle(s|U(t)|s)(s'|U^{-1}(t)|s')\rangle;$$

$$C = C'|\mathbf{M}_{ss'}|^2(N_s - N_{s'}), \tag{3}$$

where $\langle\ldots\rangle$ denotes averaging only over the vibrational states, and N_2 is the equilibrium number of impurity centers in the state s.

We carry out the calculation of K(t) in Eq. (3) by expanding the operators U(t) and $U^{-1}(t)$ in power series in ζ and then collecting all the terms of the expansion. As the perturbation Hamiltonian it is more convenient to use instead of H_i the difference $H' = H_i - \langle H_i \rangle$, at the same time including $\langle H_i \rangle$ in the zeroth-order Hamiltonian H_0. This leads to a temperature-dependent change of the electronic levels and the Bohr frequencies, which in first approximation is given by

$$\delta\omega_{ss'} = \langle H_{s's'}\rangle - \langle H_{ss}\rangle. \tag{4}$$

In what follows we shall regard this change as included in $\omega_{ss'}$, and in U(t) we shall take H_i to mean the difference H′.

Since $\langle H' \rangle = 0$, the first term in the expansion of K(t) in powers of ζ vanishes. The second term of the expansion is determined by correlation functions of the operators $H'_{ss_1}(t) = (s|H'(t)|s_1)$ at different times (these operators depend only on the phonon variables). We shall characterize such correlators by their Fourier components:

$$\langle H'_{ss_1}(t_1)\, H'_{s_1's'}(t_2)\rangle = \int_{-\infty}^{\infty} e^{i\omega(t_1-t_2)}\varphi_{ss_1}^{s_1's'}(\omega)\, d\omega,$$

$$\langle H'_{s_1's'}(t_2)\, H'_{ss_1}(t_1)\rangle = \int_{-\infty}^{\infty} e^{i\omega(t_1-t_2)}e^{\lambda\omega}\varphi_{ss_1}^{s_1's'}(\omega)\, d\omega; \quad \lambda = \frac{1}{kT}. \tag{5}$$

Expanding U(t) and $U^{-1}(t)$ in powers of ζ, using (5), and performing an integration, we find that, to and including terms $\sim \zeta^2$, K(t) is given by

$$K(t) = 1 - K';$$

$$K' = \int_{-\infty}^{\infty} d\omega \sum_{s_1} [\varphi_{ss_1}^{s_1s}(\omega)\, B_{ss_1} + \varphi_{s's_1}^{s_1s'}(\omega)\, B_{s's_1} - 2\varphi_{ss}^{s's'}(\omega)\, B_{ss}],$$

$$B_{ss_1} = \frac{1}{2}\sum_{c=+1,-1}\left[\frac{1-\cos(\omega + c\omega_{ss_1})\,t}{(\omega + c\omega_{ss_1})^2} - ic\frac{\sin(\omega + c\omega_{ss_1})\,t}{(\omega + c\omega_{ss_1})^2}\right]$$
$$\times\left[\frac{1+c}{2} + \frac{1-c}{2}e^{\lambda\omega}\right] + \frac{1}{2}\left[\frac{1}{\omega+\omega_{ss_1}} - \frac{e^{\lambda\omega}}{\omega - \omega_{ss_1}}\right]it. \tag{6}$$

In particular, for |t| → ∞

$$K' = \frac{1}{2}\gamma_T|t| + iV^0t + 2M - iL\frac{t}{|t|};$$

$$\gamma_T = \pi\sum_{c=+1,-1}\sum_{s_1}[\varphi_{ss_1}^{s_1s}(c\omega_{ss_1})$$
$$+ \varphi_{s's_1}^{s_1s'}(c\omega_{s's_1})]\left[\frac{1-c}{2} + \frac{1+c}{2}\exp(\lambda c\omega_{ss_1})\right] - 4\pi\varphi_{ss}^{s's'}(0);$$

$$V^0 = V_s{}^0 + V_{s'}{}^0;\; V_s{}^0$$

$$= \frac{1}{2}\,\mathrm{P}\int_{-\infty}^{\infty} d\omega\left\{\sum_{s_1}\varphi_{ss_1}^{s_1s}(\omega)\left[\frac{1}{\omega+\omega_{ss_1}} - \frac{e^{\lambda\omega}}{\omega-\omega_{ss_1}}\right]\right.$$
$$\left. - \varphi_{ss}^{s's'}(\omega)\frac{1}{\omega}(1 - e^{\lambda\omega})\right\};$$

$$2L = \frac{d\gamma_T}{d(c\omega_{ss_1})} + \frac{d\gamma_T}{d(c\omega_{s's_1})} - 4\pi\left.\frac{d\varphi_{ss}^{s's'}}{d\omega}\right|_{\omega=0} \tag{7}$$

Here we have used the fact that in the cases we shall be considering changing the signs of all the coefficients in the Hamiltonians (including those of the ω_{ss_1}) and those of ω and T leaves the functions $\varphi_{ss_1}^{s_1s}(\omega)$ unchanged. For brevity we do not present the explicit expression for the quantity $2M^{ss_1}$, which determines a small ($\sim\zeta^2$) change of the intensity of the NPL, since we shall not be considering this effect.

To determine the shape and width of the NPL it is essential to know the behavior of the function K(t) for large times. Therefore in the calculation of the higher terms in the expansion in powers of ζ it is sufficient to deal only with the case of large |t|. We shall assume that $|t| \gg T_0$, where T_0 is the characteristic relaxation time for the phonon system (T_0 can be of the order of Γ_K^{-1}, where Γ_K is the damping of a phonon, or of the order of ω_K^{-1}). We can then find the general term of the expansion in powers of ζ by means of an argument just like that used in [5],[1] based on the fact that when the differences between the times used are large, averages of products of operators $H'_{ss_1}(t_i)$ taken at different times t_i approach zero rapidly (exponentially). Therefore in the 2m-fold integral over $dt_1 \ldots dt_{2m}$ which is the coefficient of ζ^{2m} in the expansion of K(t) the integrand is negligibly small except when the variables can be divided into pairs with nearly equal time values t_i: $|t_i - t_j| \sim T_0$. For $|t| \gg T_0$ there is practically no overlapping of these ranges of values of the t_i, and the multiple integral reduces to a product of double integrals (with an error $\sim \zeta^2 T_0/t$). Although along with double integrals of products of the type

$$H'_{ss_1}(t_1)H'_{s_1s}(t_2), \quad H_{ss}'(t_1)H'_{s's'}(t_2),$$

which occur in the second term of the expansion, the general term of the expansion contains products with different indices (for example,

$$H'_{ss_1}(t_1)H'_{s_1s_2}(t_2)H'_{s_2s_3}(t_3)H'_{s_3s}(t_4)$$

with $|t_1 - t_2| \sim |t_3 - t_4| \sim T_0$ in the fourth term of the expansion), such expressions will contain an

---

[1] An analogous argument has been used in a somewhat different connection in papers by Van Hove[10] and Kubo.[11]

extra exponential factor [of the type $\exp[i(\omega_{S2} - \omega_S)(t_3 - t_1)]$ in the example shown], and on the assumption we have adopted ($|\Delta\omega_B| \gg \gamma_T$) their contribution to the spectral distribution ($\sim \gamma_T / |\Delta\omega_B|$) will be negligibly small. Therefore we can keep only those double integrals that also occur in the quadratic term of the expansion and reduce to the expression K′ defined in (6) or (7).

Taking into account the possibility of different divisions of the t_i into pairs, we find that the coefficient of ζ^{2m} in the expansion of K(t) is $(K')^m/m!$ (cf. [5]), and the sum of all even terms of the expansion reduces to an exponential function

$$K(t) = e^{-K'} = e^{-2M} e^{-iV^0 t} e^{-\gamma_T |t|/2} e^{iLt/|t|} \text{ for } t \gg T_0,$$

$$\gamma_T \ll T_0^{-1}. \tag{8}$$

Here we have also used the fact that for $t \gg T_0$ we can use instead of the expression (6) for K′ the asymptotic expression (7). In the odd terms of the expansion one of the groups of times must include three times t_i, and owing to this the (2m+1)st term of the expansion will differ from the 2m-th term by a small factor $\sim iH'_{S_1S_2}T_0$. When the last condition shown in (8) is satisfied these terms (which lead to a shift $\sim H'_{S_1S_2}\gamma_T T_0$ of the maximum of the line) can be neglected.

Since, as can be seen from (3), the shape of the NPL is determined by the behavior of the function K(t) for large times ($|t| \sim 1/\gamma_T \gg T_0$), we can replace K(t) in (3) by the expression (8), which holds for large $|t|$, and neglect the error of the integrand in the region $|t| \sim T_0$. The result of the integration is

$$\sigma(\omega) = Ce^{-2M}\frac{\gamma_T \cos L - 2\omega' \sin L}{\omega'^2 + \gamma_T^2/4}; \quad \omega' = \omega - \omega_{s's} - V_0. \tag{9}$$

This expression for the spectral distribution of the NPL is valid for $\omega' \ll T_0^{-1}$. Since $L \sim \gamma_T T_0$ (as must be the case), $\sigma(\omega) > 0$.

If we are not interested in small ($\sim \zeta^2$) effects of changes in the intensity of the NPL and in its anisotropy, we can approximately set M = L = 0. Then

$$\sigma(\omega) = C\frac{\gamma_T}{\omega'^2 + \gamma_T^2/4}. \tag{10}$$

Thus in the weak-coupling case under consideration the spectral distribution is described by a Lorentz curve with the width γ_T (when the natural width γ is taken into account, it is easy to see that in Eq. (10) γ_T must be replaced by $\gamma_T + \gamma$).

Concrete calculations of the width γ_T according to Eq. (7) will be made separately for the various terms in the Hamiltonian for the interaction of the electrons with local vibrations and with vibrations of the crystal (vibrations of the continuous spectrum). In the approximation adopted here the contributions to the broadening combine additively.

3. QUADRATIC INTERACTION WITH LOCAL VIBRATIONS. CASE OF LARGE BOHR FREQUENCIES

Let us consider first the part of the Hamiltonian for the interaction of the electrons of the impurity center with local vibrations which is quadratic in the phonon operators. The corresponding contribution in H′ can be written in the form

$$H' = H_1' + H_2' + H_3'; \quad H_1' = \sum_{\varkappa} V_\varkappa(r)(n_\varkappa - \bar{n}_\varkappa);$$

$$H_2' = \sum_{\substack{\varkappa,\varkappa' \\ (\varkappa\neq\varkappa')}} V_{\varkappa\varkappa'}(r) a_\varkappa^+ a_{\varkappa'}; \; H_3' = {}^1/_2 \sum_{\varkappa,\varkappa'} (V'_{\varkappa\varkappa'} a_\varkappa^+ a_{\varkappa'}^+ + \text{Herm. adj.}), \tag{11}$$

where $n_\kappa = a_\kappa^+ a_\kappa$ and the summation is taken over the local vibrations only. The Hamiltonian $\langle H_i \rangle$, which as stated before is included in the electronic Hamiltonian H^0, is in this case equal to

$$\sum_\varkappa V_\varkappa(r)(\bar{n}_\varkappa + {}^1/_2),$$

where $\bar{n}_\kappa = (\exp[\lambda\omega_\kappa] - 1)^{-1}$. It follows from (4) that in first approximation (to which we confine ourselves for brevity) the corresponding change of the Bohr frequencies is given by

$$\delta\omega_{s's} = \sum_\varkappa (V_{\varkappa s's'} - V_{\varkappa ss})(\bar{n}_\varkappa + {}^1/_2), \tag{12}$$

where $V_{\kappa s s_1} = (s|V_\kappa(r)|s_1)$. For simplicity we shall assume that the local vibrations are nondegenerate and that the differences between their frequencies are larger than the widths of the local levels. The contribution to the broadening from the nondiagonal part of the Hamiltonian H_2' and from the Hamiltonian H_3' will be considered separately in Sec. 6, where it will be shown that when corrections $\sim \epsilon^2$ are neglected this contribution is important only when certain resonance conditions are satisfied. Here we shall consider only the Hamiltonian H_1'.

The results of the calculation are decidedly different depending on the ratio of the Bohr frequencies ω_B of the electronic levels and the widths Γ_κ of the local levels. In this section we consider the case of relatively large Bohr frequencies, for which

$$\omega_B \gg \Gamma_\varkappa, \tag{13}$$

(but ω_B can be much smaller than ω_κ), and in the next section we shall consider the opposite case.

To calculate line width caused by the Hamiltonian H_1' in (11) by using (7) and (5) we need to know the Fourier component of the correlation function of the product of operators $\bar{n}_\kappa(t) - \bar{n}_\kappa$ for two different times. According to [12] this correlation function can be written in the form

$$\langle[n_\varkappa(t_1)-\bar{n}_\varkappa][n_\varkappa(t_2)-\bar{n}_\varkappa]\rangle = \int_{-\infty}^{\infty} e^{i\omega(t_1-t_2)}\nu_\varkappa(\omega)\,d\omega,$$

$$\nu_\varkappa(\omega) = \frac{2\bar{n}_\varkappa(\bar{n}_\varkappa+1)}{\pi(e^{\lambda\omega}+1)} \times \frac{\gamma_\varkappa(\omega)+\gamma_\varkappa(-\omega)}{[\omega-\pi_\varkappa(\omega)+\pi_\varkappa(-\omega)]^2+[\gamma_\varkappa(\omega)+\gamma_\varkappa(-\omega)]^2} \tag{14}$$

where for $\omega \rightarrow 0$ the function $\pi_\kappa(\omega) \rightarrow \pi_\kappa(-\omega)$, and $\gamma_\kappa(0) = \Gamma_\kappa(\omega_\kappa) \equiv \Gamma_\kappa$, where Γ_κ is the damping of the local phonon owing to its decay processes caused by anharmonicity. Furthermore $\Gamma_\kappa \ll \omega_\kappa$, being proportional to the square of the small parameter ϵ of the anharmonicity, and in the calculation of γ_κ and π_κ only terms $\sim \epsilon^2$ are kept. The correlation functions

$$\langle[n_\varkappa(t_1)-\bar{n}_\varkappa][n_{\varkappa'}(t_2)-\bar{n}_{\varkappa'}]\rangle \quad \text{for} \quad \varkappa\neq\varkappa'$$

are of the order of ϵ^2, and can be neglected in the present approximation. In our present case the relaxation time T_0 is $\sim \Gamma_\kappa^{-1}$, and in accordance with the last criterion stated in (8) the condition of weak coupling is satisfied here for $\gamma_T \ll \Gamma_\kappa$.

It follows from (5), (11) and (14) that, when we neglect terms of higher order in ϵ, for the Hamiltonian H_1'

$$\varphi_{ss_1}^{s_1's'}(\omega) = \sum_\varkappa V_{\varkappa ss_1}V_{\varkappa s_1's'}\nu_\varkappa(\omega).$$

In the case under consideration, with the condition (13) imposed, it can be seen from (14) that $\varphi_{ss_1}^{s_1s}(c\omega_{ss_1})$ is much smaller for $s_1 \neq s$ than for equal indices $s_1 = s$ [by a factor $\sim (\omega_B/\Gamma_\kappa)^2$]. Therefore in the sum (7) over s_1 we can keep only the term with $s_1 = s$ (in the first term) and that with $s_1 = s'$ (in the second). The result is that for our present case we get the following expression for the width $\gamma_T = \gamma_1$ of the spectral line

$$\gamma_1 = \sum_\varkappa \bar{n}_\varkappa(\bar{n}_\varkappa+1)(V_{\varkappa ss}-V_{\varkappa s's'})^2/\Gamma_\varkappa. \tag{15}$$

The Lorentz shape of the spectral curve, broadened owing to the interaction with local vibrations, has also been derived for the case of weak coupling in [5], by means of the adiabatic approximation (in the adiabatic approximation a treatment could also be given for the case of strong coupling, in which the shape of the curve is decidedly not the Lorentz shape). The expression (15) for the width γ_1 also agrees with the expression (9) in [5] if we replace $V_{\kappa ss} - V_{\kappa s's'}$ by the coefficient V_κ in the difference of the adiabatic Hamiltonians of the vibrations of the initial and final states.

The maximum of the Lorentz curve (12) lies at a frequency which includes the temperature dependent line shift (12), which is proportional to ζ. In the present case of weak coupling we shall for brevity neglect the higher-order corrections to the shift, in particular the correction V^0 and the correction $\sim (V_{\kappa ss} - V_{\kappa s's'})$ owing to the odd powers in the expansion of $K(t)$ in powers of ζ.

4. QUADRATIC INTERACTION WITH LOCAL VIBRATIONS. CASE OF SMALL BOHR FREQUENCIES

As in the preceding section, we shall take as the interaction Hamiltonian the operator H_1' in (11), but we shall assume that the differences of the electronic levels is much smaller than the level width of a local phonon, so that instead of the condition (13) we have the opposite conditions

$$\omega_B \ll \Gamma_\varkappa, \qquad \omega_B \ll kT. \tag{16}$$

In this case, as can be seen from (5), (7), and (14), all of the expressions $\nu_\kappa(c\omega_{ss_1})$ and $\nu_\kappa(c\omega_{s's_1})$ for different values of s_1 are approximately equal to each other and reduce to $\nu_\kappa(0)$, and in Eq. (7) we must keep all terms in the sums over s_1, not just the diagonal terms. Therefore in this case the broadening $\gamma_T = \gamma_1'$ takes the form

$$\gamma_1' = \sum_\varkappa \frac{\bar{n}_\varkappa(\bar{n}_\varkappa+1)}{\Gamma_\varkappa} \times \Big[(V_{\varkappa ss}-V_{\varkappa s's'})^2 + \sum_{s_1\neq s}|V_{\varkappa ss_1}|^2 + \sum_{s_1\neq s'}|V_{\varkappa s's_1}|^2\Big]. \tag{17}$$

Here the broadening, unlike that in the case of large Bohr frequencies, is determined not only by diagonal but also by nondiagonal matrix elements $V_{\kappa ss_1}$. The formula (17) naturally has no analog in the theory of [5], which is based on the adiabatic approximation, since (16) is in contradiction with the criterion for application of this approximation ($\omega_B \gg \omega_\kappa$).

In the general case, when the ratio of ω_B and Γ_κ is arbitrary, and in particular when the condition (13) holds for some ω_B and the condition (16) for others, we find in an analogous way that γ_T is given by the formula (17) if in the last two sums over s_1 we replace Γ^{-1} by the respective quantities

$$2\Gamma_\varkappa(\omega_{ss_1})[\Gamma_\varkappa^2(\omega_{ss_1})+\omega_{ss_1}^2]^{-1}[1+\exp\{-\lambda\omega_{ss_1}\}]^{-1},$$

and

$$2\Gamma_\varkappa(\omega_{s's_1})[\Gamma_\varkappa^2(\omega_{s's_1})+\omega_{s's_1}^2]^{-1}[1+\exp\{-\lambda\omega_{s's_1}\}]^{-1},$$

where $2\Gamma_\kappa(\omega_{ss_1}) = \gamma_\kappa(\omega_{ss_1}) + \gamma_\kappa(-\omega_{ss_1})$ and the explicit expressions for $\gamma_\kappa(\omega_{ss_1})$ can be obtained from Eq. (A.12) in [12]. In this case the quantity L which determines the asymmetry of the curve is of the order of

$$\sum_{\varkappa}\bar{n}_\varkappa(\bar{n}_\varkappa+1)\Gamma_\varkappa\left[\sum_{s_1\neq s}|V_{\varkappa ss_1}|^2\omega_{ss_1}^{-3}+\sum_{s_1\neq s'}|V_{\varkappa s's_1}|^2\omega_{s's_1}^{-3}\right].$$

If the law of conservation of energy allows the decay of a local phonon into two crystalline phonons, then for $kT \gg \omega_\kappa$, according to [13] $\Gamma_\kappa \sim T$, i.e., the broadening γ_1 or γ_1' caused by the local vibrations is proportional to T [unlike the broadening owing to crystal vibrations, which is proportional to T^2 (see Sec. 6)]. If $T \rightarrow 0$, then $\Gamma_\kappa \rightarrow \text{const} \neq 0$, and γ_1 and $\gamma_1' \rightarrow 0$. Furthermore, Γ_κ is proportional to the square of the small anharmonicity constant ϵ, and γ_1 and $\gamma_1' \sim \epsilon^{-2}$, and therefore if the interaction of the electrons of the impurity center with local phonons is not weaker than their interaction with crystalline phonons, the corresponding broadening γ_1 or γ_1' makes the main contribution to the γ_T caused by an interaction Hamiltonian quadratic in the phonon operators (see Sec. 6). According to various estimates [13-17] $\Gamma_\kappa \sim (10^{-1}–10^{-2})kT$ for $kT > \omega_\kappa$ and $\Gamma_\kappa \sim (10^{-2}–10^{-3})\omega_\kappa$ for $T \rightarrow 0$. Accordingly the condition (16) can be satisfied only for very small electronic centers or for levels very close together. Furthermore as the temperature is raised there is the possibility of a transition from the condition (13) to the condition (16), which leads to an additional complication of the temperature dependence of γ_1.

If the frequency of the local phonon is relatively large and the law of conservation of energy does not allow the decay of the local phonon into two crystalline phonons, then Γ_κ will be much smaller than in the estimates we have given, and the broadening γ_1 or γ_1' will be especially large ($\gamma_1 \ll \Gamma_\kappa$). Furthermore there is also a change of the temperature dependence of Γ_κ and γ_1. If, for example, the local phonon can decay into three phonons, then for $kT \gg \omega_\kappa$ we have $\Gamma_\kappa \sim T^2$, and γ_1 and γ_1' do not depend on T.

If the concentration of impurity centers is large enough, it is necessary to take into account the formation of an impurity band. It can be verified that in the case in which the effective width Γ' of this band is larger than Γ_κ, we must replace Γ_κ by Γ' in Eqs. (15) and (17), which diminishes the value of γ_1 or γ_1' and alters its temperature dependence. Besides the electron-phonon broadening considered here, concentration broadening of spectral lines can also be important at high concentrations of impurity centers.

5. LINEAR INTERACTION WITH THE LOCAL VIBRATIONS

Besides the terms (11) that are quadratic in the phonon operators, the Hamiltonian of the electron-phonon interaction also contains terms that are linear in these operators. We can write the corresponding Hamiltonian for the interaction with local vibrations in the form

$$H' = \sum_{\varkappa}[W_\varkappa(r)a_\varkappa + W_\varkappa^*(r)a_\varkappa^+]. \tag{18}$$

This Hamiltonian describes processes of electronic transition accompanied by the emission or absorption of local phonons. Since in general real processes of this sort are forbidden by the law of conservation of energy, there is no corresponding broadening of the electronic levels in zeroth approximation in ϵ. If, however, one of the Bohr frequencies is close to the frequency of a local phonon, then these processes are possible and make an important (in the majority of cases the decisive) contribution to the broadening of certain spectral lines.

Whereas in the harmonic approximation for the occurrence of processes of emission or absorption of phonons it is necessary that ω_B and ω_κ be almost exactly equal (to an accuracy of the order of the natural width γ), when anharmonicity is taken into account the probability for these processes is large when the much weaker condition $|\omega_B - \omega_\kappa'| \lesssim \Gamma_\kappa$ is satisfied. Therefore, as in the preceding sections, to study the broadening effect in question it is necessary to take the anharmonicity into account explicitly. Including it also allows us to consider the effect of broadening spectral lines owing to the linear Hamiltonian (18), which appears also in cases in which the resonance condition $\omega_B \approx \omega_\kappa'$ is not satisfied.

As can be seen from (7), (5), and (18), in the case now considered the broadening γ_T is determined by Fourier components of correlation functions of the types $\langle a_\kappa(t_1)a_{\kappa'}^+(t_2)\rangle$ and $\langle a_\kappa^+(t_1)a_{\kappa'}^+(t_2)\rangle$. It is not hard to find them to the accuracy of terms in ϵ^2 [and to accuracy $\sim\epsilon^4$ in the denominators of fractions, in comparison with the small factor $(\omega - \omega_\kappa')$] by the method of temperature-dependent Green's functions. Here, as before, we shall assume that the damping and shift of the spectral lines are mainly due not to their interactions with each other, but to the interaction with crystal vibrations, which are described by the anharmonicity Hamiltonian

$$H_a = {}^1/_2 \sum_{\varkappa\varkappa'\varkappa''} (V_{\varkappa\varkappa'\varkappa''} a_\varkappa a_{\varkappa'}{}^+ a_{\varkappa''}{}^+ + {}^1/_3 V'_{\varkappa\varkappa'\varkappa''} a_\varkappa a_{\varkappa'} a_{\varkappa''} + \text{Herm. adj.}).$$

For brevity we shall neglect terms of the type $V_{\kappa\kappa\kappa''} a_\kappa a_\kappa^+ a_{\kappa''}^+$ in the Hamiltonian H_a, which in the case of small concentration of impurity centers are unimportant for the effects considered here and in Sec. 7. Then to the accuracy that has been specified

$$\varphi_{ss_1}^{s_1's'}(\omega) = \sum_\varkappa \{W^*_{\varkappa ss_1} W_{\varkappa s_1's'} \lambda_\varkappa(\omega) - W_{\varkappa ss_1} W^*_{\varkappa s_1's'} \lambda_\varkappa(-\omega) + W_{\varkappa ss_1} W_{\varkappa s_1's'} \mu_\varkappa(\omega) + W^*_{\varkappa ss_1} W^*_{\varkappa s_1's'} \mu^*_\varkappa(\omega)\} n(\omega);$$

$$\lambda_\varkappa(\omega) = \frac{1}{\pi} \frac{\Gamma_\varkappa(\omega)}{[\omega - \omega_\varkappa - P_\varkappa(\omega)]^2 + \Gamma_\varkappa^2(\omega)}; \quad n(\omega) = \frac{1}{e^{\lambda\omega} - 1};$$

$$\mu_\varkappa(\omega) = \frac{1}{\pi} \frac{\Gamma_\varkappa'(\omega)[\omega - \omega_\varkappa - P_\varkappa(\omega)][\omega + \omega_\varkappa + \bar{P}_\varkappa(\omega)]}{\{[\omega - \omega_\varkappa - P_\varkappa(\omega)]^2 + \Gamma_\varkappa^2(\omega)\}\ \{[\omega + \omega_\varkappa + \bar{P}_\varkappa(\omega)]^2 + \bar{\Gamma}_\varkappa^2(\omega)\}}. \tag{19}$$

Here the damping $\Gamma_\kappa(\omega)$ and the frequency shift $P_\kappa(\omega)$, and also $\Gamma'_\kappa(\omega)$, are regarded as functions of the frequency ω. For the Hamiltonian H_a given above the formulas for these functions are of the following forms (cf.[13]):

$$\Gamma_\varkappa(\omega) = \frac{\pi}{2} \sum_{\varkappa'\varkappa''} \{|V_{\varkappa\varkappa'\varkappa''}|^2 (1 + \bar{n}_{\varkappa'} + \bar{n}_{\varkappa''}) \delta(\omega - \omega_{\varkappa'} - \omega_{\varkappa''})$$

$$- |V'_{\varkappa\varkappa'\varkappa''}|^2 (1 + \bar{n}_{\varkappa'} + \bar{n}_{\varkappa''}) \delta(\omega + \omega_{\varkappa'} + \omega_{\varkappa''})$$

$$+ 2|V_{\varkappa'\varkappa\varkappa''}|^2 (\bar{n}_{\varkappa''} - \bar{n}_{\varkappa'}) \delta(\omega - \omega_{\varkappa'} + \omega_{\varkappa''})\},$$

$$\Gamma_\varkappa'(\omega)$$

$$= -\frac{\pi}{2} \sum_{\varkappa'\varkappa''} \{V^*_{\varkappa\varkappa'\varkappa''} V'^*_{\varkappa\varkappa'\varkappa''} (1 + \bar{n}_{\varkappa'} + \bar{n}_{\varkappa''}) [\delta(\omega - \omega_{\varkappa'} - \omega_{\varkappa''})$$

$$- \delta(\omega + \omega_{\varkappa'} + \omega_{\varkappa''})]$$

$$+ 2V_{\varkappa'\varkappa''\varkappa} V_{\varkappa''\varkappa'\varkappa} (\bar{n}_{\varkappa''} - \bar{n}_{\varkappa'}) \delta(\omega - \omega_{\varkappa'} + \omega_{\varkappa''})\}. \tag{20}$$

The formula for $\bar{\Gamma}_\kappa(\omega)$ is obtained from that for $\Gamma_\kappa(\omega)$ by changing the signs of all the ω_κ (including those in $\bar{n}_\kappa$). The expression for $P_\kappa(\omega)$ can be obtained from that for $\Gamma_\kappa(\omega)$ by replacing the factor $\pi\delta(\omega - a)$ in each term by $P(\omega - a)^{-1}$. Without loss of generality we can choose the normal coordinates in such a way that $W^*_\kappa(r) = W_\kappa(r)$ and so that the coefficients V and V′ are real.

If the renormalized frequency $\omega'_\kappa = \omega_\kappa + P_\kappa$ of a local vibration differs from one of the Bohr frequencies $\pm\omega_{ss_1}$ or $\pm\omega_{s's_1}$ by an amount $\lesssim \Gamma_\kappa$, then, as can be seen from (7) and (19), the corresponding resonance term is much larger than the other terms in the sum (7) over s_1 and c, and the other terms can be neglected. In the resonance region we can also neglect $\mu_\kappa(\omega)$ in comparison with $\lambda_\kappa(\omega)$ (if we are not interested in the asymmetry of the distribution). The contribution $\gamma_{2\kappa}$ to γ_T, which is due to a resonance interaction of the type in question with a local phonon κ, can be represented in the form of the sum of the corresponding widths of the electronic levels s and s′: $\gamma_{2\kappa} = \gamma_{2s\kappa} + \gamma_{2s'\kappa}$, and ordinarily only one of these terms is important (unless the condition $|\omega_{ss_1} - \omega_{s's_2}| \lesssim \Gamma_\kappa$ is satisfied for some s_1 and s_2 . For example, for $\omega_{ss_1} \approx \omega'_\kappa$

$$\gamma_{2s\varkappa} = 2|W_{\varkappa ss_1}|^2 \frac{\Gamma_\varkappa}{(\omega_{ss_1} - \omega_\varkappa')^2 + \Gamma_\varkappa^2} [n(\omega_{ss_1}) + 1]. \tag{21}$$

If, on the other hand, $\omega_{ss_1} \approx -\omega'_\kappa$, then in (21) we must replace $n(\omega_{ss_1}) + 1$ by $n(|\omega_{ss_1}|)$. The quantity $\gamma_{2s'\kappa}$ is obtained from (21) by replacing s by s′.

In particular, for $|\omega_{ss_1} - \omega'_\kappa| \ll \Gamma_\kappa$ Eq. (21) takes the form

$$\gamma_{2s\varkappa} = 2|W_{\varkappa ss_1}|^2 [n(\omega_{ss_1}) + 1] / \Gamma_\varkappa,$$

i.e., $\gamma_{2\kappa}$, like γ_1, is $\sim \epsilon^{-2}$. Since the coefficients $W_{\kappa ss_1}$ in the linear terms of the interaction Hamiltonian are ordinarily much larger than the coefficients $V_{\kappa ss}$ in the quadratic terms, the broadening $\gamma_{2\kappa}$ is larger than the width γ_1 or γ'_1, provided only that for some one of the Bohr differences between the electronic levels s or s′ and some level s_1 the condition of resonance with a local vibration κ is satisfied. A characteristic feature of this mechanism of resonance broadening is that it occurs only for certain lines s → s′ in the absorption spectrum, for which the initial or the final level is broadened.

For high temperatures and $|\omega_{ss_1} - \omega'_\kappa| < \Gamma_\kappa$ the width $\gamma_{2\kappa}$ is of a degree in the temperature smaller by unity than the degree of γ_1 or γ'_1, and at low temperatures $\gamma_{2s\kappa}$, unlike γ_1, goes to a nonzero limit if $\omega_{ss_1} > 0$. As can be seen from (21), for $|\omega_{ss_1} - \omega_\kappa| \gg \Gamma_\kappa$ the width $\gamma_{2\kappa}$ is proportional not to ϵ^{-2} but to ϵ^2, and is small because the anharmonicity parameter is small. The mechanism in question for the broadening of electronic levels and spectral lines is essentially due to electronic transitions accompanied by absorption or emission of local phonons, whose levels are smeared out owing to anharmonicity into bands with widths $\sim \Gamma_\kappa$.

The formulas presented in this section are equally applicable both to local and to crystalline vibrations. The consequences of these formulas that relate to crystalline levels will be considered separately in Sec. 7.

6. QUADRATIC INTERACTION WITH CRYSTALLINE VIBRATIONS

The Hamiltonian for interaction with continuous-spectrum vibrations which is quadratic in the phonon operators is also defined by (11), in which, however, the summation is not taken not over the local, but over the crystalline vibrations. Since in this case $V_{\kappa ss} \sim N_0^{-1}$, where N_0 is the number of atoms in the crystal, the broadening γ_1 or γ_1' will go to zero for $N_0 \to \infty$. A finite broadening in this case is due to the nondiagonal terms H_2' and H_3' in the Hamiltonian (11). Calculating correlation functions of the type $\langle a_\kappa^+(t_1) a_{\kappa'}(t_1) a_\kappa(t_2) \times a_{\kappa'}^+(t_2) \rangle$ in the harmonic approximation, we find from (5) and (11) that for the Hamiltonian $H' = H_2' + H_3'$ the function $\varphi_{ss_1}^{s_1 s'}(\omega)$ is of the form

$$\varphi_{ss_1}^{s_1's'}(\omega) = \sum_{\varkappa\varkappa'} [V_{\varkappa\varkappa' ss_1} V_{\varkappa'\varkappa s_1' s'} \bar{n}_\varkappa (\bar{n}_{\varkappa'} + 1) \delta(\omega - \omega_\varkappa + \omega_{\varkappa'})$$
$$+ {}^1/_2 V'_{\varkappa\varkappa' ss_1} V'^*_{\varkappa\varkappa' s_1' s'} \bar{n}_\varkappa \bar{n}_{\varkappa'} \delta(\omega - \omega_\varkappa - \omega_{\varkappa'})$$
$$+ {}^1/_2 V'^*_{\varkappa\varkappa' ss_1} V'_{\varkappa\varkappa' s_1' s'} (\bar{n}_\varkappa + 1)(\bar{n}_{\varkappa'} + 1) \delta(\omega + \omega_\varkappa + \omega_{\varkappa'})]. \qquad (22)$$

In the case of the crystalline vibrations inclusion of anharmonicity leads to only a very slight correction $\sim \epsilon^2$ (cf. [5]).

Substituting (22) in (7), we find that the broadening γ_3 caused by the quadratic interaction with the crystalline vibrations can be written in the form

$$\gamma_3 = \gamma_{3s} + \gamma_{3s'} + \gamma_{3ss'};$$

$$\gamma_{3ss'} = 2\pi \sum_{\varkappa\varkappa'} |V_{\varkappa\varkappa' ss} - V_{\varkappa\varkappa' s's'}|^2 \bar{n}_\varkappa (\bar{n}_\varkappa + 1) \delta(\omega_\varkappa - \omega_{\varkappa'});$$

$$\gamma_{3s} = \pi \sum_{\varkappa\varkappa'} \sum_{s_1 \neq s} \{2 |V_{\varkappa\varkappa' ss_1}|^2 (\bar{n}_\varkappa + 1) \bar{n}_{\varkappa'} \delta(\omega_{ss_1} - \omega_\varkappa + \omega_{\varkappa'})$$
$$+ |V'_{\varkappa\varkappa' ss_1}|^2 [\bar{n}_\varkappa + 1)(\bar{n}_{\varkappa'} + 1) \delta(\omega_{ss_1} - \omega_\varkappa - \omega_{\varkappa'})$$
$$+ \bar{n}_\varkappa \bar{n}_{\varkappa'} \delta(\omega_{ss_1} + \omega_\varkappa + \omega_{\varkappa'})]\}. \qquad (23)$$

The broadening γ_{3s} of the electronic levels is due to processes of electronic transition in which two phonons are absorbed or emitted, or else one phonon is absorbed and another is emitted. Such processes are possible only if for some s_1 we have $|\omega_{ss_1}| < 2\omega_m$, where ω_m is the maximum frequency of the vibrations. The broadening $\gamma_{3ss'}$ of a spectral line is due to fluctuation changes of the Bohr frequency caused by interaction with the vibrations, and is different from zero for arbitrary relations between the ω_B and ω_m. The formula (23) for $\gamma_{3ss'}$ agrees with the analogous formula (19) in [5], which was derived in the adiabatic approximation, if in the latter we replace the coefficients $V_{\kappa\kappa'}$ in the difference of the adiabatic Hamiltonians of the initial and final states by $V_{\kappa\kappa' ss} - V_{\kappa\kappa' s's'}$.2) It is obvious that in the adiabatic approximation when $\omega_B \gg \omega_m$ then $\gamma_{3s} = 0$.

For a comparison of the broadening γ_3 with the broadening γ_1 caused by interaction with local vibrations, it is convenient to transform the sums over κ into integrals over ω_κ, by introducing the distribution function $g(\omega)$ of the vibration frequencies. For example,

$$\gamma_{3ss'} = 2\pi N_0 \sum_\varkappa \overline{V^2} \bar{n}_\varkappa (\bar{n}_\varkappa + 1) g(\omega_\varkappa)$$
$$= 2\pi N_0^2 \int d\omega_\varkappa \overline{V^2} \bar{n}_\varkappa (\bar{n}_\varkappa + 1) g^2(\omega_\varkappa),$$

where $\bar{V}^2(\omega_\kappa)$ is the average value of $|V_{\kappa\kappa' ss} - V_{\kappa\kappa' s's'}|^2$ for $\omega_{\kappa'} = \omega_\kappa$. It can be seen from a comparison of this expression with (15) that $\gamma_{3ss'}$ differs from γ_1 by replacement of $1/\Gamma_\kappa$ by by $g(\omega_\kappa)$ [and of $(V_{\kappa ss} - V_{\kappa s's'})^2$ by $N_0 \bar{V}^2$]. Since usually $g(\omega_\kappa) \sim 1/\omega_m \ll 1/\Gamma_\kappa$ [in the case of optical bands of width $\Delta\omega$ in the corresponding frequency range $g(\omega) \approx 1/\Delta\omega$], γ_1 is much larger than γ_3 if the energies of the interactions with local and with crystalline vibrations are of the same order of magnitude. On the other hand, γ_1 can be interpreted as a broadening caused by interaction with a narrow band of a continuous spectrum with Lorentz function $g(\omega)$ having its maximum at the frequency of the local phonon and width $\sim \Gamma_\kappa$ (for $\omega_B \gg \Gamma_\kappa$). In the same way, for $\omega_B \ll \omega_m$, $\Delta\omega$ the expression (23) for γ_3 agrees with the formula (17) for γ_1', which was derived for the case of small Bohr frequencies $\omega_B \ll \Gamma_\kappa$. It can be seen from (23) that at high temperatures $\gamma_3 \sim T^2$.

---

2)We point out here that Eqs. (16) and (18) in [5] are not valid for arbitrary values of the coefficients V_κ, as indicated in [5], but only for small V_κ, when along with the condition (17) in [5] the condition $\omega_{\text{eff}}^{-2} \Sigma_{\kappa\kappa'} V_{\kappa\kappa'} V_\kappa V_{\kappa'} \ll 1$ is also satisfied. If the latter condition is not satisfied, there is an additional correction to the frequency shift V^0 in Eq. (19) of [5]. As before, however, the broadening in the harmonic approximation will be due only to the quadratic terms in the Hamiltonian $H_f - H_i$, and the formula (19) in [5] for the broadening γ_T' remains valid. I take occasion to express our gratitude to M. A. Ivanov, who called my attention to this fact.

In the case of interaction with local vibrations the Hamiltonian $H_2' + H_3'$ in the harmonic approximation can make a (divergent) contribution to γ_3 only if there is an accidental coincidence of $\omega_{ss'}$ and $\pm\omega_\kappa' \pm \omega_{\kappa'}'$. When anharmonicity is taken into account there is a resonance increase of γ_3 when the condition $|\omega_{ss'} \pm \omega_\kappa' \pm \omega_{\kappa'}'| \lesssim \Gamma_\kappa + \Gamma_{\kappa'}$ is satisfied, where ω_κ' and $\omega_{\kappa'}'$ are frequencies of local vibrations; this effect is analogous to the resonance effect caused by the linear interaction and considered in Sec. 5. When we use the expression for the Fourier component of the correlation function $\langle a_\kappa(t_1) a_{\kappa'}^+(t_2) a_\kappa^+(t_2) a_{\kappa'}(t_2)\rangle$, calculated with anharmonicity included [cf. Eq. (20) in [5]], it is not hard to show that this resonance contribution to γ_{3s} caused by interaction with local vibrations κ and κ', for example for $\omega_{ss_1} \approx \omega_\kappa' - \omega_{\kappa'}'$, is of the form

$$\gamma_{3s} = 2|V_{\kappa\kappa' ss_1}|^2 \frac{(\bar{n}_\kappa + 1)\bar{n}_{\kappa'}(\Gamma_\kappa + \Gamma_{\kappa'})}{(\omega_{ss_1} - \omega_\kappa' + \omega_{\kappa'}')^2 + (\Gamma_\kappa + \Gamma_{\kappa'})^2}. \tag{24}$$

For $\omega_{ss_1} \approx \pm(\omega_\kappa' + \omega_{\kappa'}')$ we must replace $|V_{\kappa\kappa' ss_1}|^2$ in (24) by $\frac{1}{2}|V_{\kappa\kappa' ss_1}'|^2$, and also $(\bar{n}_\kappa + 1)\bar{n}_{\kappa'}$ by $(\bar{n}_\kappa + \frac{1}{2} \pm \frac{1}{2})(\bar{n}_{\kappa'} + \frac{1}{2} \pm \frac{1}{2})$ and $-\omega_\kappa' + \omega_{\kappa'}'$ by $\mp\omega_\kappa' \mp \omega_{\kappa'}'$. When the resonance conditions are satisfied the broadening (24) is $\sim \epsilon^{-2}$ and can decidedly increase the broadening (23) caused by interaction with crystalline vibrations, but far from resonance it is $\sim \epsilon^2$ and its contribution to the total broadening is small.

As has already been pointed out in [6,5], there can also be a sharp increase of $\gamma_{3ss'}$ in cases in which quasilocal vibrations arise near impurity atoms and lead to a Lorentz peak of width $\Gamma'' \ll \omega_\kappa$ in the function $g(\omega)$.[15] The corresponding formulas for $\gamma_{3ss'}$ and for γ_3 with $\omega_B \ll \Gamma''$ can be obtained from the formulas for γ_1 or γ_1' by replacing Γ_κ by Γ'' and $(V_{\kappa ss} - V_{\kappa s's'})^2$ by $N_0\bar{V}^2$ at the frequency of the quasi-local vibration. If the sum or difference of frequencies of quasi-local vibrations is close to ω_{ss_1}, then, as can easily be seen, γ_{3s} is given by a resonance formula of the type (24) with appropriate obvious changes of the quantities involved (for example, Γ_κ is replaced by Γ'').

7. LINEAR INTERACTION WITH CRYSTALLINE VIBRATIONS

The expression (19) for the correlation function $\varphi(\omega)$ in the case of an electron-phonon interaction linear in the phonon operators is valid both for local and for crystalline vibrations. Substituting this expression in the formula (7) for γ_T and assuming that W_κ, $V_{\kappa\kappa'\kappa''}$ and $V_{\kappa\kappa'\kappa''}$ are real, we find that in the general case the broadening γ_4 caused by the linear interaction is given by the expression

$$\gamma_4 = \gamma_{4s} + \gamma_{4s'} + \gamma_{4ss'};$$

$$\gamma_{4ss'} = 4\pi \sum_\kappa (W_{\kappa ss} - W_{\kappa s's'})^2 \lim_{\omega\to 0} [\lambda_\kappa(\omega) + \mu_\kappa(\omega)]\, n(\omega),$$

$$\gamma_{4s} = 2\pi \sum_\kappa \sum_{s_1 \neq s} W_{\kappa ss_1}^2 [\lambda_\kappa(\omega_{ss_1})$$

$$- \lambda_\kappa(-\omega_{ss_1}) + 2\mu_\kappa(\omega_{ss_1})][n(\omega_{ss_1}) + 1]. \tag{25}$$

If $\pm\omega_{ss_1}$ falls in the range of frequencies of the vibrations and the anharmonicity is small ($\Gamma_\kappa \ll \omega_m$) then, as can be seen from (19), $\lambda_\kappa(\omega_{ss_1}) \approx \delta(\omega_{ss_1} - \omega_\kappa)$. Therefore when anharmonicity is neglected

$$\gamma_{4s} = \gamma_{4s}' = 2\pi \sum_\kappa \sum_{s_1 \neq s} |W_{\kappa ss_1}|^2 [\delta(\omega_{ss} - \omega_\kappa)(\bar{n}_\kappa + 1)$$

$$+ \delta(\omega_{ss_1} + \omega_\kappa)\bar{n}_\kappa]$$

$$= 2\pi N_0 \sum_{s_1 \neq s} \int_0^{\omega_m} d\omega_\kappa \overline{|W_{\kappa ss_1}|^2} [\delta(\omega_{ss_1} - \omega_\kappa)(\bar{n}_\kappa + 1)$$

$$+ \delta(\omega_{ss_1} + \omega_\kappa)\bar{n}_\kappa]\, g(|\omega_{ss_1}|), \tag{26}$$

where $\overline{|W_{\kappa ss_1}|^2}$ is the result of averaging $|W_{\kappa ss_1}|^2$ over κ at the frequency $\omega_\kappa = \pm\omega_{ss_1}$.

If, however, $\pm\omega_{ss_1}$ does not fall in the allowed range of vibrational frequencies, or else if the value of $g(\omega)$ at $\omega = \pm\omega_{ss_1}$ is small [for example, in the case of small Bohr frequencies $|\omega_{ss_1}| \ll \omega_m$, when $g(|\omega_{ss_1}|) \sim \omega_{ss_1}^2$], the main contribution to γ_4 may be that of terms $\sim \epsilon^2$ associated with the anharmonicity. Then, with $\omega_B \gg \omega_\kappa$, as we see from (19), $n(0)\lambda_\kappa(0) \gg \lambda_\kappa(\omega_{ss_1})n(\omega_{ss_1})$, $n(0)\mu_\kappa(0) \gg \mu_\kappa(\omega_{ss_1})n(\omega_{ss_1})$ ($\omega_{ss_1} \neq 0$), and the main contribution to γ_4 comes from $\gamma_{4ss'}$.

Substituting the expressions (19), (20) in the formula (25) for $\gamma_{4ss'}$, we find

$$\gamma_{4ss'} = 8\pi \sum_{\kappa\kappa'\kappa''} |W_{\kappa ss} - W_{\kappa s's'}|^2 \omega_\kappa^{-2} |V_{\kappa'\kappa\kappa''}|^2 \bar{n}_{\kappa'}(\bar{n}_{\kappa'} + 1)$$

$$\times \delta(\omega_{\kappa'} - \omega_{\kappa''}), \tag{27}$$

where the summation over κ is taken over both crystalline and local vibrations. At high temperatures $\gamma_{4ss'} \sim T^2$, and for T → 0, $\gamma_{4ss'} \sim T^9$. If $\omega_B \gg \omega_\kappa$, then $\gamma_{4ss'}$ can also be expressed in terms of the coefficients V_κ in the difference of adiabatic potentials $H_f - H_i$ (cf. [5]3)):

---

3)In Eqs. (22), (23) of [5] no account was taken of the frequency dependence of $\Gamma_\kappa(\omega)$. Inclusion of this dependence, and also of terms in $\mu_\kappa(\omega)$, leads to a change in Eq. (23) of [5] for γ_T'', the factor $\Gamma_\kappa(2n + 1)$ being replaced by the quantity $\lim_{\omega\to 0} 2\Gamma_\kappa(\omega)[2n(\omega) + 1]$, so that the result is Eq. (28).

$$\gamma_{4ss'} = 8 \sum_{\varkappa} \frac{|V_\varkappa|^2}{\omega_\varkappa^2} \lim_{\omega\to 0} \Gamma_\varkappa(\omega) n(\omega)$$

$$= 8\pi \sum_{\varkappa\varkappa'\varkappa''} \frac{|V_\varkappa|^2}{\omega_\varkappa^2} |V_{\varkappa'\varkappa\varkappa''}|^2 \bar{n}_{\varkappa'}(\bar{n}_{\varkappa'}+1)\delta(\omega_{\varkappa'}-\omega_{\varkappa''}). \quad (28)$$

The correction γ''_{4s} to γ_{4s} ($\gamma_{4s} = \gamma'_{4s} + \gamma''_{4s}$) caused by anharmonicity can be written in the form

$$\gamma_{4s} = 2\pi \sum_{\varkappa} \sum_{c=+1,\,-1} \sum_{s_1\neq s} \{W_{\varkappa ss_1}{}^2[c\lambda_\varkappa(c\omega_{ss_1}) + \mu_\varkappa(\omega_{ss_1})]$$

$$- \overline{W_{\varkappa ss_1}{}^2}\, c\lambda_\varkappa'(c\omega_{ss_1})\}[n(\omega_{ss_1})+1], \quad (29)$$

where

$$\lambda_\varkappa'(\omega_{ss_1}) = \pi^{-1}\Gamma_\varkappa(\omega_{ss_1})[(\omega_{ss_1}-\omega_\varkappa')^2 + \Gamma_\varkappa^2(\omega_{ss_1})]^{-1}$$

$$\approx \delta(\omega_{ss_1} - \omega_\varkappa'),$$

and $\overline{W^2_{\kappa ss_1}}$ is the average value of $W^2_{\kappa ss_1}$ at $\omega_\kappa = \omega_{ss_1}$. In particular, if $\omega_B \ll \omega_m$ and γ'_{4s} is much smaller than the damping caused by anharmonicity, then

$$\gamma_4 = 4\pi \sum_{\varkappa} \Big[(W_{\varkappa ss} - W_{\varkappa s's'})^2 + \sum_{s_1\neq s} W^2_{\varkappa ss_1} + \sum_{s_1\neq s'} W^2_{\varkappa s's_1} \Big]$$

$$\times \lim_{\omega\to 0} [\lambda_\varkappa(\omega) + \mu_\varkappa(\omega)] n(\omega)$$

$$= 8\pi \sum_{\varkappa\varkappa'\varkappa''} \Big[|W_{\varkappa ss} - W_{\varkappa s's'}|^2 + \sum_{s_1\neq s} |W_{\varkappa ss_1}|^2$$

$$+ \sum_{s_1\neq s'} |W_{\varkappa s's_1}|^2 \Big] \omega_\varkappa^{-2} |V_{\varkappa'\varkappa\varkappa''}|^2 \bar{n}_{\varkappa'}(\bar{n}_{\varkappa'}+1)\delta(\omega_{\varkappa'}-\omega_{\varkappa''}).$$

$$(30)$$

We note also that the results we have given here can be obtained by the method of temperature-dependent Green's functions (cf. e.g., the Appendix). A treatment carried out by this method, and also concrete calculations of the broadening of spectral lines, will be presented elsewhere.

APPENDIX

THE INFLUENCE OF LOCAL VIBRATIONS ON THE PROBABILITY OF NONRADIATIVE TRANSITIONS BETWEEN CLOSELY ADJACENT ENERGY LEVELS

An interaction with local vibrations which is quadratic in the phonon operators must have a decided effect not only on the broadening of spectral lines, but also on the probability of nonradiative transitions between closely adjacent energy levels for which the condition (16) holds, and in particular on the spin-phonon relaxation time for impurity centers. In the representation of second quantization, for the case of an interaction H_1' given by Eq. (11), the Hamiltonian H for this model is of the form

$$H = \sum_{s=1,2} \omega_s N_s + \sum_{\varkappa} \omega_\varkappa n_\varkappa$$

$$+ \sum_{\varkappa} (V_{\varkappa 12} b_1^+ b_2 + V^*_{\varkappa 12} b_2^+ b_1)(n_\varkappa - \bar{n}_\varkappa) + H_a, \quad (A.1)$$

where $N_s = b_s^+ b_s$, and b_s^+ and b_s are the Fermi operators for the electrons of the center (these results will also apply to the case of nuclear spins), which besides the usual anticommutation rules satisfy the condition $b_1^+ b_1 + b_2^+ b_2 = 1$ (there is one electron localized at the center).

We introduce the retarded Green's function

$$g = \{N_1 - {}^1\!/_2;\ N_1 - {}^1\!/_2\}$$

$$= -i\theta(t)\langle\langle[N_1(t) - {}^1\!/_2,\ N_1(0) - {}^1\!/_2]_+\rangle\rangle,$$

where $[\ldots]_+$ is the anticommutator, and $\theta(t) = 1$ for $t > 0$ and $\theta(t) = 0$ for $t < 0$. The equation of motion for this Green's function in the Fourier representation is of the form

$$\omega g(\omega) = \frac{1}{8\pi} + V_{\varkappa 12}\Big\{ b_1^+ b_2 (n_\varkappa - \bar{n}_\varkappa);\ N_1 - \frac{1}{2}\Big\}$$

$$- V^*_{\varkappa 12}\Big\{ b_2^+ b_1 (n_\varkappa - \bar{n}_\varkappa);\ N_1 - \frac{1}{2}\Big\}. \quad (A.2)$$

When we now set up the equations of motion for the Green's functions that occur in the right member of (A.2), and also for the functions obtained by taking their commutators with the operator H_a, and truncate the resulting chain of equations, we find that to terms $\sim \epsilon^2$

$$g_1 = \frac{1}{8\pi}\frac{1}{\omega - S(\omega)};$$

$$S(\omega) = 2\sum_{\varkappa} |V_{\varkappa 12}|^2 \overline{(n_\varkappa - \bar{n}_\varkappa)^2} \Big[\frac{1}{\omega + \omega_{12} - R_\varkappa(\omega) + R_\varkappa(-\omega)}$$

$$+ \frac{1}{\omega - \omega_{12} - R_\varkappa(\omega) + R_\varkappa(-\omega)} \Big]. \quad (A.3)$$

Here $R_\kappa(\omega) = \pi_\kappa(\omega) - i\gamma_\kappa(\omega)$ is defined by Eq. (A.12) in [12], and $\gamma_\kappa(0)$ is equal to $\Gamma_\kappa(\omega_\kappa) \equiv \Gamma_\kappa$ defined by our present Eq. (20). In the derivation of (A.3) we have used the fact that the broadening γ of the electronic levels is much smaller than Γ_κ.

It follows from (A.3) that in the present case, with $\omega_{12} \ll \Gamma_\kappa$, the Fourier component of the correlation function $Q(t) = \langle\langle(N_1(t) - {}^1\!/_2)(N_1(0) - {}^1\!/_2)\rangle\rangle$ in the frequency region $\omega \lesssim \Gamma_\kappa$ is given by

$$Q(\omega) = \frac{1}{4\pi}\frac{1}{e^{\lambda\omega}+1}\frac{\sigma(\omega)}{\omega^2 + \sigma^2(\omega)}.$$

$$\sigma(\omega) = 4\sum_{\varkappa} |V_{\varkappa 12}|^2 \bar{n}_\varkappa(\bar{n}_\varkappa + 1)\frac{2\Gamma_\varkappa}{\omega^2 + 4\Gamma_\varkappa^2}. \quad (A.4)$$

It follows from this that in our present case, with $\sigma \ll \Gamma_\kappa$ and $\sigma \ll kT$, for $t \lesssim \sigma^{-1}$ we have $Q(t) = {}^1\!/_8 \exp[-\sigma(0)t]$. Comparing this result with the equation

$$\dot{N}_1 - \dot{N}_2 = 2W_{21}N_2 - 2W_{12}N_1 \approx 2W(N_2 - N_1),$$

where $W \equiv W_{12} = W_{21}\exp(\lambda\omega_{12}) \approx W_{21}$, we find that the probability W for a nonradiative transition between closely adjacent levels caused by interaction with local vibrations is given by the formula

$$W = \sigma/2 = \sum_{\varkappa} | V_{\varkappa 12} |^2 \bar{n}_\varkappa(\bar{n}_\varkappa + 1)/\Gamma_\varkappa. \qquad (A.5)$$

The probability (A.5) can be compared with the probability of nonradiative transitions owing to interaction with crystalline vibrations. It is easy to see that in this case the interaction linear in the phonon operators leads to a transition probability equal to the quantity γ_{4s} defined by Eq. (26), and the quadratic interaction to the probability γ_{3s} defined by Eq. (23). Furthermore, in the case of closely spaced levels γ_{4s} is small because of the smallness of $g(|\omega_{12}|)$, and when the interactions with crystalline and local vibrations are of the same order of magnitude γ_{4s} can be much smaller than W (by a factor $\sim \omega_m/\Gamma_\kappa$ or $\sim \Delta\omega/\Gamma_\kappa$). Therefore at high temperatures the mechanism now under consideration can be the main mechanism of relaxation in the case of impurity centers that have local vibrations. Unlike the probability γ_{3s}, which is proportional to T^2 for $kT > \omega_m$, W is proportional to T at high temperatures (if the concentration of impurity centers is small).

We also note here that in the case in which the difference ω_{12} of the levels is close to the renormalized frequency ω'_κ of the local phonon, the transition probability coincides with the quantity $\gamma_{2s\kappa}$ defined by (21), and shows a resonance increase.

---

[1] E. O. Kane, Phys. Rev. **119**, 40 (1960).

[2] K. Nishikawa and R. Barrie, Can. J. Phys. **41**, 1135, 1823 (1963).

[3] R. H. Silsbee, Phys. Rev. **128**, 1726 (1962); **129**, 2935 (1963).

[4] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

[5] M. A. Krivoglaz, FTT **6**, 1707 (1964), Soviet Phys. Solid State **6**, 1340 (1964).

[6] Yu. Kagan, JETP **47**, 366 (1964), Soviet Phys. JETP **20**, 243 (1965).

[7] D. E. McCumber, J. Math. Phys. **5**, 221, 508 (1964); Phys. Rev. **133**, A163 (1964).

[8] D. E. McCumber and M. D. Sturge, J. Appl. Phys. **34**, 1682 (1963).

[9] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[10] L. Van Hove, Physica **21**, 517, 901 (1955); **22**, 343 (1956); **23**, 441 (1957).

[11] R. Kubo, in Collection: Lectures in Theoretical Physics, Vol. I, W. E. Brittin and L. G. Dunham, eds., Interscience, New York, 1959, pages 120-203.

[12] M. A. Krivoglaz, JETP **46**, 637 (1964), Soviet Phys. JETP **19**, 432 (1964).

[13] M. A. Krivoglaz, JETP **40**, 567 (1961), Soviet Phys. JETP **13**, 397 (1961). V. N. Kashcheev and M. A. Krivoglaz, FTT **3**, 1528 (1961), Soviet Phys. Solid State **3**, 1107 (1961).

[14] P. G. Klemens, Phys. Rev. **122**, 443 (1961).

[15] Yu. Kagan and Ya. Iosilevskiĭ, JETP **44**, 284 (1963), Soviet Phys. JETP **17**, 195 (1963).

[16] A. A. Maradudin, in Collection: Astrophysics and the Many-body Problem, 1962 Brandeis Lectures, Vol. 2, W. A. Benjamin, Inc., New York, pages 107-320.

[17] W. M. Visscher, Phys. Rev. **134**, A965 (1964).

Translated by W. H. Furry
42