THE URBACH RULE FOR LOCALIZED EXCITATIONS IN CRYSTALS

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Abstract

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1. In theoretical studies of the form of light-absorption spectra by localized excitations in crystals, begun in works ([1,2]), a theory was developed for the shape of the light-absorption band near the absorption maximum. In subsequent works the refinement of the theory was reduced to taking into account the change in the frequencies of the lattice vibrations of the crystal upon electronic excitation ([3–6]) and to taking into account the anharmonicity of the lattice vibrations ([7,8]), without extending the theory to the region of frequencies far from the absorption maximum.

Urbach ([9]), in studying the coefficient of light absorption in silver-halide crystals, found the empirical formula

$$\chi(\omega) = \chi(\omega_0) \exp\{-\sigma(\omega_0 - \omega)/kT\}, \tag{1}$$

which determines, over a broad region of frequencies $\omega < \omega_0$, the dependence of the absorption coefficient on the frequency ω and the temperature T. It was subsequently found that formula (1), which received the name "Urbach rule," surprisingly accurately describes significant changes (by 4–6 orders of magnitude) of the absorption coefficient with changing frequency in the long-wavelength edges of the first bands of intrinsic (excitonic or localized excitations) and impurity absorption of many types of crystals.

Despite numerous attempts (see, for example, ([10–14])), the Urbach rule has until recently received no theoretical explanation. In a recent work by one of the authors ([15]), an elementary theory of the Urbach rule was proposed for the absorption of light by localized excitations in crystals. To simplify the calculations in work ([15]), on the basis of the Einstein model of a crystal, transitions from vibrational sublevels of the crystal lattice only to the level of the first electronic excitation were considered. Below a more rigorous theory is developed, in which the change in the frequencies of the normal vibrations of the lattice when an excitation appears is taken into account, as are all transitions from vibrational sublevels of the ground electronic state of the crystal to vibrational sublevels corresponding to an electronic excitation upon absorption of light of

a definite frequency. In doing so, using the general theory, which correctly describes the absorption curve near the maximum, and without introducing additional hypotheses, we shall obtain on the long-wavelength side, far from the absorption maximum, a dependence of the absorption coefficient on frequency and temperature that coincides with the Urbach rule.

2. Let the functions $|0\rangle$ and $|f\rangle$ represent the ground electronic state of the crystal and the state in which there is a localized excitation. Then, in the adiabatic approximation, the lattice vibrations in these states are described by the Hamiltonian operators (below we use units in which $\hbar = 1$)

$$H_0 = V_0 + \sum_s \Omega_s^0 \left(b_s^+ b_s + \tfrac{1}{2}\right),$$

$$H_f = V_f + \sum_s \Omega_s^f \left(b_s^+ b_s + \tfrac{1}{2}\right) - \tfrac{1}{2} \sum_s \xi_s \Omega_s^f (b_s^+ + b_s),$$

where V_0 and V_f are the zeroth terms of the expansion (in the displacements of atoms from equilibrium positions) of the potential energy of the crystal without electronic excitation and in its presence; ξ_s and $\Omega_s^f - \Omega_s^0$ are quantities characterizing the displacement of the equilibrium positions and the frequencies of the normal vibrations of the lattice when a localized electronic excitation appears in the crystal*; b_s^+ and b_s are the creation and annihilation operators of phonons of the s-th branch of normal vibrations.

According to the general theory developed in papers ([2–4, 7]), in the adiabatic approximation the absorption coefficient of light of frequency ω by a crystal, with the formation in the crystal of a localized electronic excitation, can be represented in the form of the product

$$\chi(\omega) = d_{f0}^2 F(\omega), \tag{2}$$

where d_{f0} is a quantity proportional to the vector of the electric dipole moment of the transition from the state $|0\rangle$ to the state $|f\rangle$;

$$F(\omega) = \frac{2}{\Gamma} \int_0^\infty d\mu \{ i\mu[\omega - \omega_0] + g(\mu) - {}^1/_2 \mu\Gamma \}, \tag{3}$$

where Γ is the radiation width;

$$\omega_0 = V_f - V_0 + \frac{1}{2} \sum_s (\Omega_s^f - \Omega_s^0) - \frac{1}{2} \sum_s \xi_s^2 \Omega_s^f + \sum_s \bar{n}_s (\Omega_s^f - \Omega_s^0)$$

is the energy of the zero-phonon transition;

$$g(\mu) = \frac{1}{2}\sum_s \xi_s^2\{(\bar{n}_s+1)e^{-i\Omega_s^f\mu} + \bar{n}_s e^{i\Omega_s^f\mu} - (2\bar{n}_s+1)\}, \tag{4}$$

$$\bar{n}_s = (e^{\beta\Omega_s^0}-1)^{-1}, \qquad \beta \equiv 1/kT. \tag{5}$$

In previous papers by the authors ([3, 7]), expression (3) was investigated near the frequency ω_0 of the zero-phonon transition. It was shown that under the conditions

$$B^2 \gg \max\{(\Omega_s^f)^2\}, \qquad (\omega_r-\omega)^2 < 4B^2$$

expression (4) is represented by a Gaussian curve

$$F(\omega) = \frac{\Gamma\sqrt{\pi}}{4B}\exp\left\{-\left[\frac{\omega_r-\omega}{2B}\right]^2\right\}, \tag{6}$$

where $\omega_r = \omega_0 + A$ is the frequency at the maximum of the absorption curve,

$$A = \frac{1}{2}\sum_s \xi_s^2\Omega_s^f, \qquad 2B^2 = \sum_s \xi_s^2(2\bar{n}_s+1)(\Omega_s^f)^2.$$

3. We shall investigate the dependence of function (3) on frequency and temperature far from ω_r, at the long-wavelength edge of the absorption band. To simplify the calculation, we consider the Einstein model of a crystal. We set $\Omega_s^f = \Omega$, $\Omega_s^0 = \Omega_0$, and introduce the notation:

$$\bar{n} = \bar{n}_s, \qquad a = \frac{1}{2}\sum_s \xi_s^2, \qquad b = (\bar{n}+1)a, \qquad c = \bar{n}a, \qquad g_0 = c+b. \tag{7}$$

Then function (4) takes the form

$$\exp g(\mu) = e^{-g_0}\sum_{m,m_1}\frac{b^m c^{m_1}}{m!m_1!}\exp\{i\mu[m_1-m]\Omega\}.$$

Substituting this value into (3), after integration we find the general expression for the function

$$F(\omega) = e^{-g_0}\sum_{m,m_1}\frac{b^m c^{m_1}}{m!m_1!}\{[\omega-\omega_0+(m_1-m)\Omega]^2+\Gamma^2/4\}^{-1}.$$

* For simplicity we do not take into account the off-diagonal terms of 2nd order $\Delta_{ss'} b_s^+ b_{s'}$ in the operator H_f

In the frequency region $\omega \ll \omega_0$ this function can be written in the form

$$F(\omega) = e^{-g_0} \sum_{p=0}^{\infty} \left(\frac{c}{b}\right)^{p/2} \frac{I_p(2\sqrt{bc})}{(\omega - \omega_0 + p\Omega)^2 + \Gamma^2/4}, \tag{8}$$

where $I_p(x)$ is the Bessel function of order p of imaginary argument.

Function (8) represents a system of equidistant Lorentzian curves, the positions of whose maxima correspond to the frequencies $\omega = \omega_0 - p\Omega$. The terms containing Bessel functions of low order correspond to frequencies close to the frequency of the phononless transition. They give expression (6).

We are now interested in the frequencies of the long-wavelength "tail" of the absorption curve, i.e., terms containing Bessel functions of order $p = (\omega_0 - \omega)/\Omega \gg 1$. Under the conditions

$$p = (\omega_0 - \omega)/\Omega \gg 1, \qquad 2\sqrt{be} = 2a\sqrt{\bar{n}(\bar{n}+1)} > 1 \tag{9}$$

one may use the asymptotic value ([16], p. 86)

$$I_p(x) = (\pi\sqrt{2})^{-1}(p^2 + x^2)^{-1/4} \exp\{\sqrt{p^2 + x^2} - p \operatorname{ar\,sh}(p/x)\} (\pi + O(1/x))$$

of the Bessel function of large order. Then, for a fixed value of p and frequency $\omega = \omega_0 + p\Omega$, the maximum of function (8) has the form

$$F_p(\omega) = 4(2\pi)^{-1/2}\Gamma^{-2} e^{-g_0} \exp\{p \ln \bar{n} - p \ln(p/ae)\}.$$

Substituting the values of p in (7), we transform this expression to the form

$$F_p(\omega) = \frac{4e^{-g_0}}{\Gamma^2\sqrt{2\pi}} \exp\left\{-\frac{\omega_0 - \omega}{kT}\left[\frac{\Omega_0}{\Omega} + \xi\right]\right\}, \tag{10}$$

where

$$\xi = \frac{kT}{\Omega} \ln\left(\frac{\omega_0 - \omega}{ae\Omega(\bar{n}+1)}\right)$$

is a function that depends only weakly on the frequency ω.

If the frequencies Ω are small, then the envelope function (10), taking (2) into account, gives a dependence of the absorption coefficient on frequency that coincides with Urbach' s rule (1), for

$$\sigma = [\Omega_0/\Omega + \xi] > 1. \tag{11}$$

Expression (10) differs from the expression obtained by A. S. Davydov ([15]) by a more elementary method (without allowance for the vibrational structure of the excited state and with $\Omega = \Omega_0$) by the common factor e^{-g_0} and by the factor $(\bar{n}+1)^{-1}$ under the logarithm sign.

At sufficiently low temperatures, inequality (9) is replaced by the inequality

$$2\sqrt{bc} = 2a\sqrt{\bar{n}(\bar{n}+1)} \ll 1. \tag{12}$$

In this case, in investigating expression (8) one may use the asymptotic value of the Bessel function in the form

$$I_p(x) = (p!)^{-1}(x/2)^p\{1 + x^2/4(p+1)\}.$$

Then, applying Stirling' s formula, for the frequency $\omega = \omega_0 - p\Omega$, with $p \gg 1$, we again obtain expression (10).

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REFERENCES

[1] K. Huang, A. Rhys, Proc. Roy. Soc., **204A**, 406 (1950).
[2] A. S. Davydov, ZhETF, **24**, 197 (1953).
[3] A. S. Davydov, Fiz. sborn. Kievsk. univ., **7**, 5 (1955).
[4] A. F. Lubchenko, Izv. AN SSSR, ser. fiz., **18**, 718 (1954).
[5] A. S. Davydov, A. F. Lubchenko, Ukr. fiz. zhurn., **1**, 5, 15, 111 (1956).
[6] K. Kubo, Y. Toyozawa, Progr. Theor. Phys., **13**, 160 (1955).
[7] A. F. Lubchenko, Phys. Stat. Sol., **6**, 319 (1964); **7**, 105 (1964).
[8] M. A. Krivoglaz, FTT, **6**, 1707 (1964).
[9] F. Urbach, Phys. Rev., **92**, 1324 (1953); F. Moser, F. Urbach, Phys. Rev., **102**, 1519 (1956).
[10] D. L. Dexter, Nuovo Cim. Suppl., **7**, 245 (1958).
[11] Y. Toyozawa, Progr. Theor. Phys., **20**, 53 (1958); **22**, 455 (1959); Progr. Theor. Phys. Suppl., **12**, 111 (1959).
[12] G. D. Maham, Phys. Rev., **145**, 602 (1966).
[13] K. Thomas, Phys. Rev., **144**, 582 (1966).

[14] V. M. Agranovich, Yu. V. Konobeev, FTT, **3**, 360 (1961).
[15] A. S. Davydov, Phys. Stat. Sol., in press.
[16] H. Bateman, *Higher Transcendental Functions*, 2, N. Y., 1953.
[17] H. Mahr, Phys. Rev., **125**, 1510 (1962).

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