Exciton absorption of light in layered crystals

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A mechanism of exciton absorption of light in layered crystals, which takes into account the real phonon and exciton spectra, is proposed. It is shown that temperature dependence of the integrated intensity, peak position, and half-width of the exciton absorption band in GaSe, GaTe, InSe, PbI_2, and HgI_2 is the result of the high efficiency of exciton scattering by layer flexural vibrations that are not peculiar to layered structures and by low-energy optical phonons.

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The physical principles of exciton absorption of light in organic and inorganic semiconductors and in dielectrics have by now been thoroughly studied.[1] There exists, however, a unique type of structure, occupying an intermediate place between ionic and molecular crystals, between three-dimensional and two-dimensional compounds, namely layered crystals (LC). The distinguishing property of these structures is the difference, by almost two orders of magnitude, between the elastic constants in the layer and between the layers. Numerous experimental investigations of exciton spectra in such substances make it possible to conclude unequivocally that ordinary three-dimensional Wannier excitons are excited in them, with radii spanning over several layer packets.[2] The quasi-two-dimensional character of the structure, however, leads to the appearance of a rather interesting and specific features in the photon spectra of these crystals. Foremost is the presence of flexure waves in the acoustic spectrum of the phonons, which are membrane vibrations of the layer.[3] The idea of flexure waves (FW) and of LC was first employed by I. M. Lifshitz[4] to explain the anomalies in the temperature dependence of the heat capacity of such substances. The main distinguishing property of FW is quadratic dispersion law and a high density of states in the low-frequency region. An important feature of the phonon spectrum of an LC is also the presence of low-energy optical phonons corresponding to vibrations of complete sandwiches relative to one another (rigid mode).[5] These vibrations are due to the presence of several translationally nonequivalent layers which are contained in the unit cell of the crystal. It is natural to expect, in this connection, the dynamic properties of the excitons, particularly in the exciton-phonon interaction, to have some anomalies. They should manifest themselves primarily in the temperature dependence of the parameters of the exciton absorption band. Experimental investigations of exciton absorption in LC has
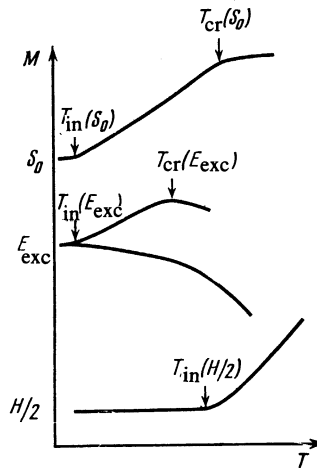

FIG. 1. Generalized temperature dependences of the exciton absorption band parameters in layered crystals.

indeed revealed anomalies in the temperature dependence of its integral characteristics. Among the most interesting are the following. (a) The presence of a temperature dependence of the integral absorption intensity (S_0), which, according to classical theory of excitons, should be missing. The anomaly of this dependence, namely the increase of the integral intensity with increasing temperature within the range of variation of the latter from the initial $T_{in} \approx 10$ K to a certain T_{cr} (the values of T_{cr} for various substances are given in Table I below). (b) The presence of a rather noticeable temperature shift of the absorption band (E_{exc}) at sufficiently low temperatures. It is remarkable that both the growth of the integral intensity of the band and its shift into the region of low temperatures are not accompanied by a broadening of the band $(H/2 = \text{const})$. These pecularities are shown schematically in Fig. 1.

TABLE I.

	GaSe [6]			InSe [7]			GaTe [8]			PbI_2 [15]			HgI_2 [16]		
	S_0	E_{exc}	$H/2$	S_0	E_{exc}	$H/2$	S_0	E_{exc}	$H/2$	S_0	E_{exc}	$H/2$	S_0	E_{exc}	$H/2$
T_{in}	20	> 6	55	<70	15	60	20	20	55	—	10	60	—	15	60
T_{cr}	190	45	—	100	60	—	170	55	—	—	40	—	—	35	—

At the present time these anomalies, particularly that of $S_0(T)$, has been interpreted by resorting to polariton concepts.[6-8] However, the polariton theory does not explain the cause of such high T_{cr} for substances with low values of the longitudinal-transverse splitting (GaSe, GaTe, InSe, and others), and does not explain the presence of a temperature shift of the band at low temperatures. When explaining the regularities of the shift of the exciton band in semiconducting crystals, it is proposed in practically all the papers that the anomalies are reflections of the temperature-induced change of the width of the forbidden band.[9-11] This makes necessary an artificial distinction between the temperature investigations of the shift and of the broadening of the absorption bands. In the former case, the calculations are performed within the framework of ordinary band theory, whereas the band shape function is calculated within the framework of the exciton model of excitation. Such an interpretation of the temperature dependence of the integral characteristics of the absorption band in LC is not convincing enough and to explain the same experimental material it becomes therefore necessary to resort to different and as yet incompatible theoretical models. On the other hand, no account is taken of the principal and distinguishing feature of the investigated crystals, namely their quasi-two-dimensionality.

In this paper we propose a physical picture of the temperature origin of the spectra of the exciton absorption in layered crystals, which explains, from unified viewpoints and with account taken of the concrete properties of the elementary excitations in the crystal, the observed anomalies of the temperature dependence of the parameters of the exciton absorption band.

1. THEORY

The proposed theory of exciton absorption of light in layered crystals is based on a unified exciton approach and presupposes high efficiency of the exciton-phonon interaction. The observed anomalies of the exciton absorption spectrum are attributed to the variety of mechanisms whereby the crystal-excitation energy is dissipated.

This is manifest primarily in the important role of indirect phototransitions in such crystals, i.e., the activity of the phonon subsystem is so high that, in addition to ordinary phototransitions, one or several phonons are produced in the course of absorption. The integral absorption intensity increases in this case with increasing temperature in accord with the increased role of the indirect phototransitions.[12] The reason is that in the model considered the indirect phototransitions are real, and not virtual arising in different orders of perturbation theory. This is precisely why the Hamiltonian of the interaction of the medium with light contains terms that are responsible for simultaneous interaction of three quasiparticles (photon-exciton-phonon), and S_0 acquires a temperature dependence that is completely absent if account is taken of only virtual processes of exciton scattering by a phonon are considered. Since the temperature dependence of the absorption band is determined by the occupation numbers of the phonons, it follows that with

increasing temperature the processes of phonon-phonon scattering become vital. Phonon-phonon interaction leads to transitions between stationary phonon states and to a redistribution of the energy among the phonon branches. The anharmonicity effects, which open up an additional excitation-energy relaxation channel, lead to existence in the crystal of a temperature T_{cr} starting with which a qualitative change takes place in the character of the temperature dependence of the integral characteristics of the absorption band.[13]

The analysis of the exciton absorption band will be carried out here on the basis of the theory of spectral moments (Ref. 1, $\S$ 53). Using the calculation procedure of Refs. 12 and 13, we obtain for the integral absorption

$$S_0 = 2\pi T_0^2 \left\{ 1 + 2\sum_q \Pi(q, -q) N_q \left[1 - \frac{24}{\omega_q} \sum_{q_1} V_a(q, q_1) N_{q_1} \right] \right\},$$

(1)

where T_0 is the matrix element of the exciton-photon interaction; $\pi(q, -q)$ is a function that characterizes the ternary photon-exciton-phonon interaction (indirect phototransition); $N_q = 1 + 2n_q$, n_q are the occupation numbers of the harmonic phonons with energy ω_q and momentum q; $V_a(q, q_1)$ is the strength constant of the phonon anharmonicity. Consequently, for crystals in which indirect phototransitions play an important role, there should exist in the high-temperature region a temperature T_{cr} above which the integrated intensity approaches saturation. Moreover, with further temperature rise the integrated absorption may decrease.

An investigation shows that the absorption-band temperature shift depends substantially on the exciton-excitation relaxation mechanism.[14] Thus, for an exciton-phonon interaction linear in the displacements of the atoms, the center of gravity of the absorption curve S_1/S_0 (S_1 is the first moment of the absorption curve) does not depend on the temperature. The shift of the maximum of the absorption band is made possible here only by a change in its asymmetry, and the direction of the shift is determined by the sign of the effective mass of the exciton. More important for $E_{exc}(T)$ is the relaxation mechanism corresponding to the exciton-phonon interaction, which is quadratic in the displacement of the atoms. Such an interaction leads to a change, with increasing temperature, of the position of the center of gravity of the absorption curve (to a shift of the band as a whole)[14]:

$$E_{exc}(T) = \frac{S_1}{S_0} - A_{exc} = E_{exc}(0) - A_{exc}(T)$$

$$+ \sum_q V_2(q, -q) N_q \left[1 - \frac{24}{\omega_q} \sum_{q_1} V_a(q, q_1) N_{q_1} \right].$$

(2)

Here $V_2(q, -q)$ is a function of the exciton-phonon coupling which is quadratic in the phonons and $A_{exc}(T)$ is the band shift due to the band asymmetry. According to (2), depending on the sign of the coupling function, the absorption band shifts to the long-wave ($V_2 < 0$) or to the short-wave ($V_2 > 0$) side of the spectrum, while the anharmonicity of the phonons leads to a nonmonotonic variation of the shift with in-

creasing temperature. Calculation of the relaxation mechanisms of the second central moment of the absorption curve, which characterizes the temperature dependence of the half-width of band, leads in this scheme to the expression.

$$M_2/S_0 = \sum_q \left[|V_1(q)|^2 + \sum_{q_1}{}' |V_2(q, q_1)|^2 N_{q_1} \right] N_q, \qquad (3)$$

where $V_1(q)$ the exciton-phonon interaction function in the approximation linear in the displacements.

2. DISCUSSION OF EXPERIMENTAL RESULTS

In Table I below are shown the published and our experimental values of the characteristic points T_{in} and T_{cr} (Fig. 1) of the temperature (in °K) dependence of the parameters of the exciton absorption band.

We begin the discussion of the results with the characteristics $E_{exc}(T)$ and $H(T)/2$. First, both the shift and the broadening of the absorption band are determined by the exciton-phonon interaction. It might seem at first glance that the temperature shift of the band should be accompanied by its broadening. This is not observed, however, in a layered crystal. Figure 2 shows the most interesting anomalous temperature shift of the exciton absorption band, observed by us in the PbI$_2$ cyrstal. The temperature dependence of the band shift has a clearly pronounced nonmonotonic character: when the temperature is raised to 40 K the band shifts to the short-wave side, and with further increase of temperature the shift direction is reversed. An attempt to explain this anomaly was undertaken in Ref. 17, where the short-wave shift was attributed to a manifestation of the anharmonicity of the phonons, and the long-wave shift to a unique influence of the Debye-Waller factor. Such an approach is surprising, since it calls for resorting to phonon-phonon interaction in a temperature region located below the region where the phonons themselves appear (the Debye-Waller factor). In addition, the Debye-Waller factor should lead primarily to a sharp decrease of the integral absorption with increasing temperature (Ref. 18, Chap. VIII), something not observed in experiments with layered crystals. On

the other hand, this explanation of the band shift does not explain the absence of broadening in this temperature region.

It is useful to attribute the differences in the behavior of $E_{exc}(T)$ and $H(T)/2$ to an anomaly of the exciton-phonon interaction in layered crystals. Such a anomaly is indeed possible if account is taken of the exciton scattering by flexure waves. A pecularity of the flexural vibrations is that they do not cause, in the approximation linear in the displacements, a change in the relative dimensions in the plane of the layer. In accordance with strain thermodynamics, the free energy of a bent plate does not contain terms that are linear in the strain tensor (Ref. 3, p. 645 of Russ. orig.). This means that the mechanism of energy relaxation of the exciton excitation on flexure waves is determined only by an interaction quadratic in the displacements. It is this, in accordance with (2), which leads to the low-temperature shift of the exciton band. On the other hand, the temperature dependence of the half-width of the absorption curve (3) is determined mainly by the function V_1 (obtained in an approximation linear in the displacements), i.e., scattering of excitons by all the remaining phonon branches s. Therefore, by virtue of the inequality $\sum_s V_1^2(s) \gg V_2^2$ (flexure waves), the temperature shift of the exciton band is not accompanied by its broadening if the scattering of the excitons in this temperature region is from the flexure waves.

Recognizing that the temperature of the excitation of the flexure waves is low enough ($T^D(\text{PbI}_2) \sim 15$ K,[19] the role of the phonon-phonon scattering increases strongly with increasing temperature. This, according to (2), causes reversal of the temperature shift at $T > 40$ K. Starting with 55 K, the band broadens and a shift component (A_{exc}) due to scattering of the excitons by the remaining phonons appears.

To check on the foregoing assumptions, we have investigated experimentally intercalated crystals. It is known that the presence of a weak coupling in the layered crystals makes it possible for foreign substances to penetrate into the space between the layers. This technological processing (intercalation), on the one hand, increases the distance between layers, and on the other, equalizes the inelastic constants between the layers and within the layers. The last circumstance causes vanishing of those phonon-spectrum anomalies which are due to the quasi two-dimensionality of the crystal. A unique "freezing-out" of the flexure waves takes place. In turn, this should lead to a decrease or even to a vanishing of the temperature shift of the excited band in the region of the lowest temperatures. This is precisely the situation observed experimentally and shown in Fig. 2, where the characteristics E_{exc} and $H/2$ of the initial PbI$_2$ crystals (a) and of those interclated with Na (b) are shown for comparison. This indicates unambiguously that the flexure waves participate in the formation of the exciton absorption band.[1]

We proceed now to discuss the temperature dependence of the integral intensity of the exciton absorption. As mentioned above, the published explanations of $S_0(T)$ are made in the framework of the polariton model of light absorption. The main condition for the appearance of a polariton (a mixed state of a photon and an exciton) in the absorption
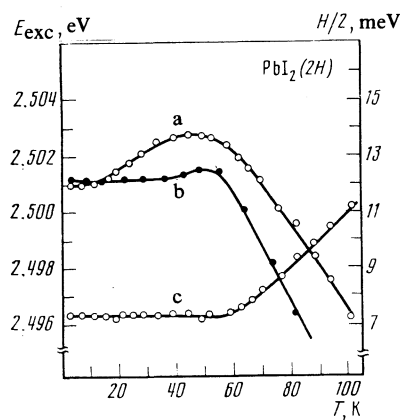

FIG. 2. Characteristics of the temperature shift of the exciton absorption band of PbI$_2$ crystals (a) and of intercalated PbI$_2$ (b); curve c shows the temperature dependence of the half-width of the exciton band.

spectra of light is the weak excitability of the dissipative subsystem. The quantity T_{cr} in the temperature dependence of the integrated absorption is defined in this approach as the ratio of the oscillator strength of the exciton transition to the relaxation parameter[22]: the smaller the ratio (i.e., the more effective the exciton scattering), the lower the temperature region in which the polariton effects manifest themselves. There is no doubt that this approach is correct for semiconductors with large longitudinal-transverse splitting (such as CdS, Ref. 23) to explain the spectral features in a region of very low temperatures.

It is almost useless to resort to the polariton absorption mechanism of light absorption to explain $S_0(T)$ in layered crystals such as GaSe, InSe, GaTe, and others, whose critical temperatures are high enough and whose characteristic parameters that indicate the degree of polariton formation are negligible. It is logical to assume that the onset of a temperature dependence in such layered crystals is due to the large specific gravity of the indirect phototransitions, i.e., to simultaneous excitation, in the course of a light absorption, of the exciton and phonon subsystems. The value of T_{cr} is determined in this case mainly by the properties of the phonon subsystem: the energy state of the phonon and the constant of its anharmonicity (1). Judging from the onset of the temperature dependence (see Table I), such phonons can be the low-energy phonons which exist in these crystals, and whose energy is of the order of 20 cm^{-1} (Ref. 24).

Thus, on the basis of an analysis of the temperature dependence of the integrated characteristics of the exciton band, we have formulated the physical principles of the light absorption process and determined the concrete mechanisms of the relaxation of the exciton-excitation energy in an unusual type of structure, namely layered crystals. We have indicated for the first time ever that temperature-induced irregularities in the exciton absorption of light in layered crystals are due to the presence of flexural acoustic vibrations and of low-energy optical phonons in such crystals.

[1] To analogous conclusions lead also investigations of the heat capacity of layered crystals, whose intercalation leads to vanishing of the anomalies in the temperature dependence of the latter,[20] as well as investigations of spin-lattice relaxation in layered crystals.[21]

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