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Abstract

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ON THE PROBABILITY OF A PHONONLESS TRANSITION IN IMPURITY CENTERS OF CRYSTALS

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After the Mössbauer experiments it became clear that, in the probability density for a change in the vibrational state of a crystal upon emission (or absorption) of a γ-quantum by a nucleus, a delta-shaped feature corresponds to a phononless transition; this was justified with the aid of Lamb' s theory (^{1}). The formal analogy of this theory with the theory of luminescence or absorption by impurity centers in crystals makes it possible to hope for the discovery of narrow phononless-transition lines also in optical spectra. It should be emphasized, however, that the formulations of the problems differ. Whereas, in the emission (absorption) of a γ-quantum, the change in the vibrational state of the crystal is associated with the recoil momentum of the γ-quantum, in optical transitions the interaction with lattice vibrations is due to a change in the adiabatic potential. The similarity of the theories of these phenomena is a consequence of the invariance of the oscillator energy $^1/_2\omega(p^2+q^2)$ with respect to replacement of momentum by coordinate.

1. Let us consider an impurity center in a crystal. Denote by $X^{(1)}$ the set of coordinates of the equilibrium positions of the nuclei for the ground state of the center, and by X^2 the set of the same quantities for the excited state. These equilibrium positions correspond to the minima of the adiabatic potentials in the ground and excited states of the center, and the differences $\Delta X = X^{(2)} - X^{(1)}$ determine the degree of interaction of the electronic state with the lattice vibrations. We shall assume that the spectrum of normal-vibration frequencies differs insignificantly for the ground and excited states of the center. Then, if $Q^{(1)} = \{q_\alpha\}$ denotes the set of normal coordinates for the ground state, the normal coordinates in the excited state may be represented in the form $Q^{(2)} = Q^{(1)} + \Delta Q$, where the displacements $\Delta Q = \{\Delta q_\alpha\}$ correspond to the displacements ΔX. Let $m = \{m_\alpha\}$ be the set of vibrational quantum numbers. Then the probability of a change in the vibrational state of the crystal $m^{(1)} \to m^{(2)}$ in the electronic transition $(1) \to (2)$, in the Condon approximation, is evidently equal to

$$W_{m^{(1)}m^{(2)}} = \left| \int \chi_{m^{(1)}}(Q)\chi_{m^{(2)}}(Q+\Delta Q)\, dQ \right|^2 , \tag{1}$$

where χ_m are the vibrational wave functions of the crystal. The transition $m^{(1)} \to m^{(2)}$ is accompanied by a change in the vibrational energy of the crystal by the amount

$$E_{m^{(2)}} - E_{m^{(1)}} = \sum_\alpha \omega_\alpha \left(m_\alpha^{(2)} - m_\alpha^{(1)} \right) . \tag{2}$$

We shall restrict ourselves to consideration of the branches of crystal vibrations as the most essential for our problem. It can be shown that allowing for local vibrations, which may arise near the defect, leaves the result obtained in the work unchanged.

If we fix the initial vibrational state $\chi_{m(1)}$ and sum (1) over all final states $\chi_{m(2)}$ satisfying the condition

$$\omega - \omega_0 \leqslant E_{m(2)} - E_{m(1)} \leqslant \omega - \omega_0 + d\omega,$$

then we obtain the probability that, in the electronic transition (1) → (2) with frequency ω_0, the vibrational energy of the crystal will change by an amount lying in the interval $\omega - \omega_0,\ \omega - \omega_0 + d\omega$. The corresponding probability density, as is known, has the form $^{(2)}$

$$W(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i(\omega-\omega_0)t + f(t)}\, dt, \tag{3}$$

where

$$f(t) = \sum_\alpha \frac{\Delta q_\alpha^2}{2} \left[\pm i \sin \omega_\alpha t - (2m_\alpha + 1)(1 - \cos \omega_\alpha t) \right] , \tag{4}$$

(the upper sign corresponds to absorption, the lower to emission). Averaging over the initial states is carried out by replacing m_α by

$$\overline{m_\alpha} = \frac{1}{e^{\omega_\alpha / kT} - 1}.$$

$W(\omega)$ is a normalized spectral distribution that determines the shape of the absorption or emission band. It is not difficult to find the moments of this distribution. Indeed, since

$$e^{f(t)} = \int_{-\infty}^{\infty} e^{i(\omega-\omega_0)t} W(\omega)\, d\omega, \tag{5}$$

the moments of the function $W(\omega)$ are expressed through the derivatives of $\exp f(t)$ at the point $t = 0$. In particular,

$$\mu_0 = \int_{-\infty}^{\infty} W(\omega)\, d\omega = 1,$$

$$\mu_1 = \int_{-\infty}^{\infty} (\omega - \omega_0) W(\omega)\, d\omega = \pm \sum_{\alpha} \frac{\Delta q_\alpha^2}{2}\, \omega_\alpha,$$

$$\mu_2 = \int_{-\infty}^{\infty} (\omega - \omega_0)^2 W(\omega)\, d\omega = \sum_{\alpha} \frac{\Delta q_\alpha^2}{2}\, \omega_\alpha^2 (2m_\alpha + 1) \tag{6}$$

and so on.

2. Let us now find the probability of a phononless transition. As is easy to see, (3) is a divergent integral, since

$$\lim_{t \to \pm\infty} \exp f(t) \neq 0.$$

We shall show that the divergence of this integral is due to a δ-shaped singularity at the point $\omega = \omega_0$. Indeed, if the summation over normal vibrations in (4) is replaced by integration, then $f(t)$ can be represented in the form

$$f(t) = \int_0^{\omega_{\max}} F(\omega) \left[\pm i \sin \omega t - (2\overline{m} + 1)(1 - \cos \omega t)\right] d\omega, \tag{7}$$

where

$$F(\omega)\, d\omega = {\sum_{\alpha}}' \frac{\Delta q_\alpha^2}{2},$$

the summation being carried out over those vibrations whose frequencies lie in the interval $\omega, \omega + d\omega$. Obviously, the terms with $\sin \omega t$ and $\cos \omega t$ in (7), as a result of averaging (with weight $F(\omega)$) over a finite interval of frequencies, tend to 0 as $t \to \pm\infty$. Consequently,

$$\lim_{t \to \pm\infty} f(t) = -\int_0^{\omega_{\max}} F(\omega)(2\overline{m} + 1)\, d\omega = -\sum_{\alpha} \frac{\Delta q_\alpha^2}{2} (2\overline{m}_\alpha + 1). \tag{8}$$

Now $W(\omega)$ can be represented in the form

$$W(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i(\omega-\omega_0)t}\{e^{f(t)} - e^{f(\infty)}\}\,dt + \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i(\omega-\omega_0)t}e^{f(\infty)}\,dt. \quad (9)$$

The first integral remains finite at $\omega = \omega_0$. With the aid of (8) we find that the second integral is equal to

$$\delta(\omega-\omega_0)\exp\left[-\sum_\alpha \frac{\Delta q_\alpha^2}{2}(2\overline{m}_\alpha + 1)\right] \quad (10)$$

and has the meaning of the probability density of a phononless transition. Consequently, the probability $P(\omega_0)$ of a phononless transition, to which in absorption and luminescence there should correspond a narrow line $\omega = \omega_0$, is equal to

$$P(\omega_0) = \exp\left[-\sum_\alpha \frac{\Delta q_\alpha^2}{2}(2\overline{m}_\alpha + 1)\right]. \quad (11)$$

3. Let us determine the conditions under which the probability of a phononless transition (11) may prove to be an appreciable quantity, i.e., when in the luminescence and absorption spectra one can observe the narrow line $\omega = \omega_0$. It follows from (11) that $P(\omega_0)$ decreases with increasing temperature. Let us consider the most favorable case $T = 0$. Then $m = 0$ and

$$P(\omega_0) = \exp\left[-\int_0^{\omega_{\max}} F(\omega)\,d\omega\right]. \quad (12)$$

At zero temperature the entire absorption spectrum lies to the right of the frequency ω_0, and the luminescence spectrum to the left of ω_0. The frequency ω_0, both in the absorption spectrum and in the luminescence spectrum, corresponds to the narrow line of the phononless transition. To estimate the intensity of the phononless transition, let us consider the relation between the value of the probability $P(\omega_0)$ and the moments of the spectral curve. The first moment, which determines the center of gravity of the spectral distribution, or half the Stokes losses, according to (6), is equal to

$$\mu_1 = \sum_\alpha \frac{\Delta q_\alpha^2}{2}\omega_\alpha = \int_0^{\omega_{\max}} F(\omega)\omega\,d\omega = \omega_{\text{av}}\int_0^{\omega_{\max}} F(\omega)\,d\omega, \quad (13)$$

where ω_{av} is some average frequency lying in the interval $(0, \omega_{\max})$. Comparing (12) and (13), we obtain

$$P(\omega_0) = e^{-\mu_1/\omega_{\text{av}}}. \tag{14}$$

Thus, the probability of a phononless transition will be the greater, the smaller the Stokes losses and the larger the value of the average vibrational quantum. By comparing $P(\omega_0)$ with the second and higher moments of the spectral curve, one can find a relation between the temperature dependence of $P(\omega_0)$ and the temperature change in the band shape.

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Note: Figure translations are in progress. See original paper for figures.