EESTI NSV TEADUSTE AKADEEMIA TOIMETISED. XVII KÖIDE
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ИЗВЕСТИЯ АКАДЕМИИ НАУК ЭСТОНСКОЙ ССР. ТОМ XVII
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INFLUENCE OF THE DEPENDENCE OF ELECTRONIC MATRIX ELEMENT ON VIBRATIONAL COORDINATES UPON RESONANT SECONDARY RADIATION OF THE IMPURITY CENTRE

I. TEHVER. ELEKTRON-MAATRIKSELEMENDI VONKEKOORDINAATIDEST SÕLTUVUSE MÕJU LISANDITSENTRI SEKUNDAARSELE KIIRGUSELE RESONANTSIJUHUL

И. ТЕХВЕР. ВЛИЯНИЕ ЗАВИСИМОСТИ ЭЛЕКТРОННОГО МАТРИЧНОГО ЭЛЕМЕНТА ОТ КОЛЕБАТЕЛЬНЫХ КООРДИНАТ НА РЕЗОНАНСНОЕ ВТОРИЧНОЕ СВЕЧЕНИЕ ПРИМЕСНОГО ЦЕНТРА

In [1-4] the resonant secondary radiation (the Rayleigh and Raman scattering in the main) has been examined in the Condon approximation (the dependence of the electronic matrix element on the vibrations is not taken into account), in [1,5] the non-resonant scattering has been studied with the dependence of electronic matrix elements on the vibrations as a necessary condition having been taken into consideration. The present paper is a sequel of the mentioned papers [1-5]. It deals with the role of the deviation from the Condon approximation in the Raman scattering in case of excitation in the absorption band and near it.

In case of excitation in the impurity absorption band, the secondary radiation spectrum is determined by the expression

$$W(\omega_0\Omega)=\frac{N_I\omega_0^4}{(2\pi)^2c^3}\sum_{\substack{\alpha\beta\\ \gamma\delta}} i_\alpha i_\beta E_\gamma E_\delta \int\limits_{-\infty}^{\infty} d\mu e^{i(\Omega-\omega_0)\mu}\iint\limits_{0}^{\infty} d\tau d\tau' e^{-i\omega_0(\tau'-\tau)-\gamma(\tau'+\tau)} A(\tau\tau'\mu), \qquad (1)$$

where

$$A(\tau\tau'\mu)=\left< M_\delta e^{\frac{i}{\hbar}\tau' H_1} M_\beta e^{\frac{i}{\hbar}\mu H_0} M_\alpha e^{-\frac{i}{\hbar}\tau H_1} M_\gamma e^{-\frac{i}{\hbar}(\mu+\tau'-\tau)H_0}\right>. \qquad (2)$$

The expression (1)—(2) is a direct generalization of the formulae (3.1)—(3.2) [1] with respect to the dependence of electronic matrix elements on vibrational coordinates. (N_I is the number of impurity centres in the crystal, E_γ, i_α and ω_0, Ω are the unit vectors of polarization and the frequencies of the exciting and scattered lights respectively, γ is the radiation width of the excited electronic level, H_0 and H_1 — the vibrational Hamiltonians of the ground and the excited electronic states.) As it can be seen, only one excited electronic level is taken into account in (1). Such an approximation proves to be correct if this level is far from the others.

Thus, the task is reduced to the calculation of correlator $A(\tau\tau'\mu)$ (2). We have calculated the mentioned correlator for the following model. In case of electronic transition, only the variation of nuclear equilibrium states is taken into consideration. The harmonic approximation is made use of. In connection with that, the case of an absence of local vibrations is studied (see [1]). The dependence of the electronic matrix elements M_δ on the vibrational coordinates is presented in the form of expansion over annihilation (a_i) and creation (a_i^+) operators of the phonons

$$M_\delta \simeq M_\delta^0 + \sum_i M_{\delta,i}\,(a_i + a_i^+) + \frac{1}{2} \sum_{ij} M_{\delta,ij}\,(a_i + a_i^+)\,(a_j + a_j^+). \tag{3}$$

Of the formulae obtained, we present here only those which are used for quantitative estimations. Those are the formulae of the integral intensity of the resonant Raman spectrum of the first and the second order for the centre with appreciable Stokes losses:

$$I_n = I_n^C + I_n^{\neq C} \tag{4}$$

($n = 1{,}2$ is the order of the spectrum).

Here

$$I_1^C = \frac{B}{\sigma^2}\{\pi z^2 e^{-2z^2} + [1 - 2zw(z)]^2\}$$

$$I_2^C = \frac{B}{\sigma^2}\left\{\frac{\pi}{4}(1 - 2z^2)^2 e^{-2z^2} + [z + (1 - 2z^2)\,w(z)]^2\right\} \tag{5}$$

are the integral intensities in the Condon approximation calculated in [1] ($B = (N_l \omega_0^4 : 2\pi c^3) \sum_{\alpha\beta\gamma\delta} i_\alpha\, i_\beta\, E_\gamma\, E_\delta\, M_\alpha^0\, M_\beta^0\, M_\gamma^0\, M_\delta^0$, $z = b/\sigma\sqrt{2}$, b is the distance of the exciting frequency from the maximum of the absorption band, σ^2 is the second central momentum of the absorption band, $w(z) = e^{-z^2}\int_0^z dx e^{x^2}$),

$$I_n^{\neq C} = \frac{B}{\sigma^2} \sum_i \xi_i \left\{ \left(\frac{M_{\alpha,i}}{M_\alpha^0} + \frac{M_{\gamma,i}}{M_\gamma^0} \right) \left[(2\bar{n}_i + 1)\,\omega_i \frac{d}{db} + \omega_i^2 \frac{d}{d\sigma^2} \right] (I_n^C + I_{n-1}^C) + 2^n \frac{M_{\gamma,i}}{M_\gamma^0}\,\omega_i^2 \frac{I_n^C}{\sigma^2} \right\} \tag{6}$$

(ξ_i^2 are the dimensionless Stokes losses).

We give here only the linear terms since they make a main supplementing correction in the resonance region. The eliminated terms ($\sim M_{\alpha,i} M_{\gamma,j}$; $\sim M_{\alpha,ij}$), playing a main role for the scattering distant from resonance [1], make (according to our estimations) a contribution which is smaller by an order in the region under study.

Approximated estimations can be carried out as based on the one-oscillator model *. We considered $|\sum_i M_{,i}|^2 \simeq 0{,}01\ M_0^2$, $|\sum_{ij} M_{,ij}|^2 \simeq 0{,}01\ |\sum_i M_{,i}|^2$; $\xi^2 = 25$ and restricted the examination to zero temperature ($T = 0$; $\bar{n} = 0$). The relative contributions of terms $I_1^{\neq C}$, $I_2^{\neq C}$ depending on the distance between the exciting line and the maximum of the absorption

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* The use of a one-oscillator model for the estimation of the contribution of terms $I_n^{\neq C}$ to the resonant Raman scattering is possible only after finding the formulae (5)—(6). The use of this model for finding (5)—(6) leads to an incorrect physical picture.

band (dimensionless parametre $z = b/\sigma\sqrt{2}$ is used instead of b) are given in the following table:

	$z = 0$;	0,1;	0,5;	1;	1,5;	2
$M_{\alpha, i}\Delta_1 : I_1^C$	0	—0,03	—0,13	—0,24	—0,34	—0,41
$M_{\gamma, i}(\Delta_1 + 2\xi^{-1} I_1^C) : I_1^C$	0,04	0,01	—0,09	—0,20	—0,30	—0,37
$M_{\alpha, i}\Delta_2 : I_2^C$	0	—0,06	—0,16	—0,25	—0,34	—0,36
$M_{\gamma, i}(\Delta_2 + 4\xi^{-1} I_2^C) : I_2^C$	0,08	0,02	—0,08	—0,17	—0,26	—0,28

($\Delta_n \equiv \frac{1}{\sqrt{2}}\left(1 - \frac{z}{\xi\sqrt{2}}\right)\frac{d}{dz}(I_n + I_{n-1})$, sign "—" corresponds to $M_{\alpha, i}$ ($M_{\gamma, i}$) > 0)

It follows from the table that the deviation from the Condon approximation makes an essential contribution already in the case of an excitation in the absorption band.

It should also be mentioned that the deviaton from the Condon approximation in the resonance case ($0 < z < \xi\sqrt{2}$) increases together with an increase of Stokes losses.

Thus, we come to the conclusion that the neglecting of the dependence of the electronic matrix element on the vibrational coordinates is possible only if the excitation is in the maximum or in the vicinity of the maximum of the absorption band and if the Stokes losses are not too appreciable. The mentioned mistake may be even greater for some angles of the scattering, especially for one of the components of the polarization if the exciting light is polarized.

Although the role of the deviation from the Condon approximation in the spectrum of the resonant Raman scattering is smaller than it is in the non-resonance case, it is still markedly greater than that in the case of allowed processes of the first order [7, 8], and therefore a correct theory should take it into account.

It should be mentioned that the basic results of the theory of the resonant secondary radiation [1, 4] pertaining to the classification (the integral intensity of the total secondary radiation equals to the intensity of absorption, the separation of luminesence from the secondary radiation spectrum), remain in force also in case of taking into account the deviation from the Condon approximation. But, at the same time, the deviation from the Condon approximation may essentially affect the Rayleigh and Raman spectra. At this the intensity of the Rayleigh scattering, determined by the absorption spectrum in the Condon approximation, is determined by a more complicated function in case of deviation from the Condon approximation. Only the forward Rayleigh scattering is determined by the absorption spectrum as before, that also following from the optical theorem [9].

REFERENCES

1. Rebane K., Hizhnyakov V., Tehver I., ENSV TA Toimet. Füüs. * Matem. **16**, Nr. 2, 207 (1967).
2. Техвер И. Ю., Тр. Ин-та физ. и астрон. АН ЭССР, № 32, 31 (1967).
3. Техвер И., Хижняков В., Изв. АН ЭССР. Сер. физ.-матем. и техн. наук, **15**, 9 (1966).
4. Hizhnyakov V., Tehver I., Phys. stat. sol., **21**, 755 (1967).

5. Ребане К. К., Техвер И. Ю., Тр. Ин-та физ. и астрон. АН ЭССР, № 29, 54 (1964).
6. Дзюб И. П., Лубченко А. Ф., ФТТ, 3, 3602 (1961).
7. Ребане К. К., Сильд О. И., Техвер И. Ю., Тр. Ин-та физ. и астрон. АН ЭССР, № 27, 23 (1964).
8. Федосеев В. Г., Хижняков В. В., Тр. Ин-та физ. и астрон. АН ЭССР, № 29, 90 (1964).
9. Давыдов А. С., Квантовая механика, М., Физматгиз, 1963.

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А. ЛАЙСААР

ВЛИЯНИЕ ДАВЛЕНИЯ НА ВРЕМЯ ЗАТУХАНИЯ ЛЮМИНЕСЦЕНЦИИ O_2^--ЦЕНТРОВ В KBr

A. LAISAAR. RÕHU MÕJU O_2^--TSENTRITE LUMINESTSENTSI KUSTUMISAJALE KAALIUMBROMIIDIS

A. LAISAAR. EFFECT OF PRESSURE ON THE DECAY TIME OF LUMINESCENCE OF THE O_2^- CENTRES IN KBr

В последнее время все больший интерес вызывают молекулярные центры свечения (O_2^-, S_2^-, NO_2^- и др.) в щелочногалоидных кристаллах. В частности, было изучено температурное тушение люминесценции примесных молекул O_2^- в различных основаниях [1–3]. Было установлено, что в тушении свечения этих систем существенную роль играют изоэнергетические безызлучательные переходы, идущие со значительным нарушением классического принципа Франка—Кондона («электронно-колебательные туннельные» переходы). При комнатной температуре свечение кислородных центров оказывается в значительной мере потушенным.

Нами было впервые изучено влияние высокого гидростатического давления на время затухания люминесценции τ центров O_2^- в KBr при комнатной температуре, т. е. в области температурного тушения.

Для определения τ использовалась методика осциллографирования единичных импульсов люминесценции [4, 5]. Монокристалл KBr-O_2^-, выращенный по методу Киропулоса, возбуждался через светофильтры УФС-1 и водный раствор $NiSO_4$ очень короткими импульсами конденсированной медной искры. Импульсы люминесценции принимались фотоумножителем M12FQS35 через светофильтры ЖС-4 и ЖС-16. Сигналы с нагрузочного сопротивления фотоумножителя подавались через катодный повторитель на вход скоростного осциллографа ДЭСО-1. С экрана