EESTI NSV TEADUSTE AKADEEMIA TOIMETISED. XVI KÖIDE
FÜÜSIKA * MATEMAATIKA. 1967, NR. 2

ИЗВЕСТИЯ АКАДЕМИИ НАУК ЭСТОНСКОЙ ССР. ТОМ XVI
ФИЗИКА * МАТЕМАТИКА. 1967, № 2

https://doi.org/10.3176/phys.math.1967.2.13

*K. REBANE, V. HIZHNYAKOV, I. TEHVER*

# PROBLEMS OF THE THEORY OF SECONDARY RADIATION BY IMPURITY CENTRES IN CRYSTALS

## I. Introduction

The aim of the present paper is to give a survey of the results in the theoretical study of the vibrational structure of Raman spectra of impurity centres in crystals carried out at the Institute of Physics and Astronomy of the Estonian S. S. R. Academy of Sciences during the last 2—3 years. References to earlier work are given in the review article [1] *.

The role of the vibrations of crystal is as great in determining the structure of Raman spectra as it is in determining the absorption and luminescence spectra of impurity centres. As in the case of absorption and luminescence spectra, it is essential to take into consideration the distortion in crystal (i. e. continuum) vibrations and the existence of local vibrations (see [1] for references).

The interaction between optical electrons and vibrations is very often so strong that it is not expedient to describe it by means of the perturbation method. A consistent theory must proceed from the important role of multi-phonon processes. Such "subtle" factors of vibronic (electronic-vibrational) interaction as the dependence of the probability of electronic transition on vibrations and anharmonic vibrational relaxation acquire great significance in the theory of Raman scattering.

There are two essentially different limit cases in the theory of scattering by impurities in crystals as well as in the general theory of scattering of light: scattering when the light frequency coincides with the absorption band of the impurity (resonance scattering) and scattering in conditions of a considerable difference between the frequency of the incident light and the absorption frequency of the impurity centre (non-resonance scattering). In the first case there arises the fundamental question of the separation of the scattered light from the ordinary luminescence [4, 5]; in the second case the task is reduced to the calculation of some first terms of the expansion of the polarizability operator in powers of nuclear coordinates and momenta [6].

The dependence of the probability of electronic transition on vibrations becomes the basic cause of scattering in the non-resonance case, since it is precisely through it that the dependence of electronic polarization on vibrations is expressed. In the resonance case the interaction

---

* We shall not examine the selection rules for the vibrations in Raman scattering. For references see, e. g. [2, 3].

with vibrations is well taken into account by means of the variation of the adiabatic potential in electronic transition. For that it is necessary to use such a model of vibrations which describes the rapid vibrational relaxation in the excited state [7, 8].

We see that owing to the rapid relaxation of vibrational excitations localized in the impurity centre, the division of secondary radiation into luminescence and scattering is indeed possible. The fundamental significance of processes of relaxation in intermediate states for the classification of secondary radiation is especially clearly shown in the works of Stepanov and Apanasevich [5]. However, in these papers (as well as in all other works known to us) the relaxation in intermediate states does not take place proceeding from the characteristics of the model examined, but is introduced as a certain supplementary property.

In dealing with the problem of classifying secondary radiation the case of the impurity centre has a certain advantage when compared, for example, with molecular gases and solutions. This advantage lies in the fact that the relaxation as well as the structure of the impurity spectrum is determined by the vibrations of the crystal. The vibrational motion of the crystal can easily be described on the basis of the theory of small vibrations. In particular, the relaxation of the localized vibrational packet within the crystal in the absence of local vibrations is described already in the simplest approximation of N independent harmonic oscillators [9] (N — the number of degrees of the freedom of the crystal vibrations). If there are local vibrations, a part of the vibrational excitation relaxes in the crystal owing to its anharmonic interaction with the crystal vibrations. Methods of calculating these interactions have now also been well elaborated (see, e. g. [10]).

The luminescence arising in the impurity centre in case of optical excitation is usually described in the first order of the perturbation method according to the interaction between light and substance (see, e. g. [11]). The whole process of secondary radiation is divided into three stages: the absorption of the photon of frequency $\omega_0$ (1), the vibrational relaxation in the impurity centre until the establishment of thermal equilibrium (2), the emission of the photon of frequency $\Omega$ (3). In such a treatment (which is wholly sufficient for the description of luminescence) absorption and emission are essentially two independent processes. Accordingly, two theoretical tasks are solved. The task of finding the absorption spectrum by means of one or another variant of the quantum-mechanical perturbation method assuming as an initial condition that there is thermal equilibrium in the impurity centre before absorption, and precisely the same task for emission, but with a new initial condition — the assumption of thermal equilibrium for vibrations in an excited electronic state at the time of radiation.

As is generally known, the description of scattering requires the second approximation of the perturbation method. In that case secondary radiation is regarded as an indivisible process. In connection with this it is necessary to take into account two essential factors. Firstly, secondary radiation in the general case obviously also comprises luminescence, for the latter was obtained in the first order of the perturbation method and described in full correspondence with the experiment; a more precise theoretical description cannot lead to its loss. It is also obvious that luminescence constitutes an overwhelming part of the summary intensity of secondary radiation if only the frequency of incident light is in resonance with the absorption band. Secondly, the assumption of thermal equilibrium of the lattice in the impurity centre before the act of photon emission cannot be introduced now. A consistent theory should obtain all the results proceeding from the properties of the model and from the one single initial condition — the condition of thermal equilibrium in the crystal before the interaction with the incident light. If there is relaxation it must naturally be allowed by the properties of the model. The ordinary contour of the luminescence spectrum corresponding to the thermal equilibrium of vibrations in the excited electronic state in the theory of the first order must now also be obtained in the natural way by assuming the equilibrium of vibrations only in the ground electronic state before the interaction between the impurity centre and the incident light. It is precisely this programme that is carried out in the papers [7, 8].

The vibrational relaxation in the impurity centre does not depend on the properties of the crystal only, but also on the characteristics of the exciting light. The present survey deals mainly with monochromatic excitation. A more detailed analysis of the situation of vibrational relaxation depending on the characteristics of exciting light is given in section V.

The resonance secondary radiation of impurity centres on the basis of the second order of the interaction between the electromagnetic field and substance has been examined earlier in papers * [12–17]. In these papers only Rayleigh and Raman scattering were obtained. In fact, the formulae worked out by the authors [12–17] comprise luminescence but their analysis has not been completed, the terms (the greatest) proportional to $\gamma_1^{-1}$ ($\gamma_1$ — the radiative width of the excited electronic state) describing luminescence have not been taken into consideration. At the same time the authors [13, 17] examine in detail the models which on principle cannot describe luminescence on the basis of the second order perturbation theory — the model of zero-dispersion vibrations [13], the one-oscillator and the two-oscillator models in the harmonic approximation [17]. The paper [12] merits particular attention as the author has shown that in case of continuous excitation the spectral structure of secondary radiation coincides for the most part exactly with the spectrum of ordinary impurity luminescence. However, the author [12] has not interpreted this spectrum as luminescence.

## II. Raman Scattering in Case of Excitation Distant from Resonance [18]

Let us examine the spectrum of light scattered by an impurity crystal where in case of excitation with a monochromatic wave of light the transition $0v \rightarrow ev'' \rightarrow 0v'$ takes place. Here 0 and $e$ denote the ground and all the possible intermediate electronic states, $v$ — the vibrational state of the system crystal + impurity. As usually, we examine the process in adiabatic approximation. The concentration of impurities in the crystal is considered to be small, so that the interaction between impurities and the interference of the scattered light by different impurities may be neglected.

We proceed from the usual formula for the intensity of the scattered radiation per unit of the solid angle [19]

$$W(\omega_0, \Omega) = \frac{N_l \omega_0^4}{2\pi c^3} \sum_{\substack{\alpha\beta \\ \gamma\delta}} n_\alpha n_\beta E_\gamma^- E_\delta^+ i_{\alpha\gamma,\beta\delta}(\omega_0, \Omega), \tag{2.1}$$

---

* The paper [16] contains some essential inaccuracies (see [8]).

where $\omega_0$, $\Omega$ are respectively the frequencies of the light falling on the crystal and the light scattered by it; $N_I$ — the number of impurity centres in the crystal; $\vec{n}$ — the unit vector of polarization of the scattered radiation; $E^+$ and $E^-$ — the amplitudes of the electromagnetic field of radiation ($\vec{E}=\vec{E}^+e^{i\omega_0t}+\vec{E}^-e^{-i\omega_0t}$). The function $i_{\alpha\gamma,\beta\delta}$ is connected with the tensor of polarizability $P_{\alpha\beta}$ in the following way

$$i_{\alpha\gamma,\beta\delta}(\omega_0,\ \Omega)=\sum_{v,v'}w(v)<v'\,|\,P^*_{\alpha\gamma}\,|\,v><v\,|\,P_{\beta\delta}\,|\,v'>\delta(\omega-\omega_{vv'}), \qquad (2.2)$$

$w(v)$ is the Boltzmann factor, $\omega=\Omega-\omega_0$, $\omega_{vv'}=E_0^v-E_0^{v'}$.

Making use of the integral representation of the $\delta$-function, the following rewriting is possible

$$i_{\alpha\gamma,\beta\delta}=\frac{1}{2\pi}\int\limits_{-\infty}^{\infty}dte^{i\omega t}<P_{\beta\delta}\,(t)\,P^*_{\alpha\gamma}\,(0)>. \qquad (2.3)$$

Here $P_{\alpha\beta}\ (t)$ is operator $P_{\alpha\beta}$ in Heisenberg's representation

$$P_{\alpha\beta}=\sum_{ev''}\left\{\frac{<0\,|\,M_\beta\,|\,ev''><ev''\,|\,M_\alpha\,|\,0>}{\omega_{e0}+\omega_{v''v}-\omega_0+\frac{i\gamma_e}{2}}+\frac{<0\,|\,M_\alpha\,|\,ev''><ev''\,|\,M_\beta\,|\,0>}{\omega_{e0}+\omega_{v''v'}+\omega_0+\frac{i\gamma_e}{2}}\right\}. \qquad (2.4)$$

where $\vec{M}$ is the operator of the dipole momentum of the crystal, $\gamma_e$ — the radiative width of the excited electronic level *, $\omega_{e0}=E_e-E_0$ — the energy of the pure-electronic transition ($\hbar=1$).

Examining the spectrum in case of excitation distant from resonance, we can in (2.3) expand the denominator in a power series making use of conditions

$$\omega_0\ll\Omega_{e0}$$

$$\omega_{v''v}\ll\Omega_{e0}-\omega_0$$

(in this case the radiative width can be neglected) and sum up over intermediate vibrational states. We obtain (see also [20])

$$P_{\alpha\beta}=\sum_{n=0}^{\infty}\sum_{e}\left\{\frac{(M_\beta)_{0e}(H_e-E_0^v-\Omega_{e0})^n(M_\alpha)_{e0}}{(\Omega_{e0}-\omega_0)^{n+1}}+\right.$$

$$\left.+\frac{(M_\alpha)_{0e}(H_e-E_0^{v'}-\Omega_{e0})^n(M_\beta)_{e0}}{(\Omega_{e0}-\omega_0)^{n+1}}\right\}. \qquad (2.5)$$

Here $H_e$ denotes the vibrational Hamiltonian of the system crystal + impurity in the electronic state $e$, $E_0^v$ denotes the vibrational energy of the $v$ level of the ground electronic state, $\Omega_{e0}=\omega_{e0}+C$ denotes the distance between the adiabatic potentials in the minimum point of the initial adiabatic potential.

---

* Unlike [19] we introduced $\gamma_e$ in order to use the formula (2.3) also in the resonance case.

The given formula is somewhat different from the usual Placzek formula [6] which is obtained by replacing $E_{ev'',0v}$ simply by $E_{e0}$ (neglecting fully the variation of the vibrational energy) and expanding the electronic matrix elements in a power series of the nuclear coordinates. In addition we take into account here the variation of vibrational Hamiltonians in electronic transition that leads to the dependence of the polarizability tensor on nuclear momenta. This expands the sphere of application of the given formula.

On the basis of the formula (2.5) it is not difficult to draw the conclusion that the Condon approximation (according to which the dependence of $(M_\alpha)_{0e}$ on the vibrational coordinates is fully neglected) is considerably less precise in the case of non-resonance Raman scattering than in the theory of the absorption of light by the impurity centre. Indeed, it can be seen from (2.2) and (2.5) that when $v \neq v'$, the main term of the expansion $(n=0)$ is equal to zero in the Condon approximation. Consideration of the dependence of the electronic matrix element on the coordinates of nuclear vibrations is consequently the more essential, the farther the frequency of the incident light $\omega_0$ is from the absorption band.* It is not difficult to understand that this must really be so: if $\omega_0$ is not in resonance with the vibronic frequencies, the electronic polarizability whose vibrational modulation is given by the dependence of the electronic wave functions on the nuclear coordinates plays an important role.

On the basis of the formulae (2.3), (2.5) it is easy to carry out thermal averaging and to find expressions for the intensities of one-, two-, etc. phonon transitions.

Let us choose the Hamiltonians as follows:

$$\begin{gathered}
H_0 = \sum_i \omega_i \left( a_i^+ a_i + \frac{1}{2} \right) + \frac{1}{3!} \sum_{ijk} v_{ijk} (a_i + a_i^+)(a_j + a_j^+)(a_k + a_k^+) + \\
+ \frac{1}{4!} \sum_{ijkl} w_{ijkl} (a_i + a_i^+)(a_j + a_j^+)(a_k + a_k^+)(a_l + a_l^+), \\
V = H_e - H_0 - \Omega_{e0} = \sum_i b_i^{(e)} (a_i + a_i^+) + \\
+ \frac{1}{2} \sum_{ij} \varepsilon_{ij}^{(e)} (a_i + a_i^+)(a_j + a_j^+).
\end{gathered} \tag{2.6}$$

Here the anharmonicity of the third and the fourth order and the variation of the equilibrium positions and frequencies as well as the mixing of normal coordinates in electronic transitions are taken into account.

Expanding electronic matrix elements in powers of vibrational coordinates we obtain the following formulae for the Rayleigh (zero-phonon) line and for the first and second order Raman spectra:

$$i^{(0)} = \left[ \sum_e \left( \frac{D_\alpha D_\beta}{\Omega_{e0} - \omega_0} + \frac{D_\beta D_\alpha}{\Omega_{e0} + \omega_0} \right) \right]^2 \delta(\omega), \tag{2.7}$$

where $D_\alpha$ is the first (constant) term of the expansion of the electronic matrix element $(M_\alpha)_{0e}$.

---

* The same conclusion has been drawn earlier by Shorygin and Krushinski on the analysis of experimental data [21].

$$i^{(1)} = \sum_i (P_{q_i} + P_{p_i})^2 [\bar{n}_i \varphi(\omega - \omega_i) + (\bar{n}_i + 1)\varphi(\omega + \omega_i)];$$

$$P_{q_i} = \sum_e \{ (D_\alpha D_\beta)_i [\Delta_e^- + \Delta_e^+] + b_i^{(e)} [(\Delta_e^-)^2 + (\Delta_e^+)^2] \}; \tag{2.8}$$

$$P_{p_i} = \sum_e b_i^{(e)} \omega_i [(\Delta_e^-)^2 + (\Delta_e^+)^2]; \ \Delta_e^\pm = (\Omega_{e0} \pm \omega_0)^{-1};$$

$D_{\alpha,\,i}$ is determined by the formula $D_{\alpha,\,i}(a_i + a_i^+) = (M_\alpha)_{0e,i} q_i$;

$$\varphi(\omega \pm \omega_i) = \frac{1}{\pi} \frac{\Gamma_i}{(\omega \pm \bar{\omega}_i)^2 + \Gamma_i^2};$$

$\bar{n}_i = \{\exp(\omega_i/kT) - 1\}^{-1}$ and $\bar{\omega}_i = \omega_i + \Pi_i$ is the renormalized frequency and

$$\Pi_i = \frac{1}{2} P \sum_{k,m} \Big\{ v_{ikm}^2 \Big[ \frac{1 + \bar{n}_k + \bar{n}_m}{\omega - \omega_k - \omega_m} - \frac{1 + \bar{n}_k + \bar{n}_m}{\omega + \omega_k + \omega_m} + 2 \frac{\bar{n}_k - \bar{n}_m}{\omega + \omega_k - \omega_m} \Big] -$$

$$- 2 v_{iik} v_{kmm} \cdot \frac{2\bar{n}_m + 1}{\omega_k} + \delta_{mk} w_{iikk} (2\bar{n}_k + 1) \Big\},$$

$$\Gamma_i = \frac{\pi}{2} \sum_{k,m} v_{ikm}^2 \{ (1 + \bar{n}_k + \bar{n}_m)[\delta(\omega - \omega_k - \omega_m) - \delta(\omega + \omega_k + \omega_m)] +$$

$$+ 2(\bar{n}_k - \bar{n}_m)\delta(\omega + \omega_k - \omega_m) \}.$$

$$i^{(2)} = \sum_{i,k} \{ (P_{q_i q_k} + P_{p_i q_k})^2 (\bar{n}_i + 1)(\bar{n}_k + 1)\varphi'(\omega + \omega_i + \omega_k) +$$

$$+ (P_{q_i q_k} - P_{p_i q_k})^2 \bar{n}_i \bar{n}_k \varphi'(\omega - \omega_i - \omega_k) + 2P_{q_i q_k}^2 \bar{n}_i (\bar{n}_k + 1)\varphi'(\omega - \omega_i + \omega_k) \},$$

where $P_{q_i q_k} = \sum_e \{ (D_\alpha D_\beta)_{ik} [\Delta_e^- + \Delta_e^+] + [(D_\alpha D_\beta)_i b_k^{(e)} + \frac{1}{2} \varepsilon_{ik}^{(e)}][(\Delta_e^-)^2 +$

$$+ (\Delta_e^+)^2] + b_i^{(e)} b_k^{(e)} [(\Delta_e^-)^3 + (\Delta_e^+)^3] \}, \tag{2.9}$$

$$P_{p_i q_k} = \sum_e \{ [(D_\alpha D_\beta)_k b_i^{(e)} \omega_i + \frac{1}{2} \varepsilon_{ik}^{(e)} \omega_i][(\Delta_e^-)^3 + (\Delta_e^+)^3] \},$$

$$\varphi'(\omega \pm \omega_i \pm \omega_k) = \int \varphi(x \pm \omega_i)\varphi(\omega - x \pm \omega_k)\, dx.$$

It is evident from the formulae (2.8), (2.9) that the importance of the variation of vibrational Hamiltonians is that much the greater, the closer the exciting frequency is to the absorption band and the higher the order of the Raman scattering.

These formulae easily convince one that the Raman spectrum of impurity centres may have a quasiline structure.

As can be seen from (2.6), the Rayleigh line has a finite intensity. The line corresponding to the variation of the state of a local vibration (transitions, accompanied by creation or destruction of the quanta of the local vibration) has also a finite intensity as the coefficients $b_i, \varepsilon_{ik}, D_i, D_{ik}$ in (2.8), (2.9) are finite for local vibrations. The intensity of the line corresponding to the variation of one crystal vibration by one quantum is of the order $N^{-1}$. Indeed, the coefficients $b_k, D_k$; $\varepsilon_{ik}, D_{ik}$ for crystal vibrations have the order $N^{-1/2}$, $N^{-1}$ respectively. The density of frequencies in the spectrum of crystal vibrations (outside singular points) is proportional to $N$. Therefore the total contribution to the intensity by crystal vibrations whose frequencies are in the interval $\omega$, $\omega+\Delta\omega$ is finite. The scattering which is accompanied by the emission or the absorption of the phonons of crystal vibrations leads to a continuous background. The background may of course also have a structure caused either by singularities of the phonon spectrum of the host crystal or by Raman-active pseudolocal vibrations.

Thus, we arrive at the conclusion that in the absence of local vibrations the spectrum of the scattered light consists of a quasi-continuous background conditioned by the Raman scattering on crystal vibrations and of a sharp Rayleigh line corresponding to the scattering without variation of the vibrational state of the lattice and which in this respect is analogous to the Mössbauer line. In case there are local vibrations, the picture described above is supplemented by vibrational recurrences of the zero-phonon line which correspond to scattering with variation of the vibrational state of the local oscillators only. These quasilines represent an analogue to the vibrational recurrences of the zero-phonon line in the Mössbauer and Shpolski effect.

Hence, we can certainly speak of the quasiline vibrational structure of the Raman spectrum which is in many respects analogous to the vibrational structure in the vibronic and in the Mössbauer spectra of absorption and radiation.

There are, however, two essential differences.

Firstly, the quasiline is formed by real transitions between different vibrational levels of the ground electronic state. Therefore the quasiline can have a structure only as a result of the anharmonicity of vibrations in the ground electronic state. Excited electronic states with their vibrational structure occur only as virtual states and do not directly influence the structure of the quasiline. In particular, it should be pointed out that no influence is exerted by the inequality of frequencies in different electronic states which may cause the decay of the quasiline into separate components in the absorption and luminescence spectra.

Secondly, the width of the quasiline is determined by the width of the line of the incident light as well as by the width of the corresponding vibrational level (in case of local vibration) or by the vibrational wave packet (in case of pseudolocal vibration). The first width is for ordinary sources of light of the order of the width of vibrational levels. It is far greater than the radiative width of the line. For that reason the investigation of details in the quasiline structure of the Raman spectrum and that of the Rayleigh line in particular is obviously one of the tasks that can successfully be solved by means of lasers.

It must be mentioned that the non-resonance case does not appear to be appropriate for the experimental Raman scattering by impurity centres: it is difficult to distinguish between the spectrum of the impurity centre and that of the host crystal. Even when the host crystal lacks a first order spectrum, one cannot be sure that the observed spectrum (of the first order) belongs to the impurity which interests us, for accidental impurities and defects occurring in minor quantities may turn out to be in resonance with the excitation and produce noticeable luminescence or scattering.

The resonance case of the excitation of Raman scattering represents a far more promising subject in the investigation of impurities.

## III. Resonance Scattering [7, 8, 22]

### 1. Luminescence in the Resonance Secondary Radiation of the Impurity Centre

As in the previous section, we shall describe the process of interaction between light and crystal by means of the second order formula (2.1) and use an adiabatic approximation for the study of vibronic states of the impurity crystal. In connection with the fact that the resonance case will be examined, it is possible to introduce some additional simplifications. We shall take into account only the resonance intermediate electronic transition. In the formula (2.4) let us omit the second term in brackets as in this case it is small when compared with the first term and let us neglect the dependence of the electronic matrix element on the vibrational coordinates ($(M_\alpha)_{e0} = \text{const}$ — the Condon approximation).

With these assumptions it is possible to rewrite the formula (2.1) as follows (see [15]):

$$W(\omega_0, \Omega) = \frac{B}{2\pi} \int_{-\infty}^{\infty} d\mu \exp\left[i(\Omega - \omega_0)\mu\right] \int\int_0^{\infty} dt dt' \times \tag{3.1}$$

$$\times \exp\left[-i\omega_0(t' - t) - \frac{\gamma_1}{2}(t' + t)\right] A(tt'\mu),$$

where

$$A(tt'\mu) = \left< e^{it'H_1} e^{i\mu H_0} e^{-itH_1} e^{-i(\mu + t' - t)H_0} \right>_0, \tag{3.2}$$

$$B = \frac{N_l \omega_0^4}{2\pi c^3} \left| \left< 0 \right| \vec{E}\vec{M} \left| 1 \right> \left< 1 \right| \vec{n}\vec{M} \left| 0 \right> \right|^2, \tag{3.3}$$

$$\left< \ldots \right>_0 \equiv Sp(\ldots\, e^{-H_0/\kappa T}) \,/\, Sp(e^{-H_0/\kappa T}). \tag{3.4}$$

It is evident that in case of excitation in the absorption band of the impurity, ordinary luminescence should arise as the main part of secondary radiation as a whole. Therefore, any consistent theory of the resonance secondary radiation of impurity centres must, first of all, provide a correct description of luminescence.

Let us show that the main part of the secondary radiation given by the formula (3.1) belongs indeed to ordinary impurity luminescence.* To do that let us rewrite the formula (3.2) for $A(tt'\mu)$ in the following form:

$$A(tt'\mu) = \left< e^{it'H_1} S^+(\mu) e^{-it'H_1} S(\mu + t' - t) R \right>_1, \tag{3.2a}$$

where

$$\left< \ldots \right>_1 \equiv Sp(\ldots e^{-H_1/\kappa T}) / Sp(e^{-H_1/\kappa T}), \tag{3.4a}$$

$$S^+(\mu) = e^{i\mu H_0} e^{-i\mu H_1}, \tag{3.5}$$

$$S(\mu + t' - t) = e^{i(\mu + t' - t)H_1} e^{-i(\mu + t' - t)H_0}, \tag{3.5a}$$

$$R = S^+(i/kT)\, Sp(e^{-H_1/\kappa T}) / Sp(e^{-H_0/\kappa T}). \tag{3.6}$$

---

* The proof adduced here is of a more general character than that provided in the papers [7, 8].

It is easy to be convinced of the correctness of (3.2a) if we use (3.4a) — (3.6).

We shall regard $\mu$, $\mu + t' - t$ and $t'$ as the new independent variables. In that case $A(tt'\mu)$ is a double-time correlator parametrically dependent on $\mu$ and on $\mu + t' - t$:

$$A(tt'\mu) = \langle a(t')b(0)\rangle_1, \tag{3.7}$$

where

$$a = S^+(\mu),\ b = S(\mu + t' - t)R.$$

We shall separate the part which does not damp with an increase of $|t'|$ from the correlator $\langle a(t')b(0)\rangle_1$:

$$A^{(1)}(tt'\mu) = \lim_{t'\to\infty} A(tt'\mu) = \langle a(\infty)b(0)\rangle_1 = \\ = \langle a\rangle_1 \langle b\rangle_1 = \langle S^+(\mu)\rangle_1 \langle S(\mu + t' - t)\rangle_0. \tag{3.8}$$

The remaining part damps if $|t'|$ increases. We shall denote the region of the values of $|t'|$ as $\Delta\varepsilon^{-1}$ in which $A^{(2)}(tt'\mu) = A(tt'\mu) - A^{(1)}(tt'\mu)$ is considerably different from zero. If local vibrations are missing, $\Delta\varepsilon \gtrsim \bar{\omega}$ where $\bar{\omega}$ denotes the mean frequency of the lattice vibrations in the excited state. It must be stressed that $\Delta\varepsilon$ may considerably exceed $\bar{\omega}$ in case of strong electron-phonon interaction as then the main contribution to $A^{(2)}(tt'\mu)$ is made by multi-particle correlators whose speed of damping is higher. If local vibrations are present, $A^{(2)}(tt'\mu)$ contains terms damping only on account of the anharmonicity of vibrations. In that case $\Delta\varepsilon \gtrsim \Gamma$ where $\Gamma$ denotes the anharmonic damping constant of local vibrations.

Let us point out that $A^{(1)}(tt'\mu)$ represents the product of characteristic functions of absorption ($I_\varkappa(\mu + t' - t) = \langle S(\mu + t' - t)\rangle_0$) and luminescence ($I_y(\mu) = \langle S^+(\mu)\rangle_1$) of the impurity centre [23].

For further discussion it is essential that in case of impurity centres there usually exists the inequality

$$\Delta\varepsilon \gg \gamma_1. \tag{3.9}$$

The condition (3.9) expresses the fact that thermal averaging with regard to vibrations (vibrational relaxation) is established far more quickly than that for electronic states. Indeed, even in case of local vibrations when $\Delta\varepsilon = \Gamma \gtrsim 10^{-3}\bar{\omega} \sim 10^{10}$ sec$^{-1}$ the radiative width $\gamma_1$ does not usually exceed $10^8$ sec$^{-1}$.

At present it is not clear whether the condition (3.9) may not be realized for some kind of impurity centres. We are of the opinion that the violation of this condition may most probably be expected in special cases of molecular impurities possessing intramolecular vibrations of very high frequency.

Attention should be drawn to the following interesting possibility of describing resonance secondary scattering if cases really become known where the condition, the reverse of (3.9) : $\Gamma \ll \gamma_1$ is fulfilled for vibrations of high frequency. It is possible to apply an adiabatic approximation for the second time [24], considering the above-mentioned vibrations of high frequency to be a rapid sub-system. Then we may interpret the resonance electronic transition as a resonance electronic + vibrational transition for high frequency vibrations. In that case the corresponding vibronic matrix elements occur instead of electronic matrix elements and the Hamiltonians $H_0$ and $H_1$ are the vibrational Hamiltonians of the slow vibrational sub-system only. In other words, the theory remains the same but only the concrete sense of parameters is changed.

Let us show that owing to the condition (3.9) in case of excitation in the phonon wing of the absorption band, the main contribution to the spectrum of the resonance secondary scattering yields $A^{(1)}(tt'\mu)$.

In this case the essential values of $|\mu+t'-t|$ are small ($|\mu+t'-t| \lesssim \Delta\varepsilon^{-1}$). It is easy to be convinced of this if one takes into account that

$$A(tt'\mu) = < S(t') e^{i(\mu+t'-t)H_0} S^+(t) e^{-i(\mu+t'-t)H_0} >_0$$

consists of the term equal to $<S(t')>_0 <S^+(t)>_0$ which does not damp with an increase of $|\mu+t'-t|$ and the term which damps in the region of $|\mu+t'-t| \lesssim \Delta\varepsilon^{-1}$. Indeed, after integrating in (3.1) over $\mu+t'-t$ both terms make a contribution of the order $\lesssim \Delta\varepsilon^{-1}$ — that being the determination of the region of essential values of $|\mu+t'-t|$.

Let us put $A^{(1)}(tt'\mu)$ into (3.1). Since $A^{(1)}(tt'\mu)$ does not damp in case of an increase of $t'$ the integrand will be noticeably different from zero on the integration plane over $t$ and $t'$ in the region of $|\mu+t'-t| \lesssim \Delta\varepsilon^{-1}$, $t' \lesssim \gamma_1^{-1}$. At the same time $A^{(2)}(tt'\mu)$ differs from zero in the far smaller region of $|\mu+t'-t| \lesssim \Delta\varepsilon^{-1}$, $t \lesssim \Delta\varepsilon^{-1}$. Therefore the contribution $A^{(2)}(tt'\mu)$ to the Fourier transform of the spectrum (and, consequently, to the spectrum itself) is of the order of magnitude $\Delta\varepsilon/\gamma_1 \gtrsim 10^4$ times smaller than that made by $A^{(1)}(tt'\mu)$.

Let us examine in greater detail the spectrum determined by $A^{(1)}(tt'\mu)$. Introducing the variables $t'-t=x$, $t'+t=y$ and using the Fourier transformation

$$< S(\mu+t'-t) >_0 = \int_{-\infty}^{\infty} dz\, F(z) e^{i(\mu+x)z}, \tag{3.10}$$

$$< S^+(\mu) >_1 = \int_{-\infty}^{\infty} dz\, F'(z) e^{i\mu z} \tag{3.11}$$

we integrate over $x$ and $y$. Then we make the reverse Fourier transformation and integrate over $z$. We obtain

$$W^{(1)}(\omega_0, \Omega) = \frac{B}{2\pi\gamma_1} \int_{-\infty}^{\infty} d\mu\, e^{i\Omega\mu} < e^{i\mu H_0} e^{-i\mu H_1} >_1 \times$$
$$\times \int_{-\infty}^{\infty} d\tau\, e^{-i\omega_0\tau} < e^{i\tau H_1} e^{-i\tau H_0} >_0 \exp\{-\tfrac{\gamma_1}{2}|\tau-\mu|\}. \tag{3.12}$$

In view of the fact that upon excitation of the phonon wing the essential values of $|\tau|$ are small ($|\tau| \lesssim \Delta\varepsilon^{-1} \ll \gamma_1^{-1}$), it is possible to replace $\exp\{-\frac{\gamma_1}{2}|\tau-\mu|\}$ by $\exp\{-\frac{\gamma_1}{2}(|\tau|+|\mu|)\}$. Hence, the formula (3.12) leads to the product of the absorption spectrum

$$I_x(\omega_0) = \frac{B}{\gamma_1} \int_{-\infty}^{\infty} d\tau\, e^{-i\omega_0\tau - \frac{\gamma_1}{2}|\tau|} < e^{i\tau H_1} e^{-i\tau H_0} >_0 \tag{3.13}$$

and of the normalized luminescence spectrum

$$I_y(\Omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\mu \, e^{i\Omega\mu - \frac{\gamma_1}{2}|\mu|} < e^{i\mu H_0} e^{-i\mu H_1} >_1. \tag{3.14}$$

Therefore in case of excitation in the phonon wing of the absorption band, the main part of the secondary radiation $W^{(1)}(\omega_0, \Omega)$ represents ordinary impurity luminescence:

$$W^{(1)}(\omega_0, \Omega) = I_x(\omega_0) I_y(\Omega). \tag{3.15}$$

The appearance of the absorption band in the formula (3.15) has an evident physical significance: the constant factor $I_x(\omega_0)$ (in the sense of independence from $\Omega$) expresses the number of photons of frequency $\omega_0$ "absorbed" by luminescence centres. If the absorption of frequency $\omega_0$ is not small as often happens for $\omega_0$ in the absorption band of an actual activated crystal of sufficient thickness and with noticeable concentration of impurities, $I_x(\omega_0)$ is trivially replaced by the factor which takes account of the actual number of photons absorbed by the impurities of the given type. The general considerations here are the same as in the discussion of the correspondence of luminescence excitation spectrum to the absorption spectrum of a single impurity centre.

Let us also stress the following circumstance. As shown by a number of papers (see [12, 13, 22]), the integral intensity of the secondary radiation determined by the formula (3.1) is exactly equal to the probability of absorption. On the basis of the formula (3.15) it becomes evident that the integral intensity of the whole secondary radiation (i. e. of luminescence and scattering but not only of scattering!) coincides with the probability of absorption.

We do not intend to carry out a detailed investigation of the resonance secondary radiation spectrum in case of excitation in the region of the pure-electronic line. Such a study can be found in [8]. We shall give only the general characteristics of the above-mentioned spectrum.

As is also the case with excitation in the phonon wing, the spectrum that is distant from the pure-electronic line represents the vibrational wing of luminescence and is described by the formula (3.15) on condition that $\Omega \neq \omega_{10}$ ($\omega_{10}$ is the frequency of the pure-electronic transition, it depends on the temperature in the general case; the formula for $\omega_{10}$ can be found in [8]).

In the region of the pure-electronic transition the spectrum consists of a pure-electronic line of the width $\gamma_1 + \gamma_v$ ($\gamma_v$ — being its vibrational broadening connected with the variation of elastic constants and with the anharmonicity of vibrations [25, 26, 8]) and the Rayleigh line. The total relative probability of both lines in the spectrum is equal to the relative probability of the pure-electronic line in the luminescence spectrum in case of excitation in the phonon wing. The relative probability of the Rayleigh and the pure-electronic line is equal to $\gamma_1/\gamma_v$. The width of the pure-electronic line is usually some orders greater than the radiative width $\gamma_1$. Owing to this circumstance the main part of the resonance secondary scattering is ordinary impurity luminescence also in case of excitation in the region of the pure-electronic line.

### 2. *Rayleigh and Raman Scattering* [8]

The part of the resonance secondary radiation not included in (3.15) is of noticeable interest as it can occur in another spectral region than luminescence and can be experimentally observed despite its relatively small intensity. Below we shall examine the secondary radiation spectrum in case $\Omega = \omega_0$ and in the region of frequencies near $\omega_0$ within a range of several $\omega_L$ ($\omega_L$ — the maximum frequency of normal modes). In other words, we shall examine the spectral region where the frequencies of Rayleigh and Raman scattering are located. However, it is obvious that the spectrum near the Rayleigh line should be interpreted as the Raman spectrum only when it differs essentially from the wing of the luminescence band of this region. In particular at low temperatures and $\omega_0 > \omega_{10}$ the luminescence does not make any contribution to the spectrum in the region of $\omega_0$. So at least in this case the spectrum of the secondary radiation can be considered as Raman scattering.

It can easily be seen that the spectrum of the secondary radiation contains (in case of monochromatic excitation) a δ-shaped Rayleigh line $W_R(\omega_0, \Omega) = I_R(\omega_0)\delta(\Omega - \omega_0)$. The probability of Rayleigh scattering $I_R(\omega_0)$ is determined by the asymptotic value of $\lim\limits_{\mu\to\infty} A(tt'\mu) = < S(t') >_0 \times$ $\times < S^+(t) >_0$

$$I_R = B \left| \int_0^\infty dt\, e^{-i\omega_0 t - \frac{\gamma_1}{2} t} < S(t) >_0 \right|^2 = B \left| \Phi(\omega_0) \right|^2. \qquad (3.16)$$

Here

$$\Phi(\omega_0) = P \int_{-\infty}^{\infty} d\omega \frac{I'_\varkappa(\omega)}{\omega - \omega_0} + i\pi I'_\varkappa(\omega_0), \qquad (3.17)$$

$I'_\varkappa = 2\pi\gamma_1 / B I_\varkappa$ is the normalized absorption spectrum.

In this way the intensity of Rayleigh scattering can be easily calculated if the absorption spectrum of the impurity is known.

It should be mentioned that Rayleigh scattering can be considered as an elastic scattering by impurities. Therefore it is possible to use a well-known optical theorem for finding the cross section of the above-mentioned scattering, which also leads to (3.16).

Let us now examine the vibrational wing of the Rayleigh line. To do this it is necessary to evaluate the correlator $A(tt'\mu)$. Taking into account that

$$S(t) = T_{(-)} \exp\{i \int_0^t ds V(s)\}, \qquad (3.18)$$

$$S^+(t) = T \exp\{-i \int_0^t ds\, V(s)\} \qquad (3.19)$$

where $V(s)$ denotes the operator $V = H_1 - H_0$ in Heisenberg's representation, $T$ and $T_{(-)}$ being operators of the positive and negative chronological arrangement respectively, we obtain

$$A(tt'\mu) = < T_{ss'} \exp\{i \int_0^{t'} ds\, V(s) - i \int_0^t ds' V(s' + \mu + t - t')\} >_0. \qquad (3.20)$$

Here $T_{ss'}$ is the operator of the negative chronological arrangement for $V(s)$ and of the positive chronological arrangement for $V(s')$ that places the operators of moment $s$ to the left of the operators of moment $s'$.

We can rewrite $A(tt'\mu)$ in the following form:

$$A(tt'\mu) = < S(t') >_0 < S(-t) >_0 \exp[K(tt'\mu)], \tag{3.21}$$

where

$$< S(-t) >_0 = < S^+(t) >_0,$$

$$K(tt'\mu) = \int_0^t ds \int_0^t ds' [< V(s)\, V(s'+\mu+t'-t) >_0 - < V >^2] + \dots . \tag{3.22}$$

If we neglect the variation of elastic constants in the formula (3.22), then only the first term differs from zero in the harmonic approximation [15]. Consideration of variations of elastic constants and the anharmonicity of vibrations leads to the infinite expansion (3.22).

It is evident that the higher the approximation in $V$ we use for $\exp[K(tt'\mu)]$, the broader the spectral distribution we obtain near the Rayleigh line. The width of the above-mentioned distribution for the fixed approximation depends then on the model of the impurity centre used for the description. Taking account of the variation of elastic constants in the harmonic approximation increases the above-mentioned region two times in comparison with the model which takes into account only the variations of the nuclear equilibrium positions. Indeed, if we neglect the variation of elastic constants in the $k$-th order, we obtain the $k$-particle correlators; taking account of variations of elastic constants it is necessary to add to $V$ the quadratic terms of creation and destruction operators. Hence, $2k$-particle correlators which attain a two times broader spectral distribution appear in the $k$-th order. The above-mentioned region is analogously increased also by the vibrational anharmonicity.

Thus, in the frequency region $|\Omega'| > \omega_L$ $(\Omega' = \omega_0 - \Omega)$ the variation of elastic constants and the vibrational anharmonicity make a contribution in lower orders than the variation of the equilibrium states of nuclei. Hence it follows that the relative influence of the variation of elastic constants and the vibrational anharmonicity is the weaker the smaller is $\Omega$* on condition that $|\Omega'| > \omega_L$. Therefore it is possible to restrict ourselves to the second approximation in $V$ for $K(tt'\mu)$ in the region under study (small $|\Omega'|$) not only in case of a weak electron-phonon interaction but also in case of a strong interaction. In contrast to that we cannot restrict ourselves to the second approximation in $\ln(< S(t') >_0 < S^+(t) >_0)$ in case of a strong interaction as the main contribution to $< S(t) >_0$ is made by terms of higher orders in $V$ where the influence of the variation of elastic constants and the vibrational anharmonicity is relatively great.

Let us carry out the Fourier transformation in (3.22)

$$< V(s)\, V(s'+\mu+t'-t) >_0 - < V >_0^2 = \int_{-\infty}^{\infty} d\omega\, J(\omega)\, e^{i\omega(s'-s+\mu+t'-t)}. \tag{3.23}$$

After integrating over $s$ and $s'$ we obtain the formula for $K(tt'\mu)$

$$K(tt'\mu) = \int_{-\infty}^{\infty} d\omega\, \frac{J(\omega)}{\omega^2}\, e^{i\omega\mu} \left(1 + e^{i\omega(t'-t)} - e^{i\omega t'} - e^{-i\omega t}\right). \tag{3.24}$$

---

* Here we take into account that the contribution to the intensity of Raman scattering decreases with an increase of the order in the expansion of $\exp[K(tt'\mu)]$ in $V$. See below, section III.4.

Let us expand $A(tt'\mu)$ in powers of $K(tt'\mu)$:

$$A(tt'\mu) = <S(t')_0><S(-t)>_0 \sum_{n=0}^{\infty} \frac{K^n(tt'\mu)}{n!}. \tag{3.25}$$

We call the contribution made by the term of number $n = k$ the $k$-th order spectrum. It is easy to see that the zero order spectrum represents the Rayleigh line. The first and second order spectra are determined by the formulae

$$W_1(\omega_0, \Omega') = B \frac{I(\Omega')}{(\Omega')^2} \mid \Phi(\omega_0) - \Phi(\omega_0 - \Omega') \mid^2, \tag{3.26}$$

$$W_2(\omega_0, \Omega') = \frac{B}{2} \int_{-\infty}^{\infty} dx \frac{I(x) J(\Omega' - x)}{x^2 (\Omega' - x)^2} \mid \Phi(\omega_0) + \Phi(\omega_0 - \Omega') - \\ - \Phi(\omega_0 - x) - \Phi(\omega_0 + x - \Omega') \mid^2. \tag{3.27}$$

The higher order spectra can be found analogously.

Formulae determining the vibrational wing of the Rayleigh line will be simplified in the essential case of low temperatures ($J(\omega)$ is considerably different from zero only for positive $\omega$) and for small frequencies $|\Omega'|$. Indeed, if

$$|\Omega'| \ll \left| \int_0^{\infty} dt\, e^{i\omega_0 t - \frac{\gamma_1}{2} t} < S(t) >_0 \right|^2 \tag{3.28}$$

then the function $K(tt'\mu)$ in the formula (3.25) can be expanded in powers of $t$ and $t'$ and restricted to the terms that are the first ones differing from zero. In doing so we obtain

$$W_k(\omega_0, \Omega') = \frac{B}{k!} J_k(\Omega') \left| \int_0^{\infty} dt\, t^k e^{i\omega_0 t - \frac{\gamma_1}{2} t} < S(t) >_0 \right|^2. \tag{3.29}$$

Here $J_k(\Omega')$ is the folding of the $k$-th order of the function $J(\Omega')$: $J_0(\Omega') = \delta(\Omega')$, $J_1(\Omega') = J(\Omega')$, $J_2(\Omega') = \int_{-\infty}^{\infty} dx\, J(x)\, J(\Omega' - x), \ldots$ . Thus, the shape of the spectrum in the immediate proximity of the Rayleigh line is determined by the sum of $J(\Omega')$ * and its foldings.

For comparison it should be mentioned that the partial spectra of the first, second, etc. orders in the phonon wings of the absorption and luminescence spectra of the impurity centre are determined by the foldings of the function $J(\pm(\Omega - \omega_{10})) / (\Omega - \omega_{10})^2$.

If local or pseudolocal modes are present, the function $J(\omega)$ has narrow maxima at corresponding frequencies. Every such maximum will appear in the spectrum forming a series of quasilines, i. e. local and pseu-

---

* In [8] the formula for $J(\omega)$ has been obtained, the variations of the equilibrium states and elastic constants in electronic transition and also the vibrational anharmonicity having been taken into consideration.

dolocal modes must lead to a quasiline structure in the resonance Raman spectrum.

The formulae (3.26), (3.27) and (3.29) allow us to calculate the resonance Raman spectra if the frequency dependence of the function $J(\omega)$ and the absorption spectrum of impurities are known.

As examples let us now consider the spectra of the secondary radiation of impurity centres in two concrete cases: (1) the one-oscillator model, (2) the centre with appreciable Stokes losses.

### 3. *Spectrum of Resonance Secondary Radiation for a One-Oscillator Model* [7]

For simplicity's sake let us consider here the case where upon electronic transition only the nuclear equilibrium states are changed, whereas the elastic constants remain the same. In that case the vibrational Hamiltonians $H_0$ and $H_1$ are connected with unitary transformation of the displacement:

$$H_1 = e^{\nabla} H_0 e^{-\nabla} + \omega_{10}, \tag{3.30}$$

where $\nabla = \sum_{m\alpha} q_{0m\alpha} \frac{\partial}{\partial q_{m\alpha}}$, $q_{m\alpha}$ and $q_{0m\alpha}$ denote respectively the coordinates of the cartesian component $\alpha$ of nucleus number $m$ and its variation in electronic transition.

In the approximation (3.30) the correlator $A(tt'\mu)$ can be presented in the following form

$$A(tt'\mu) = < e^{\nabla(-t')} e^{-\nabla} e^{\nabla(\mu)} e^{-\nabla(\mu - t)} >_0 e^{i\omega_{10}(t'-t)}, \tag{3.31}$$

where $\nabla(\mu) = \exp(i\mu H_0) \nabla \exp(-i\mu H_0)$.

In further calculation of $A(tt'\mu)$ let us restrict ourselves to the approximation of pair correlators. Then

$$A(tt'\mu) = \exp\{g(-t) + g(t') + g(\mu) + g(\mu + t' - t) - g(\mu + t') - \\ - g(\mu - t)\} \exp[i\omega_{10}(t' - t)]. \tag{3.32}$$

Here

$$g(\mu) = < \nabla(0) \nabla(\mu) >_0. \tag{3.33}$$

Here we are considering the model where $g(\mu)$ is the correlator of one damping oscillator. For simplicity's sake let us restrict ourselves to the approximation of exponential damping and examine the zero temperature $(T = 0)$. In that case

$$g(t) = \xi^2 [\exp(i\omega t - \Gamma |t|) - 1] \tag{3.34}$$

($\xi^2$ denotes Stokes losses).

The correlator $g(t)$ may have the form (3.34) if optic electrons are in interaction either with a single local mode or with a single pseudolocal one. In the first case $\Gamma$ is the anharmonic damping constant of the local mode, in the second case $\Gamma$ differs from zero already in the harmonic approximation.

Let us place the formula (3.31) into (3.1) taking account of (3.34). After expanding $A(tt'\mu)$ in powers of $g(t)$ and integrating, we obtain

$$
\begin{gathered}
W(\omega_0,\,\Omega)=\frac{B}{2\pi}e^{-2\xi^2}\sum_{\substack{m,m',l,l',\\ p,k=0}}^{\infty}(-1)^{l+l'}\frac{\xi^{2(m+m'+l+l'+p+k)}}{m!\,m'!\,l!\,l'!\,p!\,k!}\times\\
\times\{[i(\Omega-\omega_{10}+\omega(p-m+l'))-\tfrac{\gamma_1}{2}-\Gamma(p+m+l')]^{-1}\times\\
\times[(i\omega(m-m'+l-l')+\gamma_1+\Gamma(m+m'+l+l')]^{-1}(f(m+l'+k)-\\
-f(m'+l'-k)+f(m'+l'+k)f^*(m-l-k)-\\
-f(m'+l'-k)f^*(m+l+k)]-\\
-[i(\Omega-\omega_0+\omega(p+k+l+l'))-\\
-\Gamma(p+k+l+l')]^{-1}f(m'+l'+k)f^*(m-l-k)+Cc\}
\end{gathered}
\tag{3.35}
$$

where $f(m'\pm l'\pm k)\equiv[i(\omega_{10}-\omega_0+\omega(m'+l'+k))-\frac{\gamma_1}{2}-\Gamma(m'\pm l'\pm k)]^{-1}$; $Cc$ denotes complex conjugated terms.

Let us examine the terms corresponding to $m=m'=l=l'=0$ (i. e. $g(-t)+g(t')-g(\mu+t')-g(\mu-t)=0$) in case of $\omega_0\neq\omega_{10}$. The main contribution to (3.35) is made by the following terms: *

$$
\begin{gathered}
W^{(1)}(\omega_0,\,\Omega)=\frac{B}{2\pi\gamma_1}e^{-2\xi^2}\sum_{p=0}^{\infty}\frac{\xi^{2p}}{p!}\cdot\frac{1}{i(\Omega-\omega_{10}+\omega p)-\frac{\gamma_1}{2}-\Gamma p}\times\\
\times\sum_{k=1}^{\infty}\frac{\xi^{2k}}{k!}\left[\frac{1}{i(\omega_{10}-\omega_0+\omega k)-\frac{\gamma_1}{2}-\Gamma k}-\frac{1}{i(\omega_{10}-\omega_0+\omega k)-\frac{\gamma_1}{2}+\Gamma k}\right]+Cc\approx\\
\approx\frac{B}{2\pi\gamma_1}e^{-2\xi^2}\sum_{p=0}^{\infty}\frac{(\gamma_1+2\Gamma p)\xi^{2p}/p!}{(\Omega-\omega_{10}+\omega p)^2+\left(\frac{\gamma_1}{2}+\Gamma p\right)^2}\sum_{k=1}^{\infty}\frac{2\Gamma k\xi^{2k}/k!}{(\omega_{10}-\omega_0+\omega k)^2+(\Gamma k)^2}\,.
\end{gathered}
\tag{3.36}
$$

The factor containing the sum over $p$ gives luminescence and the sum over $k$ corresponds to the absorption spectrum. Hence the secondary radiation spectrum contains luminescence.

It is easy to see that the terms $m$, $m'$, $l$, $l'\neq 0$ contain the Rayleigh line ($\Omega=\omega_0$) and its vibrational recurrences ($\Omega=\omega_0-\omega P$).

Let us discuss as an example the intensity of these lines if the frequency of the exciting light coincides with the maximum of one of the absorption lines, i. e. $\omega_{10}-\omega_0+M\omega=0$ ($M=m+l+k=m'+l'+k$). Then the intensity of the line of number $P<M$ ($P=p+k+l+l'\neq 0$) is expressed by the formula

$$
\begin{gathered}
W_P=\frac{B}{\pi\Gamma^3PM}e^{-2\xi^2}\sum_{k=0}^{P}\sum_{l=0}^{P-k}\sum_{l'=0}^{P-k-l}(-1)^{l+l'}\times\\
\times\frac{\xi^{2[P-l-l'+2(M-k)]}(P+M-k)}{k!\,l!\,l'!(M-l-k)!\,(M-l'-k)!\,(P-l-l'-k)!(M-k)(P+M-2l-2k)}\,.
\end{gathered}
\tag{3.37}
$$

---

* The omitted terms are all at least $\Gamma/\gamma_1$ times smaller.

Comparing the formulae (3.36) and (3.37) we are convinced that the Raman scattering is indeed $\Gamma/\gamma_1$ times weaker than the luminescence.

If the absorption band consists of the non-overlapping quasilines ($\omega \gg \Gamma$) and if the exciting light falls between the absorption bands $I_\varkappa(\omega_0)$ is practically equal to zero in (3.15), (3.36). It is easy to notice that then $\Gamma$ can be neglected. This gives the results obtained by E. Trifonov and K. Peuker [17]. Thus the model used in [17] is applicable only in this particular case.

## 4. Appreciable Stokes Losses

Let us examine Rayleigh and Raman scattering by the impurity centre with appreciable Stokes losses (when $I_\varkappa(\omega_0)$ is described by a Gaussian).

In this case $\langle S(t)\rangle_0 = \exp\left[it(b+\omega_0) - \frac{\sigma^2}{2}t^2\right]$ where $b$ is the difference between the exciting frequency and the maximum of the absorption band, $\sigma^2$ — the second central moment of the absorption band. The condition for appreciable Stokes losses is $\sigma \gg \omega_L$. If we restrict ourselves to the second order terms in the expansion of $\ln\langle S(t)\rangle$ then

$$b = \langle V\rangle_0 - \omega_0, \quad \sigma^2 = \int_{-\infty}^{\infty} J(\omega)\,d\omega.$$

In the case under consideration the total intensity of the Rayleigh line is equal to

$$I_R = \frac{2B}{\sigma^2}e^{-2z^2}\left[\frac{\sqrt{\pi}}{2} + i\int_0^z e^{x^2}dx\right]^2, \quad z = \frac{b}{\sigma\sqrt{2}}. \tag{3.38}$$

The analysis of this formula shows that the intensity of the Rayleigh line is highest in case of excitation in the maximum of the absorption band ($z=0$), with an increase of $|z|$ the intensity of the Rayleigh line decreases quickly: at $|z|<1$ — exponentially ($\sim\exp(-2z^2)$), at $|z|>1$ as $\sim\exp(-2z^2)\left[\int_0^z \exp(x^2)\,dx\right]^2$. The temperature dependence of the Rayleigh line is the following: at $|z|<1{,}4$ its intensity decreases with the increase of the temperature, at $1{,}4<|z|<3$ it increases and at $|z|>3$ it does not essentially depend on the temperature (more exactly, it decreases slowly).

Let us now consider the spectrum of Raman scattering. Owing to the condition (3.28), the formula (3.29) is correct for $|\Omega'|$ in the region from zero to several $\omega_L$ (at $z=0$ — the excitation in the maximum of the absorption band, the condition (3.28) is replaced by $|\Omega'| \ll \sigma$, at $z \neq 0$, $|\Omega'|$ may be greater). In this region the total intensity of the $k$-th order spectrum $I_k$ is equal to

$$I_k = \frac{B}{2^{k-1}k!\sigma^2}\left|\frac{d^k}{dz^k}\left\{e^{-z^2}\left[\frac{\sqrt{\pi}}{2} + i\int_0^z e^{x^2}dx\right]\right\}\right|^2. \tag{3.39}$$

In particular,

$$
\begin{aligned}
I_1 &= \frac{B}{\sigma^2}\{\pi z^2 e^{-2z^2} + [1 - 2zw(z)]^2\},\\
I_2 &= \frac{B}{\sigma^2}\{(1-2z^2)^2 e^{-2z^2}\frac{\pi}{4} + [z + (1-2z^2)w(z)]^2\}.
\end{aligned}
\tag{3.40}
$$

The function $w(z) = e^{-z^2}\int\limits_0^z e^{x^2}dx$ is tabulated in [27].

As we can see, the relation between the total intensities of the first, second and higher order Raman spectra of a centre with appreciable Stokes losses is determined by two parametres of the absorption spectrum: its half-width and maximum position. The temperature dependence of total intensities is analogous to that of the Rayleigh line. The relation of total intensities $I_2/I_1$ is the highest possible ($\pi/4$) in case of excitation at the maximum of the absorption band, it decreases with the increase of $|z|$.

The spectral distribution of intensities of the first, second and higher order scattering is determined as shown in section III, 2 by the foldings of the function $J(\Omega')$.

The experimental study of the resonance Raman scattering by impurity centres may provide us with new information about their vibronic states. That concerns especially the centres with strong electron-phonon interaction.

Indeed, it follows from the formulae (3.29), (3.39) that the contribution of multi-phonon transitions to the region of the first-order Raman scattering may be small. That considerably facilitates the task of restoring the function $J(\omega)$ on the basis of the Raman scattering spectra as compared with the absorption and luminescence spectra. It must be stressed that the finding of $J(\omega)$ is of noticeable interest since this function gives us detailed information about the local dynamics and electron-phonon interaction of the impurity centre.

## IV. Calculation of Resonance Raman Scattering by F-Centres in KCl and NaCl

The number of experiments on the resonance scattering by luminescence centres is very modest. Among works specially devoted to this promising trend of investigating impurity centres one should mention the experiments of Stekhanov and his collaborators in the field of the Raman spectra of alkali halide crystals activated with $Li^+$, $Br^-$, $J^-$, $Na^+$ [28], etc. and the experiments of Worlock and Porto [29]. Using helium-neon and argon lasers as the sources of excitation, Worlock and Porto examined the resonance Raman spectra of F-centres in NaCl and KCl.

For purposes of comparing the results of the above-presented theory with those of Worlock and Porto, a concrete calculation of the corresponding resonance Raman spectra of F-centres in KCl [30] and NaCl has been carried out. *

As is known, the electron of the F-centre is in strong interaction with lattice vibrations. That enabled us to choose the relatively simple model of appreciable Stokes losses examined in the previous section. We calculated the spectral distribution of intensities of one- and two-phonon transitions which is determined by the formulae (3.26), (3.27) as was shown

---

* The calculation for NaCl has been made by K. Loide.

above. Taking account of the lack of local modes in the F-centre in KCl and NaCl, we are justified in restricting ourselves to the harmonic approximation. Then

$$J(\omega) = \xi^2(\omega)\,\omega^2[n(\omega)+1]\,\frac{\omega}{|\omega|} \tag{4.1}$$

where $\xi^2(\omega)$ is the distribution function of Stokes losses [1].

When calculating $\xi^2(\omega)$ we took into consideration that a totally symmetric variation of equilibrium states of the six $K^+$ (or $Na^+$) ions nearest to the vacancy takes place in electronic transition. In that case

$$\xi^2(\omega) = \frac{1}{2} M d^2 e^2(\omega)\,\omega, \tag{4.2}$$

where $e^2(\omega)$ determines the dependence of the coefficient of the expansion in normal coordinates of the totally symmetric combination of reduced shifts of the nearest neighbours on the vibrational frequency $\omega$; $M$ is the mass of ions $K^+(Na^+)$, $d$ is the shift of the equilibrium position of the totally symmetric coordinate under discussion in electronic transition.

The function $e^2(\omega)$ has been calculated, taking into account the distortion of vibrations near the F-centre and assuming the interaction between the nearest neighbours. We have used the formula obtained in [31]

$$e^2(\omega) = \frac{1}{6\pi} ImG(\omega)\{[1 - pReG(\omega)]^2 + [pImG(\omega)]^2\}^{-1}. \tag{4.3}$$

Here $G(\omega)$ denotes the linear combination of the classical Green functions. We had the opportunity of using the Green functions calculated by Zavt for KCl and by Loorits and Loide for NaCl.* Constant $p$ is determined by the temperature dependence of the second central moment of the absorption bands of F-centres on the basis of the experimental data of Markham and Konitzer [33]. The relation of total intensities of one-phonon and two-phonon transitions is expressed by the formulae (3.40) ($I_2/I_1 \simeq 0{,}2$ for KCl and $I_2/I_1 \simeq 0{,}6$ for NaCl).

Contours of the Stokes component of the Raman spectrum calculated on the basis of the formulae (4.1)—(4.3) and (3.26), (3.27) and the Green functions [31] are presented in Figures 1—2. For comparison the experimental curves of Worlock and Porto are added. The comparison of the calculated curve with experimental data shows that the contour of the spectrum is mainly determined by one-phonon transitions, two-phonon transitions make a considerable contribution only to the high-frequency region of the spectrum: for KCl higher than 150 cm$^{-1}$, for NaCl — 200 cm$^{-1}$. The maximum of one-phonon transitions of the calculated curve is near 75 cm$^{-1}$ for KCl, coinciding with the experimentally observed maximum at 60—90 cm$^{-1}$ and at 165 cm$^{-1}$ for NaCl (the experimental datum is $\sim$ 170 cm$^{-1}$).

Taking into account the degree of the exactness of the experiment and the relative simplicity of the model used, the agreement of the theory with the experiment for KCl can be considered satisfactory.

---

* The Green functions for KCl have been calculated in [31] in the approximation of the interaction between the nearest neighbours (both central and non-central interactions having been taken into account). The Green functions for NaCl have been calculated on the basis of the tables of dispersion laws calculated by Maradudin in the approximation of deformed ions of Karo and Hardy [32].

In case of NaCl the theoretical curve lacks an experimentally observed maximum in the low-frequency region. The observed dependence on the polarization of light and the exciting frequency also remains unaccounted for. It results from the formula (3.1) that only the intensity of the scattered light, but not the spectral distribution, depends on its polarization in the Condon approximation. It can be supposed that in case of NaCl side by side with ordinary $F$-centres also $F_A$- or $F_2$-, $R$-, etc. centres make a contribution to scattering, a fact which would explain the observed dependence upon polarization. The relative increase in the intensity of the longer-wave region of the scattering spectrum in case of the longer-wave exciting light in Worlock's and Porto's experiments speaks in favour of assuming the existence of scattering centres whose absorption bands are on the longer-wave side from excitation.

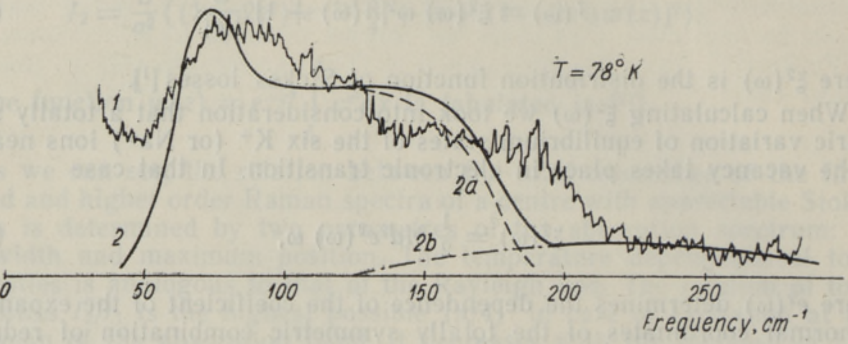

Fig. 1. The resonance Raman spectrum of the F-centre in KCl (the Stokes component) in case of the exciting light of wave-length λ = 6328 Å:
1 — the spectrum measured by Worlock and Porto (the unpolarized spectrum); 2 — the calculated spectrum (2a — the one-phonon region of the calculated spectrum, 2b — the two-phonon region of the calculated spectrum).

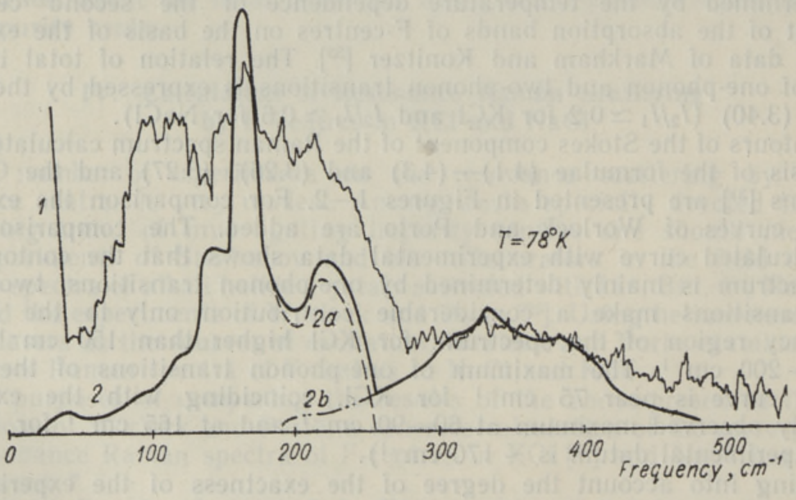

Fig. 2. The resonance Raman spectrum of the F-centre in NaCl (the Stokes component) in case of the exciting light of wave-length λ = 5145 Å (notations are the same as in Fig. 1).

## V. Conclusion

### *1. On the Classification of Secondary Radiation*

We are not of the opinion that secondary scattering should always be divided into luminescence and scattering. On the contrary, secondary scattering represents an entity in the general case, attempts to divide it may prove to be fruitless because they may be senseless. As is generally known, a physically reasonable division is possible in case of non-resonance excitation. Then there exists practically no luminescence, but only scattering. Division is possible and physically reasonable sometimes also in case of resonance excitation. We have shown above that it is possible in the impurity centre under certain sufficiently broad conditions.

We have examined the classification of the secondary radiation from a purely spectral aspect. It is evident that various other approaches are also possible. One should first of all take into consideration the classification according to the temporal feature — according to the speed of the radiation damping as compared with the period of light vibrations. That has been used as one of the two basic features in the classical definition of luminescence by Vavilov (see, e. g. [4]). It should be mentioned, however, that the experiment is usually set so that namely the time-averaged radiation spectrum is measured. Therefore the spectral feature (in those cases when it is possible to use it) must be equivalent to the temporal criterion.

The classification of the secondary radiation by the impurity centre according to the time and character of the afterglow in case of excitation by a pulse of light has recently been elaborated by Purga [34].

The secondary radiation excited by a pulse of light represents an interesting and prospective phenomenon for the examination of the luminescence centre. In particular, the methods of quantum beats belong here. However, this interesting field of study is not included in the present survey.

### *2. Generalization for the Exciting Line of Finite Width*

We have examined the secondary radiation by impurity centres in case of monochromatic excitation. The generalization of the results for the concrete case of an exciting line with a finite spectral width is expressed by the formula

$$W(\Omega) = [n(\Omega) + 1] \int d\omega_0 W(\omega_0, \Omega), \tag{5.1}$$

where $W(\Omega)$ is the secondary radiation spectrum, $n(\Omega)$ — the function of density of the number of photons, $\Omega$ and $\omega_0$ include directions of wave vectors and the index of the polarization of photons. In this formula the term proportional to $n(\Omega)$ describes stimulated processes (stimulated Raman scattering and stimulated emission).

We are not going to discuss here the results to which the formula (5.1) leads in case of non-monochromatic excitation outside resonance. They are rather trivial. Let us dwell briefly upon the resonance case.

In case of excitation in the phonon wing of the absorption band, the main part of the secondary radiation represents luminescence independent of the exciting spectrum. Moreover, the spectrum contains much

($\Delta\varepsilon/\gamma_l$ times) weaker Rayleigh and Raman scattering whose spectrum is dependent on the position, form and width $\Delta\omega_0$ of the exciting spectrum. However, if the exciting line is sufficiently narrow ($\Delta\omega_0 \ll \Gamma$), the Raman scattering spectrum does not depend on $\Delta\omega_0$ and is determined by the formulae in section III.

If the excitation takes place in the region of pure-electronic transition, the secondary radiation spectrum in the region of $|\Omega - \omega_{10}| \gg \gamma_l + \gamma_v$ also represents luminescence (the phonon wing of the latter). The spectrum near $\omega_{10}$ depends, however, essentially on the width of the exciting line. If $\Delta\omega_0 \ll \gamma_l + \gamma_v$ the spectrum contains a Rayleigh line of width $\Delta\omega_0$ and a pure-electronic line of width $\gamma_l + \gamma_v$. The relation of their finite intensities is equal to $\gamma_l/\gamma_v$. If $\Delta\omega_0 \gg \gamma_l + \gamma_v$, the spectrum in the region of $\omega_{10}$ is a pure-electronic line.

### *3. Spectral Width of the Photon Packet of Excitation and Vibrational Relaxation*

Let us consider the process of interaction of the impurity centre with a photon wave packet of finite width $\Delta\omega_0$; we pay particular attention to the mutual relation between the vibrational relaxation resulting from electronic transition and the width of the photon packet of excitation.

To begin with, let us examine the situation from the point of view of the classical theory of vibrations. In this case it is important to stress that the vibrational relaxation starts already from the very beginning of the interaction between the photon packet and the centre. It is interesting to examine to what range the vibrational excitation spreads as a result of relaxation during the interaction between the luminescence centre and the incident photon packet, i. e. our aim is to obtain an estimate of the thermal spike of the crystal in the impurity region after the electronic transition.

Let us study the case where the impurity does not create local or well-expressed pseudolocal vibrations. Here we may take the speed of sound $v \sim 10^5$ cm sec$^{-1}$ as the spreading speed of vibrational waves in the vicinity of the impurity centre. The duration of the interaction between the photon packet of width $\Delta\omega_0$ and the luminescence centre is obviously of the order $\Delta\omega_0^{-1}$. Consequently, the linear dimensions ($L$) of the thermal spike region during electronic transition is of the order

$$L \sim 2v/\Delta\omega_0, \tag{5.2}$$

where we take $v \simeq 5 \cdot 10^5$ cm sec$^{-1}$ for purpose of estimation.

(1) Highly non-monochromatic excitation.

In case of an exciting packet of width $\Delta\omega_0 \gtrsim 10^{-1}$eV ($\Delta k \gtrsim 10^3$cm$^{-1}$) the time of the interaction with the impurity centre is $\lesssim 10^{-14}$ sec. Then $L \lesssim 10^{-8}$ cm. In case of such an excitation for centres with appreciable Stokes losses, the redundant local thermal spike may constitute several thousand degrees*. But already $\sim 10^{-12}$ sec after electronic transition the excitation spreads over the region $L \sim 10^{-6}$ cm. As a result, the local thermal spike decreases to the practically insignificant value of order $10^{-2}$ degrees.

---

* One cannot, of course, speak in the strict sense of the temperature of an impurity centre during a smaller time interval than the period of vibrations $\sim 10^{-13}$ sec. As redundant temperature we regard here only the mean redundant (in relation to thermal equilibrium) vibrational energy of the impurity centre.

(2) Sufficiently monochromatic excitation.

If the exciting photon packet has a width $\Delta\omega_0 \sim 10^{-3}$eV($\Delta k \sim 10$ cm$^{-1}$) the time of its interaction with the centre is $\sim 10^{-12}$ sec. Within this time the vibrational excitation spreads to a distance of order $10^{-6}$ cm. Therefore the local thermal spike does not exceed several hundredths of a degree immediately after electronic transition. It is important to note that in case of the interaction of a light packet of width $\Delta\omega_0 \sim 10^{-3}$ eV$\gg\gamma_l$ even with a centre which has appreciable Stokes losses, the redundant temperature does not rise over some tenths of a degree at any moment (we regard a time moment as a time interval of $\sim 10^{-13}$ sec). In case of a more monochromatic excitation, the local thermal spike is still smaller. Consequently, at $\Delta\omega_0 \lesssim 10^{-3}$ eV the thermal equilibrium of the impurity centre with regard to vibrations in general is not appreciably violated (neither during nor after electronic transition).

The given estimates are, of course, but rough estimates. They cannot be applied in case of pseudolocal or local modes. In that case the share of redundant energy belonging to the above-mentioned modes as a result of electronic transition may be one or two (but sometimes even more) times greater. Nevertheless, even in case of sufficiently monochromatic excitation (during which $\Delta\omega_0$ may still be far greater than the radiative width $\gamma_l$) the thermal equilibrium of vibrations is not violated after electronic transition.

In case of a quantum theoretical examination of the problem, it is best to base the discussion on the width $\Delta\varepsilon$ of the wave packet of energetic states of the impurity centre arising upon excitation with a photon packet whose width is $\Delta\omega_0$. It is natural to assume $\Delta\varepsilon \lesssim \Delta\omega_0$. The sufficiently stationary state of the impurity centre corresponds to the sufficiently monochromatic excitation.

If $\omega_0$ falls on the narrow levels of local or clearly expressed pseudolocal modes, a well localized vibrational excitation arises also in case of small $\Delta\omega_0$. The impurity centre receives considerable vibrational energy, a strong local thermal spike occurs and ordinary relaxation — the gradual departure of the redundant vibrational energy from the centre during $\tau(\tau \simeq 10^{-11} - 10^{-12}$ sec) takes place. Since $\tau \gg \gamma_l^{-1}$, the theory presented in III.1 is correct and luminescence forms the main part of the secondary radiation. However, the formula (3.29) in III.2 for the secondary radiation supplementary to luminescence is not applicable since the condition (3.28) is violated already in the frequency interval $|\Delta\Omega'| = \Delta\omega_0$. It can be supposed on the basis of physical considerations that some part of the radiation (of order of the relation between the time of the vibrational relaxation and the optical life-time) will correspond to the emission of the "heated" centre.

If $\omega_0$ falls on the region of the energy spectrum without narrow levels, the arising state is sure to be matched by corresponding fairly extensive vibrational packet. In the limit case $\Delta\omega_0 = \Delta\varepsilon = 0$ a stationary vibrational state arises with a determined set of quantum numbers of crystal vibrations to which corresponds the excitation of the vibration of the whole crystal and the insignificantly small thermal spike of the impurity centre. If we turn our attention to the corresponding estimations of the finite values of $\Delta\omega_0$, it can easily be seen that they are reduced to the estimation obtained above on the basis of the classical theory of vibrations.

Thus, also a quantum theoretical study leads to the conclusion that in case of excitation with sufficiently monochromatic light ($\Delta\omega_0 \simeq 10^{-3}$ eV,

$\Delta k \simeq 10\ \text{cm}^{-1}$) of an impurity centre which does not contain local or clearly expressed pseudolocal vibrations, there is no noticeable local thermal spike whatever. Consequently, there is no considerable relaxation of redundant vibrational energy either.

Thus, the wide-spread opinion that thermal equilibrium is violated in the impurity centre as a result of optical absorption is incorrect if the excitation is sufficiently monochromatic. In the latter case there is no need, when describing luminescence, for an intermediate process of vibrational relaxation after the absorption of the photon.

It should be stressed that what has been said above does not depreciate the role of vibrational relaxation in explaining luminescence. We should like to point out that the latter must not be considered only as a relaxation after electronic transition.

After all, it is important from the point of view of the secondary radiation (both for luminescence as well as for scattering) that the localized vibrational excitation arising in some way in the centre could decay quickly in comparison with the optical life-time. The property of quick relaxation is then inherent among the properties of the vibrational spectrum of the impurity crystal. In case of monochromatic excitation, the localized vibrational packet does not come into being, there is no relaxation, but the property of "quick relaxation" appears to be essential in this case as well. As a result of this property, in particular, the criterion (3.9) is fulfilled, allowing us to divide the secondary radiation into scattering and luminescence.

## *4. On the Role of Thermal Quenching*

We have not examined here the case of thermally quenched luminescence centres which is topical from the experimental point of view. In order to describe such centres it is necessary to disregard the adiabatic approximation. However, it is evident from general considerations (see, e. g. [5]) that if the characteristic period of quenching $\tau_q$ (determined by the probability of non-radiation transitions) is, on the one hand, essentially smaller than the life-time of the excited state $\gamma_1^{-1}$, but on the other hand far greater than the time of establishment of thermal equilibrium with regard to vibrations $\Delta\varepsilon^{-1}$:

$$\Delta\varepsilon^{-1} \ll \tau_q \ll \gamma_1^{-1}$$

then the impurity centre will produce resonance Raman scattering, but the secondary radiation spectrum will lack luminescence.

## *5. On Scattering on Forbidden Electronic Transitions*

We have studied scattering on allowed electronic transitions. In accordance with this, the matrix elements of dipole transitions were presented as electronic matrix elements in our formulae. The formal generalization for the quadrupole, etc. interactions is trivial: it is only necessary to replace dipole electronic matrix elements by quadrupole ones. Both these as well as the others is only the parametre of the theory. Therefore all the conclusions drawn from the vibrational structure of spectra remain the same as before, but the contribution to the total spectrum of the forbidden level is far smaller than to that of the allowed level ($\alpha^4$ times where $\alpha$ has the order of the relation of atomic dimensions to the light wave length). Owing to this last factor, scattering on forbidden transitions of impurity centres is hardly ever topical. In the non-resonance case scattering on forbidden transitions is insignificant in the summary polarizability. Also in the resonance case the intensity of scattering by impurity centres is so small that it becomes extremely difficult to distinguish it against a background of non-resonance scattering of the host crystal or resonance luminescence and scattering on allowed transitions of impurities and defects which cannot be checked up.

In particular, it is difficult to obtain information about the impurity centre $Cr^{3+}$ in ruby by means of Raman scattering of frequencies near the R-line.

## REFERENCES

1. Ребане К. К., Кристофель Н. Н., Трифонов Е. Д., Хижняков В. В., Изв. АН ЭССР. Сер. физ.-матем. и техн. наук, **13**, № 2, 87 (1964).
2. Кристофель Н. Н., ФТТ, **7**, 2519 (1965).
3. Trifonov E. D., Peuker K., J. Phys., **26**, 738 (1965).
4. Вавилов С. И., Собрание сочинений, т. 2, М., 1952.
5. Степанов Б. И., Апанасевич Н. А., Изв. АН СССР. Сер. физ., **22**, 1380 (1958).
6. Placzek G., Rayleigh-Streuung und Raman-Effekt, Handbuch der Radiologie, IV, Leipzig, 1934.
7. Техвер И., Хижняков В., Изв. АН ЭССР. Сер. физ.-матем. и техн. наук, **15**, № 1, 9 (1966).
8. Hizhnyakov V., Tehver I., Phys. stat. sol., **21**, 2 (1967).
9. Завт Г. С., ФТТ, **5**, 1946 (1963).
   Пурга А. П., Тр. Ин-та физ. и астрон. АН ЭССР, № 27, 57 (1964).
10. Кащеев В. Н., Кривоглаз М. А., ФТТ, **3**, 1528 (1961).
    Иванов М. А., Квашнина Л. Б., Кривоглаз М. А., ФТТ, **7**, 2047 (1965).
11. Пекар С. И., ЖЭТФ, **22**, 641 (1952).
12. Перлин Ю. Е., ФТТ, **2**, 1915 (1960).
13. Перлин Ю. Е., Розенфельд Ю. Б., Уч. зап. Кишиневского ГУ, **75**, 1 (1964).
14. Дзюб И. П., Лубченко А. Ф., ФТТ, **3**, 3602 (1961).
15. Лубченко А. Ф., Павлик Б. М., ФТТ, **5**, 1714 (1963).
16. Lubchenko A. F., Phys. stat. sol., **9**, 879 (1965).
17. Трифонов Е. Д., Пойкер К., ФТТ, **7**, 2345 (1965).
18. Ребане К. К., Техвер И. Ю., Тр. Ин-та физ. и астрон. АН ЭССР, № 29, 54 (1964).
19. Борн М., Хуан Кунь, Динамическая теория кристаллических решеток. ИЛ, М., 1958.
20. Кондиленко И. И., Коротков П. А., Стрижевский В. Л., Опт. и спектр., **9**, 26 (1960).
21. Крушинский Л. Л., Шорыгин И. П., Опт. и спектр. **16**, 30 (1964).
22. Техвер И. Ю., Тр. Ин-та физ. и астрон. АН ЭССР, № 32, 31 (1967).
23. Lax M., J. Chem. Phys., **20**, 1752 (1952) (перевод в сборнике «Проблемы физики полупроводников», ИЛ, М., 1957).
24. Ребане К. К., Сильд О. И., Изв. АН ЭССР. Сер. физ.-матем. и техн. наук, **15**, № 2, 299 (1966).
25. Кривоглаз М. А., ФТТ, **47**, 1707 (1964); ЖЭТФ, **48**, 310 (1965).
    McCumber D. E., Phys. Rev., **A 134**, 299 (1964).
26. Техвер И., Хижняков В., Изв. АН ЭССР. Сер. физ.-матем. и техн. наук, **15**, № 4, 601 (1966).
27. Карпов К. А., Таблицы функции $w(z) = e^{-z^2} \int\limits_0^z e^{x^2} dx$ в комплексной области, Изд. АН СССР, М., 1954.
28. Стеханов А. И., Элиашберг М. Б., ФТТ, **5**, 2985 (1963), **6**, 3397 (1964); Стеханов А. И., Максимова Т. И., ФТТ, **8**, 924 (1966).
29. Worlock J. M., Porto S. P. S., Phys. Rev. Lett., **15**, 697 (1965).
30. Техвер И., Изв. АН ЭССР. Сер. физ.-матем. и техн. наук, **15**, № 4, 603 (1966).
31. Завт Г. С., Теория колебаний кристаллов типа NaCl с примесью, Диссертация, Ин-т физ. и астрон. АН ЭССР, Тарту, 1966.
32. Каго А. М., Hardy J. R., Phys. Rev., **129**, 2024 (1963).
33. Konitzer J. D., Markham J. J., J. Chem. Phys., **32**, 843 (1960).
    Markham J. J., Konitzer J. D., J. Chem. Phys., **34**, 1936 (1961).
34. Пурга А. П., Изв. АН ЭССР. Сер. физ.-матем. и техн. наук, **15**, № 2, 293 (1966).

*Институт физики и астрономии*
*Академии наук Эстонской ССР*

Поступила в редакцию
24/II 1967

*K. REBANE, V. HIŽNJAKOV, I. TEHVER*

## MÕNINGAID KRISTALLI LISANDITSENTRITE SEKUNDAARSE KIIRGUSE TEOORIA KÜSIMUSI

Artikkel kujutab endast ülevaadet meie töödest lisanditsentrite kombinatsioonhajumisteooria alal. Vaadeldakse lisanditega kristalli sekundaarse kiirguse spektrit kahel juhul: esiteks — kui kristallile langeva valguse sagedus on kaugel neeldumisribast, teiseks — kui ta langeb lisandi neeldumisribasse (resonantsjuht). Mõlemal juhul kasutatakse adiabaatilist lähendust.

Töös käsitletakse sekundaarse kiirguse teooria üldküsimusi, nagu sekundaarse kiirguse jaotamine luminestsentsiks ja hajumiseks ning võnkerelaksatsiooni osa lisanditsentri sekundaarses kiirguses.

Esitatakse sekundaarse kiirguse spektri intensiivsuse jaotuse valemid, arvestades võnkumiste anharmoonilisust, tuumade tasakaaluasendite nihkeid ja võre elastsuskonstantide muutust elektronüleminekul. Esimesel juhul on oluline arvesse võtta elektron-maatrikselementide sõltuvust võnkekoordinaatidest (s. o. arvestada kõrvalekaldumist Condoni lähendusest). On saadud parandusliikmed Placzeki lähenduses tuntud valemile, mis võivad intensiivsuse jaotust oluliselt mõjutada.

Erilist tähelepanu on osutatud resonantsjuhule. Näidatakse, et tavaliselt hajumise jaoks kasutatav teist järku valem sisaldab ka luminestsentsi. Viimase eraldamiseks on oluline arvestada võnkeergutuste spektri lõplikku laiust $\Delta\varepsilon$, eeldades, et $\Delta\varepsilon \gg \gamma_1$ ($\gamma_1$ on ergutatud elektronseisundi loomulik laius). Üksikasjalikumalt vaadeldakse sekundaarse kiirguse spektri võnkestruktuuri ühe ostsillaatori (on arvestatud elektroni interaktsiooni ühe (lokaalse) võnkumisega) ja suurte Stokesi kadudega tsentri jaoks. Kui viimase korral luminestsentsi spekter kujutab endast laia struktuurita riba, siis kombinatsioonhajumisspekter võib omada selgesti väljendatud kvasijoon-struktuuri.

On antud F-tsentri resonantshajumisspektri arvutuse tulemused KCl ja NaCl kristalli jaoks. Arvutatud kõveraid võrreldakse eksperimentaalsetega (Worlocki ja Porto eksperiment [29]).

---

*К. РЕБАНЕ, В. ХИЖНЯКОВ, И. ТЕХВЕР*

## НЕКОТОРЫЕ ВОПРОСЫ ТЕОРИИ ВТОРИЧНОГО СВЕЧЕНИЯ ПРИМЕСНЫХ ЦЕНТРОВ КРИСТАЛЛА

Статья содержит обзор цикла работ авторов по теории комбинационного рассеяния света на примесных центрах в кристалле.

Рассматриваются спектры вторичного свечения и их колебательная структура при возбуждении: 1) вдали от резонанса с полосами поглощения (нерезонансный случай), 2) в полосе примесного поглощения (резонансный случай). Используется приближение Борна и Оппенгеймера.

Обсуждаются проблема разделения вторичного свечения на люминесценцию и рассеяние и роль колебательной релаксации во вторичном свечении примесных центров.

Получены формулы для распределения интенсивностей в соответствующих спектрах с учетом ангармонизма колебаний, различия положений равновесия ядер и упругих постоянных решетки в разных электронных состояниях. В резонансном случае использовалась методика упорядоченных операторов, а в нерезонансном — разложение по степеням разности колебательных гамильтонианов. В последнем случае весьма существенен учет зависимости электронного матричного элемента от колебательных координат. Получены известные формулы комбинационного рассеяния в приближении Плачека и поправки к ним. Показано, что в резонансном случае модифицированная для кристалла формула Крамерса-Гейзенберга, используемая обычно лишь для релеевского и комбинационного рассеяний, описывает также и люминесценцию. Для выделения люминесценции из спектра вторичного свечения необходимо учесть конечную ширину $\Delta\varepsilon$ спектра колебательных возбуждений, приняв во внимание условие $\Delta\varepsilon \gg \gamma_1$ ($\gamma_1$ — радиационная ширина возбужденного электронного уровня). Подробно исследована колебательная структура спектра резонансного вторичного свечения для модели, учитывающей взаимодействие электронного перехода с одним (локальным) осциллятором, и для центра с большими стоксовыми потерями. В последнем случае спектр люминесценции представляет собой широкую бесструктурную полосу, в то время как резонансное комбинационное рассеяние может иметь четко выраженную квазилинейчатую структуру.

Приведены результаты конкретного расчета колебательной структуры спектров резонансного комбинационного рассеяния $F$-центров в NaCl и KCl. Рассчитанные кривые сравниваются с экспериментальными кривыми Ворлока и Порто [29].