

results were obtained: $k_1 = 5 \times 10^{-32} \text{ cm}^6/\text{sec}$, $k_1' \leq 2 \times 10^{-33} \text{ cm}^6/\text{sec}$, $k_1'' \leq 10^{-33} \text{ cm}^6/\text{sec}$.
 $k_2 \leq 10^{-17} \text{ cm}^3/\text{sec}$, $k_3 = (4 - 6.5) \times 10^{-11} \text{ cm}^3/\text{sec}$, $k_3' = (3 - 4) \times 10^{-12} \text{ cm}^3/\text{sec}$, $k_6 = (4.3 - 7) \times 10^{-17} \text{ cm}^3/\text{sec}$, $k_7 \leq 3 \times 10^{-6} \text{ cm}^3/\text{sec}$. 3) It was impossible to estimate the constant k_7' , since the experimental results are highly insensitive to inclusion of this reaction in the analysis [6].

A detailed description of the work will be published later.

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REPOPULATION OF HIGHLY-EXCITED VIBRATIONAL LEVELS IN A COLD LATTICE

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We consider a molecular crystal consisting, e.g., of diatomic molecules. The molecules exchange vibrational energy and this process is more probable than the conversion of the intramolecular energy into lattice energy, i.e., into phonons. One of us [1] considered the influence of anharmonicity on the lifetime of highly-excited vibrational levels in molecular crystals, and noted a strong narrowing of the energy bands for such excitations. States in which second vibrational levels (obtained, as it were, by sticking of two-single-quantum excitations) are excited were considered by Jortner and Rice [2] and later by Agranovich [3]. In the present article we consider a different aspect, connected with the fact that the number N of the vibrational quanta (abbreviated "vi-quanta") can be regarded as approximately conserved, and one can seek a stationary state at a given lattice temperature T_1 and at a given¹⁾ value of N .

The subject of our study is the distribution of the molecules over the vibrational states. By virtue of the anharmonicity, the energy of the two-quantum state is lower than the energy of two single-quantum states. A similar relation holds also for higher states. This can be expressed with the aid of the inequality

$$\Delta E_r = E_{r-1} + E_1 - E_r - E_0 > 0, \quad r > 1, \quad (1)$$

where E_r is the energy of the anharmonic oscillator. In the case of a Morse potential it is given by (in a system of unifs in which $\Omega = \hbar = 1$)

3) The constants k_3 and k_3' are given under the assumption that the corresponding reactions are binary. One cannot exclude the possibility of participation of a third body.

1) Approximate conservation of the total number of intermolecular quanta is possible, since nonradiative transitions with change of the number of vi-quanta are connected with the production of a large number of phonons N_p and are therefore highly unlikely. N_p is approximately equal to $\Omega/\omega_d \sim 20 - 30$, where Ω is the value of the vi-quantum ($\sim 2^p - 3 \times 10^3 \text{ cm}^{-1}$) and ω_d is the Debye frequency of the crystal ($\sim 10^2 \text{ cm}^{-1}$). Thus, the only process leading to a change in the number of vi-quanta is their emission. The corresponding time is $t_p \approx 10^{-2} - 1 \text{ sec}$ for molecules having a dipole moment (CO, NO, HCl) and $t_p = 10^6 - 10^7 \text{ sec}$ [4] for molecules having no dipole moment (O_2, N_2, H_2).

$$E_r = r - xr^2, \quad r \leq r_0 = 1/2x, \quad x = 1/4D, \quad (2)$$

where x is the index of the anharmonicity, D the dissociation energy, and r_0 the number of the last vibrational level. At low lattice temperatures there is realized a state with the lowest energy, i.e., at a given N there arises an anomalously large number of highly-excited molecules with large r , owing to the decrease in the number with small $r = 1, 2, \dots$. We normalize n_r (the number of r -excited molecules) to unity, so that

$$\sum n_r = 1, \quad \sum r n_r = N. \quad (3)$$

At such a normalization n_r and N are the concentrations of the r -th excitations and of the total number of quanta per molecule.

Under true thermodynamic equilibrium we have

$$n_r = c \exp(-\beta E_r), \quad \beta = 1/kT_1. \quad (4)$$

If the total number of vi-quanta is specified, then (4) takes the form

$$n_r = c \exp \beta(\mu r - E_r). \quad (5)$$

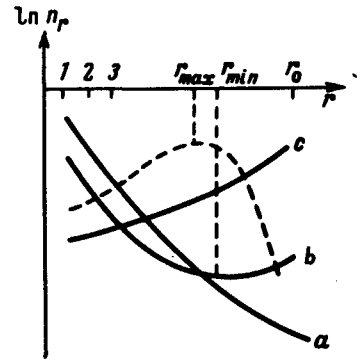
Here C and μ are determined from (4). In the harmonic case $E_r = r$ and we obtain for n_r the distribution

$$n_r = (1 - y) y^r, \quad y = N/(N + 1), \quad (6)$$

which does not depend on the temperature; this is natural, since the exchange of the vi-quanta takes place here without participation of the lattice. Under true equilibrium ($\mu = 0, N = N_1$), $n(r)$ decreases monotonically with increasing r , up to r_0 (curve a). If N exceeds the equilibrium value ($N > N_1$), then n_r reaches a minimum at a certain intermediate value $r = r_{\min} = \ln(1/N)/2x\beta < r_0$ (curve b). With decreasing temperature, r_{\min} shifts to the left and at sufficiently low temperatures ($x\beta \ll 1$) it can become equal to unity (curve c). For clarity, r_{\min} can be represented in a different form. We introduce the temperature $T_2 = T_2(N)$ at which the total number of vi-quanta is in equilibrium, and we approximately have $T_2 = \ln(1/N)$. We then obtain $r_{\min} = r_0 T_1/T_2$. For large r , and in particular for $r > r_{\min}$, in important factor is the irreversible drift of the quanta to $r = r_0$, for a change takes place in the total number of the vi-quanta when the molecule dissociation energy is reached. The rate of drift to the dissociative limit in the stationary regime is proportional to $n_{r_{\min}}$, since r_{\min} plays the role of a barrier to this process. It is easily seen that

$$n_{r_{\min}} \sim \exp(-DT_1/T_2^2). \quad (7)$$

An investigation of the situation when $r > r_{\min}$, and particularly the dissociation process, is quite difficult, since the dissociating molecule interacts strongly with its environment. There is no need for this study, however. In fact, the probability per unit time of going from $r - 1$ to r decreases strongly with increasing r . According to [1] it can be represented in the form



$$w_r = 1/r_r = 1/r_0 e^{-pr}, \quad (8)$$

where p ranges from 1 to 4 for different crystals, and $r_0 \sim 10^2/\Omega$. At the same time the emission probability increases weakly with increasing r ; at certain rather large r these probabilities become equal, and consequently there will be no condensation of the excitations above these r in practice. To determine the function in this case we start from the kinetic equation, which is analogous to the equation for the growth of drops from a supersaturated vapor [5]

$$\begin{aligned} \frac{dn_r}{dt} = & w_r n_{r-1} n_1 - w_{r+1} n_r n_1 + \bar{w}_{r+1} n_{r+1} - \bar{w}_r n_r + \frac{1}{t_p} (n_{r+1} - n_r) + \\ & + i_0 \delta_{r,1}, \quad \bar{w}_r = 1/r_r e^{-\Delta E_r \beta}; \end{aligned} \quad (9)$$

i_0 is the concentration of the identical excitations produced per unit time, say as a result of irradiation, and t_p is the radiative lifetime of the quanta (we neglect the weak dependence on r). Under stationary conditions we have

$$n_{r-1} n_1 - n_r e^{-\Delta E_r \beta} = \frac{r_r}{t_p} n_r, \quad (9a)$$

$$n_r = \frac{n_1^r e^{-E_r \beta} E_1 r \beta}{\prod_{k=2}^r \left(1 + \frac{r_k}{t_p} e^{-\Delta E_k \beta} \right)}. \quad (10)$$

It follows from (10) that when $r < r_\beta = \ln(t_p/r_0)/2x\beta + p$ the distribution of n_r coincides in the main with the equilibrium distribution (5). When $r > r_\beta$, n_r increases and reaches a maximum at

$$r_{max} = 1/2 + \sqrt{\frac{2 \ln \alpha_0}{p} - 7/4}, \quad \alpha_0 = \frac{i_0 t_p^2}{r_0}, \quad (11)$$

after which it decreases rapidly; $n_r \sim \exp(-pr^2/2)$ as $r \rightarrow \infty$. The general form of this dependence is shown in the figure (dashed curve) for excitation by radiation, $r = 1$. The system is in a strongly inverted state, a fact that can be used for an experimental observation of the condensation of the vi-quanta. It is important to note that the inversion occurs at $r > 1$, i.e., at frequencies that differ from the irradiation frequency. When the irradiation stops there occurs (or is intensified) inversion of the transition $r = 2 \rightarrow r = 1$.

In conclusion we note that the effect is most strongly pronounced at low (say, helium) temperatures) in molecular crystals consisting of diatomic molecules N_2 , H_2 , O_2 , NO . Also interesting are crystals of the HCl type, in which it is much easier to excite single-quantum levels.

Everything said above applies with certain modification also to gases and liquids. Then, however, the temperatures must be sufficiently low.

Note added in proof. Afanas'ev, Belenov, Markin, and Poluektov (ZhETF Pis. Red. 13, 462, 1970 [JETP Lett. 13, 331, 1971] consider the population of the upper vibrational levels and the dissociation following excitation of the first vibrational level; they do not, however, consider the effect of anharmonicity.

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ANOMALIES OF THERMAL EMF IN PHONON-PHONON DRAGGING

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The purpose of this research is to study the thermal emf of semiconductors under conditions of hydrodynamic flow of phonons under the influence of a temperature gradient applied to them. Under the indicated conditions, besides the usual effect of electron dragging by the phonons, another effect becomes quite significant, namely the dragging of the longer-wave phonons by thermal phonons, an effect to which no attention has been paid in the past. This effect, as will be shown below, can cause anomalously large values of the thermal emf, and even exponentially large values in the case of highly perfect crystals.

The physical picture is as follows: The thermal phonons with frequencies $\sim kT$ are scattered mainly by one another, since the conduction-electron density in intrinsic semiconductors is exponentially small. It is assumed that the frequency of the N-processes is large compared with the frequency of the U-processes. The result is a thermal-phonon distribution that is in equilibrium in a coordinate system moving with velocity u along the temperature gradient [1].

The conduction electrons interact only with phonons whose wavelength is comparable with their proper wavelength [2]. At an effective mass of the electron m on the order of the true mass and at $T > 0.1^\circ\text{K}$ the frequency of such phonons (they shall be referred to as "electronic") is low compared with kT [3]. It is precisely the non-equilibrium nature of such "electronic" phonons which leads to the anomalies predicted by L. E. Gurevich for the thermal emf at low temperatures.

In calculations of the dragging effect it is usually assumed that the interaction of the "electronic" phonons with the thermal ones leads to dissipation of the momentum of the former [2, 3]. In fact, however, it can lead only to establishment of a drift of the "electronic" phonons with the same velocity as that of the thermal-phonon flow. Thus the thermal phonons, not being in equilibrium, drag the "electronic" phonons. On the whole, the dragging of the electrons by phonons is a two-step process: the conduction electrons are dragged by the "electronic" phonons which in turns are dragged by the thermal phonons.

The kinetic equations for the thermal and "electronic" phonons are written in the form

$$s \nabla T \frac{\partial F^0(\omega)}{\partial T} = I^N \{F\} + I^U \{F\}, \quad (1)$$

$$s \nabla T \frac{\partial G^0(\omega)}{\partial T} = I^N \{G, F\} + I^U \{G\}. \quad (2)$$

Here F and G are the distribution functions for the thermal and "electronic" phonons, respectively, and the index "0" denotes their equilibrium values. The symbols I^N and I^U denote the parts of the collision integral corresponding to processes with and without conservation of the total quasimomentum, and s is the phonon velocity. In writing down Eq. (1) for the thermal phonons it is recognized that the dominant role is played by their collisions with one another, and that the influence exerted on them by the "electronic" phonons can be neglected.