

# Anomalies of phonon wings in the spectra of impurity centers

N. N. Kovaleva, K. P. Meletov, and E. F. Sheka

*Institute of Solid-State Physics, Academy of Sciences of the USSR, Chernogolovka, Moscow Province*

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Investigations were made of the temperature and composition dependences of the phonon wings in quasiline absorption and luminescence spectra of deep impurity centers with a dipole-allowed electronic transition (the impurity was  $\beta$ -methyl-naphthalene in a naphthalene crystal). It was found that the phonon wings in the absorption spectrum and in the vibronic luminescence bands were independent of the impurity concentration and that their temperature dependences could be described in the Condon approximation, which was characteristic of centers of this type. It was also established that only one band, representing the Stokes phonon wing of a purely electronic band in the luminescence spectrum, behaved anomalously: the profile of this phonon wing differed from the profiles of the phonon wings of vibronic bands (violation of the similarity law) and from the phonon wings of the related electronic band in the absorption spectrum (violation of the law of mirror symmetry of the absorption and luminescence spectra). These violations increased on increase in temperature and in the impurity concentration. The different causes of such behavior, including the difference between the lifetimes of the final states, are discussed.

## 1. INTRODUCTION

A common spectrum of impurity centers is a quasiline spectrum with bands forming groups consisting of two components:

$$I(\omega) = J(\omega) + \Phi(\omega), \quad (1)$$

where  $J(\omega)$  describes narrow no-phonon lines (NPLs) and the function  $\Phi(\omega)$  describes a phonon wing. In the case of crystals activated with simple ions it is found that  $J(\omega)$  represents transitions between electronic states of a center.<sup>1</sup> When the impurity is a complex ion (for example, a molecular  $O_2^-$  or  $S_2^-$  ion in alkali halide crystals<sup>2</sup>) or a molecule (this is true of an extensive class of molecular crystals containing impurities and of Shpol'skiĭ systems<sup>3</sup>), it is found that  $J(\omega)$  forms series due to electronic-vibrational (vibronic) transitions.

A characteristic feature of quasiline spectra is that the structure of a single vibronic group is repeated in a series. This form of spectrum is in agreement with the theory of Ref. 4 in the case when an electronic transition in an impurity center is strongly coupled to a high-frequency local vibration (in the case of molecular centers this may be an internal molecular vibration) and weakly coupled to the low-frequency phonon spectrum of the matrix and to low-frequency local and quasilocal vibrations. The structure of such a group, predicted by the main model of the theory of Ref. 4 based on the adiabatic approximation and the linear Condon approximation, should obey the similarity law in respect of phonon wings of different groups (this law follows from the independence of local and crystal matrix vibrations) as well as the law of mirror symmetry of phonon wings of related spectra.<sup>1</sup>

The main model in the microscopic theory of the spectra of impurity centers was formulated in the fifties by Pekar<sup>5</sup> and then developed in tens of papers. In the last decade a considerable progress has been made in theoretical analysis of related spectra.<sup>6</sup> The main result has been the development of a theory which describes the profiles of phonon wings and NPLs allowing both for the Franck-Condon (linear and quadratic) and the Herzberg-Teller electron-phonon

interactions.<sup>7,8</sup> It has been shown that an allowance for these two interactions results specifically in the absence of the mirror symmetry between the related spectra. Therefore, studies of such spectra make it possible to formulate a quantitative approach to the study of the electron-phonon interaction.

There has been an enormous number of experimental investigations of the phonon wings of impurity centers but the attention has been concentrated only on the absorption or luminescence spectra. The phonon wings have been studied because the profile of these wings can be used to determine the density of the phonon states of the crystal matrix.<sup>9,10</sup> In the theory of the subject a direct relationship between the density of the phonon states and the profile of a phonon wing  $\Phi(\omega)$  was obtained in the main model.<sup>6</sup> Therefore, this theory applies only in the Condon approximation, the validity of which can be established by a study of the related (absorption and luminescence) spectra.<sup>7</sup> This formulation has stimulated investigations of related spectra of various molecular crystals with impurities.<sup>11–13</sup> It has been found that the asymmetry of the related spectra, indicating breakdown of the main model, is the rule rather than the exception. In those cases when the phonon wings can be described in the Condon approximation, their profile differs considerably from the density of the phonon states of the crystal matrix. Investigations of the related spectra have demonstrated that the theoretical formulas given in Refs. 7 and 8 are valid. In some cases it has been possible to determine the principal characteristic of the electron-phonon interaction.<sup>13</sup> However, in spite of the opportunities provided by the theory, numerical parameters obtained in this way fail to give a quantitative description of the temperature dependence of the shift and broadening of an NPL in the same way as this has been done in the case of a phonon wing of a quasilocal vibration.<sup>14</sup> Therefore, it has become necessary to study the temperature effects not only in the case of NPLs but also in the case of phonon wings, and a study of this kind is reported below. The method of thermal modulation of the

spectra was used by us to reveal weak effects in a phonon wing.

## 2. EXPERIMENTS

We investigated naphthalene containing  $\beta$ -methyl-naphthalene as an impurity (N + BMN). Crystals with impurities were grown from the vapor phase and they were platelets with a highly developed (ab) plane; their thickness was 20–40  $\mu$ . The starting material was naphthalene of the analytic purity grade, which was subjected to a careful purification by a combined method<sup>15</sup> and then was doped with the BMN impurity. The impurity concentration was deduced from the absorption spectra. A study was made of two batches of crystals with the BMN concentrations of  $10^{-2}$  and 1 wt. %.

The luminescence spectra were recorded with a DFS-13 spectrograph fitted with an FEP-2 photoelectric attachment. An FEU-106 photomultiplier was used as the detector. The dispersion was 2  $\text{\AA}/\text{mm}$  and the spectral width of the instrumental function was 0.3  $\text{\AA}$ . The luminescence was excited with light from a xenon lamp of 1 kW power through an MS monochromator (linear reciprocal dispersion 13  $\text{\AA}/\text{mm}$ , relative aperture 1:3). The absorption spectra were recorded using a xenon lamp of 200-W power. A system of stabilization for the light flux made it possible to record the spectra with an error not exceeding 3%.

Thermal modulation was achieved by the transmission of rectangular current pulses of 14 Hz frequency and 13 msec duration through a metal film heater. This heater was a bismuth film 0.5  $\mu$  thick and of transverse dimensions  $5 \times 8$  mm; it was evaporated on a polished quartz cell between indium contacts. The film surface was coated by a thin insulator which prevented mechanical damage. The resistance of the film together with its leads amounted to several ohms. A sample was 20–40  $\mu$  thick and its transverse dimensions were  $4 \times 6$  mm; it was mounted on the film heater and pressed flatly against the latter by springs. The whole assembly was immersed in liquid helium. The amplitude of a temperature wave in the thermal modulation regime depended on the energy of the heat pulses and it ranged from 3 to 20 K; the minimum temperature of the investigated crystal was the bath temperature  $T_b = 4.2$  K. A detailed description of the thermal modulation method was given in Ref. 16.

## 3. EXPERIMENTAL RESULTS

The energy level scheme of a crystal with an impurity is shown in Fig. 1 and it explains the notation used below. The arrows  $J_{00}^a$  and  $J_{00}^e$  identify resonance NPLs of a purely electronic transition (electronic group) in the absorption and luminescence;  $J_{01}^e$  describes an NPL of one of the vibronic transitions (vibronic group) involving participation of an internal molecular vibration with  $\Omega = 509$   $\text{cm}^{-1}$ . This NPL is accompanied by a wide photon wing due to transitions involving phonon creation [ $\Phi_{st}^a(\omega)$  and  $\Phi_{st}^e(\omega)$ ] or annihilation [ $\Phi_{ast}^a(\omega)$  and  $\Phi_{ast}^e(\omega)$ ]. In the investigated system a BMN molecule forms a deep impurity level (which is separated from the bottom of the exciton band by  $\epsilon = -417$   $\text{cm}^{-1}$ , where  $|\epsilon| \gg M$  and  $M$  is the band width) to which a

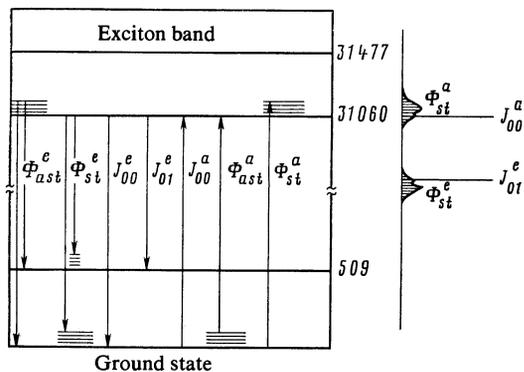


FIG. 1. Energy level scheme of a naphthalene crystal containing  $\beta$ -methyl-naphthalene as an impurity.

purely electronic transition is dipole-allowed.

**Mirror symmetry law.** Figure 2 shows the phonon wings of the “thermostationary” related spectra<sup>2)</sup> of the electronic group at 4.2 K when the impurity concentration was low (Fig. 2a). The phonon wings can be seen to be symmetric in respect of the integrated intensity and practically symmetric in shape (as observed earlier<sup>13</sup>). According to the theory of Ref. 7, these spectra can be regarded as a classical illustration of the validity of the Condon approximation. This is why they have been selected for our investigation.

When the impurity concentration was increased to 1%, the equality of the integrated intensities of the phonon wings in the luminescence spectrum found after allowance for re-absorption<sup>3)</sup> was retained, but the asymmetry of the profile became stronger (Fig. 2b). At 25 K (Fig. 2c) the asymmetry of the phonon wings became much stronger but the integrated intensities still remained equal. The asymmetry of the phonon wings, enhanced by an increase in temperature, was difficult to observe in the thermostationary luminescence spectrum when the impurity concentration was low, but it

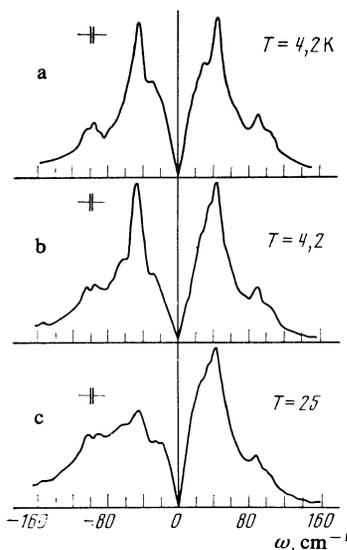


FIG. 2. Stokes phonon wings of the related electronic spectra of the  $\beta$ -methyl-naphthalene impurity in naphthalene (luminescence spectra on the left and absorption spectra on the right): a)  $T = 4.2$  K, impurity concentration  $C \sim 10^{-2}\%$ ; b)  $T = 4.2$  K,  $C \approx 1\%$ ; c)  $T = 25$  K,  $C \approx 1\%$ .

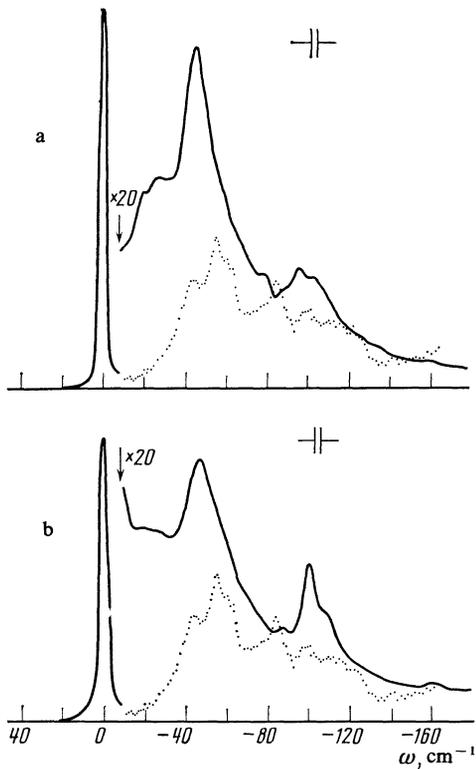


FIG. 3. Luminescence spectrum of a naphthalene crystal containing  $\beta$ -methylnaphthalene ( $\sim 1\%$ ) recorded at 4.2 K: a) electronic group; b) vibronic group,  $\nu = 509 \text{ cm}^{-1}$ . The dotted curves represent the density of the phonon states in a naphthalene crystal with weighted squares of the amplitudes of the hydrogen atoms.<sup>17</sup>

was observed quite easily in the “thermodifferential” spectra.

**Similarity law.** An investigation of the related electronic spectra showed violation of the symmetry law by the profiles of the phonon wings on increase in temperature and violation of the similarity of the phonon wings of the electronic group and of the phonon wings of the vibronic group in the luminescence spectrum was observed also at low temperatures. Figure 3 shows the electronic and vibronic groups in the luminescence spectrum recorded at  $T = 4.2 \text{ K}$ . We can see that the structure of the phonon wings in both groups is generally similar, but the details differ considerably. In all the vibronic groups that could be studied the structure of the phonon wings is identical with that shown in Fig. 3b. Unfortunately, we were unable to study the phonon wings of the vibronic transitions in the absorption spectrum because the vibronic spectrum of the impurity molecule overlapped the absorption spectrum of the crystal matrix. Violation of the similarity law for the electronic group increased on increase in the impurity concentration, whereas the phonon wings of the vibronic groups were not affected by this concentration.

The very fact that the phonon wings in the electronic and vibronic groups in the luminescence spectrum are different means that the density of the phonon states of the crystal matrix deduced from the wings ceases to be reliable.<sup>9,10</sup> Moreover, a comparison of the known density of the phonon states of a naphthalene crystal (Fig. 3) with weighted squares of the displacements of hydrogen atoms (deduced from the

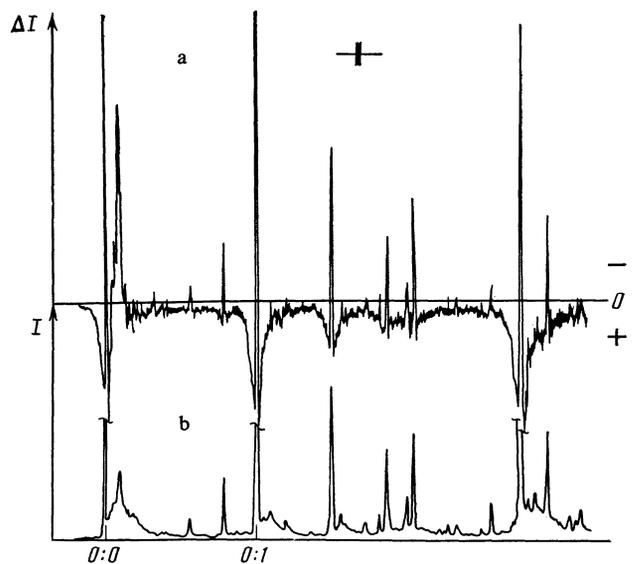


FIG. 4. Panoramic thermodifferential (a) and thermostationary (b) luminescence spectra of a naphthalene crystal with  $\beta$ -methylnaphthalene;  $T = 4.2 \text{ K}$ , modulation amplitude  $\Delta T = 15 \text{ K}$ , impurity concentration  $C \approx 1\%$ .

experimental data on inelastic noncoherent scattering of neutrons at 4.5 K reported in Ref. 17) shows that the optical phonon wings in the electronic and vibronic groups differ considerably from the density of the phonon states of the crystal matrix.

Figure 4 shows a panoramic record of the thermodifferential and thermostationary electronic-vibrational spectra of the impurity luminescence. The narrow bands in Fig. 4b represent the NPLs of the electronic and some vibronic groups in which one vibrational quantum of variable frequency participates. The similarity law is clearly obeyed by the vibronic groups in the thermodifferential spectrum in Fig. 4a. It is clear from the figure that all the vibronic groups behave in a similar manner and the negative peak representing a reduction in the intensity of a certain part of the phonon wing on increase in temperature is exhibited only by the electronic group. Therefore, in the case of a purely electronic transition the spectrum of a deep impurity level exhibits violation of the laws of symmetry and similarity of the phonon wings and this violation increases on increase in temperature and the impurity concentration.

#### 4. DISCUSSION OF RESULTS

We shall use the Condon approximation to consider the temperature dependences of the intensities and profiles of phonon wings in the thermodifferential spectra. The distribution of the intensity in an isolated group of a band (NPL + phonon wings) is described by the formula

$$\Phi_m = \mu^2 \exp[-f(T)] f^m(T) / m! \quad (2)$$

Here,  $m = 0$  applies to the NPL, whereas  $m \neq 0$  applies to the phonon wings;  $\mu$  denotes the dipole moment of a transition;

$$f(T) = \int_{-\infty}^{+\infty} \{ [n(\nu, T) + 1] v(\nu) + n(-\nu, T) v(-\nu) \} d\nu,$$

where  $n(\nu, T) = [\exp(h\nu/kT) - 1]^{-1}$  are the occupation numbers of phonons and  $\nu(\nu)$  is a one-phonon function.<sup>7</sup> The intensity of the phonon wings increases with temperature because of an increase in the phonon occupation numbers. On the other hand, it follows from Eq. (2) that there is no change in the integrated intensity of a group comprising an NPL and phonon wings when temperature is varied.

In the case of a weak electron-phonon coupling when  $f(T)$  is small the wings are practically of the one-phonon nature, the Stokes and anti-Stokes parts are described by the formulas

$$\Phi_{st}^i(\omega) = \exp[-f(T)] [n(\omega, T) + 1] \nu^i(\omega), \quad (3a)$$

$$\Phi_{ast}^i(\omega) = \exp[-f(T)] n(-\omega, T) \nu^i(-\omega), \quad (3b)$$

where the index  $i$  represents  $e$  or  $a$  for the luminescence and absorption spectra, respectively. The functions  $\nu^e(\omega)$  and  $\nu^a(\omega)$  may differ if there is a change in the phonon frequency as a result of electronic excitation of a center. This may be the reason for the absence of mirror symmetry of the profiles of the phonon wings in the related spectra.<sup>13</sup> The formulas (3) give the temperature dependence of the phonon wing profile in the one-phonon harmonic approximation. The phonon anharmonicity may result in a weak temperature dependence of the one-phonon function  $\nu(\omega)$ .

According to Eq. (3), the profile of the phonon wings in the thermodifferential absorption and luminescence spectra is described by the formulas

$$\begin{aligned} \Delta\Phi_{st}^e &= \Delta\Phi_{ast}^e(\omega, T, \Delta T) \\ &= \exp[-f(T)] \nu^e(\omega) [n(\omega, T + \Delta T) - n(\omega, T)], \end{aligned} \quad (4a)$$

$$\begin{aligned} \Delta\Phi_{ast}^a &= \Delta\Phi_{st}^a(-\omega, T, \Delta T) \\ &= \exp[-f(T)] \nu^a(-\omega) [n(-\omega, T + \Delta T) - n(-\omega, T)]. \end{aligned} \quad (4b)$$

Here  $T$  and  $\Delta T$  represent the temperature of the bath and the amplitude of thermal modulation. It follows from the above relationships that the symmetry of the phonon wings is preserved within one group in the thermodifferential spectra.

Two qualitative conclusions can be drawn from the above.

1. The integrated intensity of an isolated group in a thermodifferential spectrum is zero. The intensity of the phonon wings rises and the intensity of the NPL falls.

2. In one-phonon spectra the Stokes and anti-Stokes phonon wings in the thermodifferential case are symmetric relative to the NPL, to the extent that the functions  $\nu^e$  and  $\nu^a$  are equal.

However, it should be pointed out that these two predictions may not be satisfied by the experimental thermodifferential spectra if a change in temperature alters the population of the impurity level or the quantum efficiency of the luminescence.

In the spectra of the investigated system with impurities the phonon wings of the electronic and vibronic groups are basically due to one-phonon processes, because their relative intensities in the groups are 0.34 and 0.35, respectively. The panoramic thermodifferential spectra in Fig. 4 show that the

symmetry of the phonon wings in the vibronic groups is indeed manifested quite clearly. This symmetry is violated in the electronic group and a study of this violation as a function of the impurity concentration gave the results presented in Figs. 5 and 6.

Figure 5 shows the electronic and one of the vibronic groups in the thermodifferential luminescence spectrum of a sample with a low impurity concentration, recorded at different thermal modulation amplitudes. As pointed out already and as demonstrated in Fig. 5b, the thermodifferential spectrum has a characteristic symmetric structure in the vibronic group. The weak asymmetry of the spectrum is clearly associated with the inequality of the functions  $\nu^e$  and  $\nu^a$ , with the thermal shift and broadening of the NPL, and possibly also with factors of kinetic origin because the net intensity of the thermodifferential spectrum is not zero. The vibronic spectrum is not affected by an increase in the impurity concentration.

The behavior of the anti-Stokes part of the spectrum in the electronic group (Fig. 5a) was similar to that exhibited by the vibronic group. On the other hand, in the Stokes region there was a strong reduction in the intensity of the phonon wings on increase in temperature. This effect was observed also at extremely low concentrations of the PMN impurity ( $\sim 10^{-5}\%$ ). When the concentration was increased to 1%, the effect became much stronger (Fig. 6).

Unfortunately, methodological difficulties prevented us from recording thermally modulated absorption spectra. The electronic spectra  $\Delta\Phi_{st}^e$  and  $\Delta\Phi_{ast}^e$  were deduced as the differences between the absorption spectra recorded at different temperatures. These spectra were found to be symmetric and completely similar to the vibronic thermodifferential luminescence spectra. Therefore, we may conclude that the thermodifferential spectra of the vibronic luminescence and of purely electronic absorption of the investigated crystal can be described in the Condon approximation. A quantitative confirmation of this conclusion is provided by an experimental check of the dependence

$$a(\omega, T) = \ln\{[\Delta\Phi_{ast}^e(-\omega, T)/\Phi_{st}^e(\omega, T) + n(\omega, T_0)]^{-1} + 1\} \quad (5)$$

where  $T = T_0 + \Delta T$ , which follows from Eqs. (3a) and (4b). Figure 7 shows the dependence  $a(\omega, T)$  obtained for three different values of  $\Delta T$  ( $T_0 = 4.2$  K). It is clear from this figure that the dependence is quite accurately linear, in agreement with Eq. (5). The functions  $\Delta\Phi_{ast}^e$  and  $\Delta\Phi_{st}^e$  are assumed to be the experimental phonon wings in the thermodifferential luminescence spectrum and in the thermostationary absorption spectrum of the electronic group of a sample with an impurity concentration  $\sim 10^{-2}\%$ . The values of  $\Delta T$  deduced from the slopes of the experimental dependences are equal to the modulation amplitudes found by an independent method.<sup>16</sup>

## 5. CONCLUSIONS

It follows from the above results that the Stokes phonon wings of the electronic group in the luminescence spectrum of the BMN impurity in a naphthalene crystal behave anom-

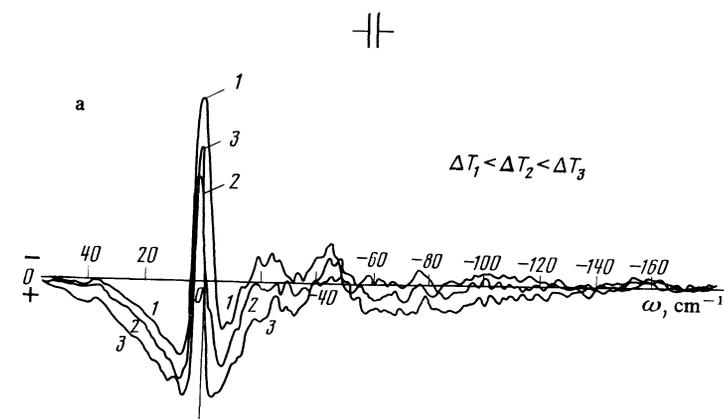
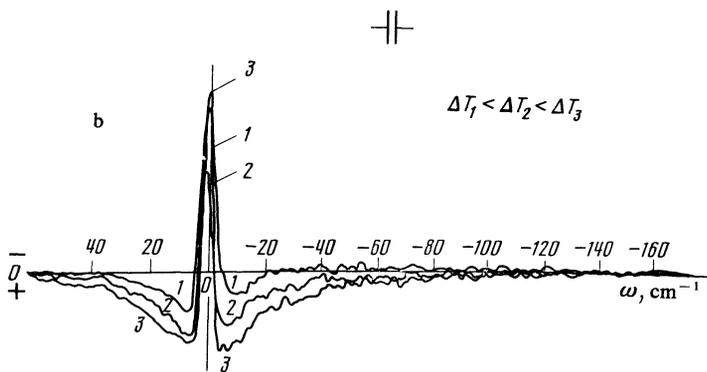


FIG. 5. Electronic (a) and vibronic (b)  $\Omega = 509 \text{ cm}^{-1}$  groups in the thermodifferential luminescence spectrum of a naphthalene crystal with  $\beta$ -methylnaphthalene ( $T = 4.2 \text{ K}$ , impurity concentration  $C \approx 10^{-2}\%$ ). Curves 1, 2, 3 represent modulation amplitudes of 7.5, 9, and 11 K, respectively.



alously in respect of the laws of symmetry and similarity of the electron-phonon spectra.<sup>4</sup> The existing theories of the electron-phonon interaction fail to account for this anomaly. However, the observed effects are small and they are clearly not a special property of the investigated system. It is natural to formulate the question of what is the basic difference which distinguishes a purely electronic transition from a vibronic transition in the luminescence or from a similar transition in the absorption. It is clear from Fig. 1 that the differ-

ence lies in the different final states. In the case of a purely electronic transition in the luminescence spectrum these states are in the phonon continuum, whereas for a vibronic transition the final state is an internal molecular local vibration superimposed on the phonon continuum, and in the case of a purely electronic transition in the absorption spectrum it is an electron-phonon state consisting of an electronic excitation and the phonon continuum.

The main quantitative characteristics of the phonon

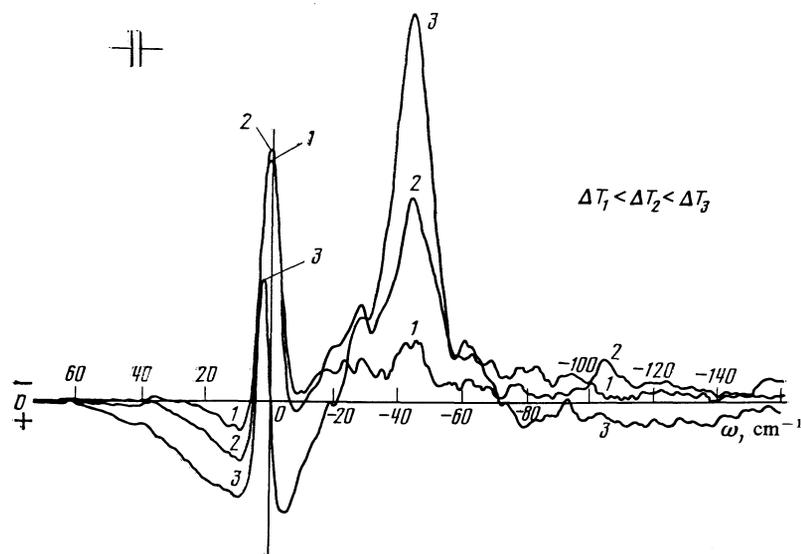


FIG. 6. Electronic group in the thermodifferential luminescence spectrum of a naphthalene crystal with  $\beta$ -methylnaphthalene ( $T = 4.2 \text{ K}$ , impurity concentration  $\sim 1\%$ ). Curves 1, 2, and 3 correspond to modulation amplitudes of 3.7, 7.5, and 11 K, respectively.

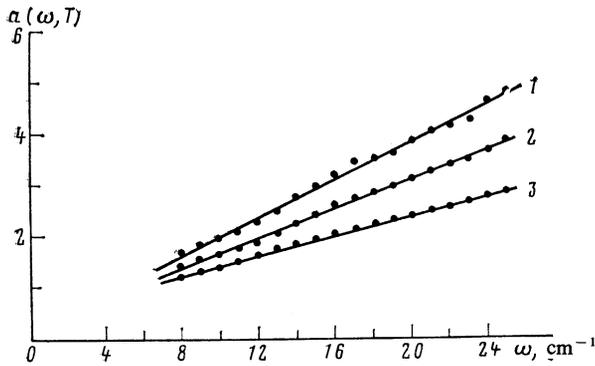


FIG. 7. Experimental (points) and theoretical (straight lines) dependences  $a(\omega)$ ; 1)  $\Delta T = 5.4$ ; 2) 12.5; 3) 17.7 K.

wings is the function of one-phonon transitions  $\nu^{a,e}$  which can be represented in the form<sup>18</sup>

$$\nu^{a,e} = \int \sum_{\nu} |\mu^{a,e}(\nu \mathbf{q})|^2 \delta(\omega - E + \Omega + \bar{\omega}(\nu, \mathbf{q})) d^3 q, \quad (6)$$

where  $\bar{\omega}(\nu, \mathbf{q})$  is a phonon belonging to a branch  $\nu$  and having a wave vector  $\mathbf{q}$  from the phonon continuum. The difference between the final states in the three transitions discussed above may naturally give rise to different values of the matrix element  $\mu^{a,e}$ . This effect does indeed take place in the electronic (exciton) and vibronic luminescence of a pure crystal and it is associated with the different selection rules governing the quasimomentum.<sup>19,20</sup> We may assume that the localization of an exciton at an impurity which accompanies impurity excitation has different effects in the case of purely electronic and vibronic transitions in the luminescence spectrum. This may account for the violation of the similarity law, but it cannot explain the existence of a negative part of the phonon wing in the thermodifferential luminescence spectrum.

The different final states of these transitions are characterized also by different lifetimes. In the case of a local vibration superimposed on the phonon continuum the lifetime of the state is governed by the relaxation time of a high-frequency local mode which amounts to  $10^{-11}$  sec or less.<sup>21</sup> The lifetime of the state of an electron coupled to the phonon continuum is of the same order of magnitude.<sup>22</sup> It should be noted that the phonon continuum of a naphthalene crystal is characterized by relaxation times from hundreds of picoseconds at frequencies between 0 and  $100 \text{ cm}^{-1}$  to tens of picoseconds for  $\omega > 100 \text{ cm}^{-1}$  (Ref. 23). It is also known that, in contrast to the cases mentioned above, these times depend strongly on temperature in the range of interest to us.<sup>24</sup> We may expect an allowance for the time dependences in Eq. (6) to account for the observed temperature effects. Moreover, the impurity-concentration dependences of the observed

anomalies may be affected also by the scattering of phonons on defects.

The authors regard it as their pleasant duty to thank L. A. Rebane, I. B. Levinson, I. S. Osad'ko, and D. V. Kazakovtsev for valuable discussions and stimulating comments.

<sup>1</sup>The related spectra are understood to be the absorption and luminescence spectra due to transitions between the ground and excited electronic states involving the participation of the same local vibration.

<sup>2</sup>The term "thermostationary" is introduced for the convenience of distinction from the "thermodifferential" spectra.

<sup>3</sup>The correctness of the allowance for the effects of reabsorption on the luminescence spectrum was supported by the fact that the band profiles were the same for crystals of different thickness.

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