

## The prediction of excitons (On the 90th birthday of Ya. I. Frenkel')

É. I. Rashba

*L. D. Landau Institute of Theoretical Physics of the Academy of Sciences of the USSR, Moscow District  
Usp. Fiz. Nauk 144, 347–357 (October 1984)*

### 1. INTRODUCTION

Ninety years have elapsed in 1984 from the birth of Yakov Il'ich Frenkel'. Already 30 years have passed since his death. But the name of Ya. I. Frenkel' is not forgotten. On the contrary, it is met ever more often in the scientific literature, and it resounds in the scientific conferences and seminars. This test of time shows convincingly that the new physical concepts and mechanisms of processes presented in Frenkel's papers have been experimentally confirmed and are an organic part of modern physics.

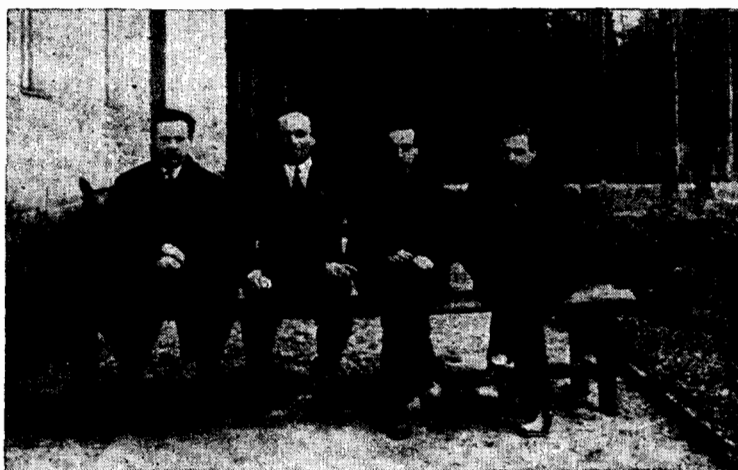
Yakov Il'ich was a physicist of broad scope. His studies encompass practically all branches of physics, and they contain a response to the most important events in different fields of physics. They include also the allied sciences: biophysics, geophysics, etc. He wrote many monographs. A view of the volume and variety of Ya. I. Frenkel's scientific creativity is given by the bibliographic index contained in Volume II of his "Collection of Selected Studies".<sup>1</sup> The most outstanding features of Yakov Il'ich's talent appear to be the remarkable pictorial quality of his physical thinking and the scientific inventiveness that one at times is compelled to view as clairvoyance.

The fate of individual studies of Ya. I. Frenkel' differs. Some of them were immediately accepted by his contemporaries

and rapidly entered the monograph literature. For example, this is what happened with the "Frenkel' defects". Others, as though resurfacing from oblivion, have naturally entered into the circle of contemporary studies. An example is the "Frenkel'-Kontorova model", which in recent years has been widely applied in studies on the structure of submonomolecular films adsorbed on the surface of crystals. Many of his studies yet await their fate.

However, the aim of this article is not a general review of the studies of Ya. I. Frenkel'. It is devoted entirely to a single problem—excitons, which perhaps are the pearl of Yakov Il'ich's creative legacy.

The concept of "waves of excitation" was advanced by Ya. I. Frenkel' in 1931<sup>2</sup> and was developed in three of his articles.<sup>2-4</sup> The term "exciton" for these waves was introduced in Ref. 4. At present the spectroscopy of excitons constitutes an extensive, rapidly developing field of solid state physics that is closely interwoven with its other branches (band theory, photoelectric phenomena, luminescence, radiation physics, etc.), while Yakov Il'ich is invariably viewed as its creator. In this estimation both Soviet and foreign physicists are united. The American physicist J. J. Hopfield, whose studies have exerted a profound influence on the development of the spectroscopy of excitons in semiconductors, wrote to me in a private letter (1978): "Excitons have



At the building of the Leningrad Physicotechnical Institute, 1928. Theoretical Division of the Physicotechnical Institute, from left to right: B. N. Finkel'shtein, Ya. I. Frenkel', L. D. Landau, D. D. Ivanenko.

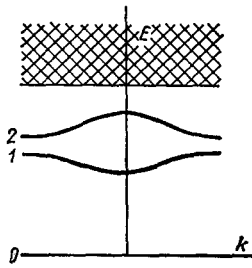


FIG. 1. Diagram of the electronic spectrum of crystalline dielectrics and semiconductors. 0—ground state, 1, 2—exciton bands. Cross-hatched area—electron-hole continuum,  $E$ —energy,  $k$ —quasimomentum.

truly become a field and not a curiosity.” The collected monograph *Excitons*<sup>5</sup> by Soviet and foreign authors begins with a sketch of Ya. I. Frenkel’, where it is noted that it was sent to press in the 50th anniversary year from the time of publication of Ya. I. Frenkel’s pioneering study.

It now seems inexpedient to present in detail the studies performed about a half century ago: both the physical understanding of the problems and the mathematical apparatus of the theory, and finally, the experimental material have radically changed since that time. At the same time it seems instructive, on looking back, 1) to examine the set of problems undertaken, 2) to understand the motivation for formulating them, 3) to trace how far it has been possible to advance toward solving them, and 4) to correlate them with the current state of the physics of excitons. An attempt of this type has been undertaken in this article.

## 2. EXCITONS

Elementary excitations of the electronic subsystem of a crystal that transport energy but not electric charge are called excitons. As a rule, the exciton levels lie in the forbidden band (gap) that separates the ground state of the crystal from the electron-hole continuum (Fig. 1).

Frenkel’ introduced the concept of an exciton in using the model of a crystal constructed of weakly interacting atoms. This allows one to use the Heitler-London approximation, and neglecting exchange, to write the multielectron wave function of a crystal in which the excitation is localized at the  $m$ th node in the form

$$\Phi_m = \psi_1 \psi_2 \dots \tilde{\psi}_m \dots \psi_N. \quad (1)$$

Here  $\psi$  and  $\tilde{\psi}$  are the wave functions of the unexcited and the excited atom, while  $N$  is the number of atoms in the crystal. Then the wave function, which possesses translational symmetry, has the form

$$\Phi_k = \frac{1}{\sqrt{N}} \sum_m \Phi_m e^{ik \cdot m}. \quad (2)$$

Here  $k$  is the quasimomentum. Then  $\Phi_k$  describes the “excitation wave” or exciton. The dispersion law of the exciton is:

$$E(\mathbf{k}) = E_0 + D + J(\mathbf{k}), \quad J(\mathbf{k}) = \sum_{\mathbf{m}_1} J_{\mathbf{m}-\mathbf{m}_1} e^{i\mathbf{k}(\mathbf{m}-\mathbf{m}_1)}, \quad (3)$$

Here  $E_0$  is the excitation energy of a free atom,  $D$  is the vapor-crystal spectral shift, and the  $J_{\mathbf{m}-\mathbf{m}_1}$  are the matrix elements for excitation transport:

$$J_{\mathbf{m}-\mathbf{m}_1} = \int \tilde{\psi}_{\mathbf{m}_1}^*(2) \psi_{\mathbf{m}}^*(1) H_{\text{int}}(1, 2) \tilde{\psi}_{\mathbf{m}}(1) \psi_{\mathbf{m}_1}(2) d(1) d(2). \quad (4)$$

Upon absorption of light, excitons are excited that satisfy the law of conservation of momentum:

$$\mathbf{k} = \mathbf{K}. \quad (5)$$

Here  $\mathbf{K}$  is the wave vector of the photon. Since  $K \ll \pi/d$ , where  $d$  is the lattice constant, we can generally set  $\mathbf{K} \approx 0$ .

An exciton constructed in this way is called a Frenkel’ exciton.

Below we must understand the motivating factors that led Frenkel’ to this model. There are two of them, the first of them clearly fixed by the title common to the first two articles<sup>2,3</sup>: “On the Transformation of Light into Heat in Solids”. In a monatomic gas the dissipation of absorbed light energy results from collisions of the second type by conversion of the energy of electronic excitation into kinetic energy of the atoms. Ya. I. Frenkel’ sought an analogous mechanism that would bring about dissipation in solids, while clearly understanding the difficulties that arise here: the trading of energy of electronic excitation for Debye phonons, whose mean energy is two orders of magnitude smaller, must be extremely hindered. The second factor—the experimental data of Becquerel,<sup>6</sup> and also of Obreimov and de Haas,<sup>7</sup> in which narrow-band absorption was found at low temperatures; it could not be explained by interband transitions with formation of electron-hole pairs without assuming that the width of both the hole and electron bands are extremely small. The first factor was decisive, and this is precisely why Frenkel’ chose the model of a solid maximally close to the model of a monatomic gas.

It is very important that both Frenkel’ and Peierls,<sup>8</sup> who first responded to Frenkel’s study and entered into the study of excitons following him, started with the weakness of secondary emission (luminescence and inelastic light scattering) of solids as an immutable experimental fact valid in the entire range of temperatures down to the very lowest. This implied practically complete conversion of absorbed light energy into heat. Here it was assumed that the mechanism of dissipation is intrinsic, i.e., it functions in a perfect crystal. Owing to this direction of the studies, the exciton became the first quasiparticle, for which a theory of strong interaction with phonons began to develop. We shall turn to this problem again in Sec. 5. Yet here we must stress that the improvement of the experimental methods of growing and studying crystals, which has taken many decades, has shown that the absence of luminescence is not a universal property of crystals, while its quenching usually occurs at certain types of impurities and defects. On the contrary, many perfect crystals exhibit a high yield of secondary emission. Owing to this, there are efficient luminophors, light diodes, injection lasers, etc., as well as intense resonance Raman scattering.

Thus the difficulties that Frenkel’ and Peierls faced in attempts to find a highly effective universal intrinsic mechanism of quenching of luminescence were not simply technical difficulties of the theory: they reflected the essence of things. At the same time, the direction of their studies is

quite natural. As eminent theoreticians/who worked in the first decade of existence of quantum mechanics and created the fundamentals of the quantum theory of crystals, they strove to construct it by starting from first principles in order to make it just as consistent and perspicuous as the quantum theory of atoms and simple molecules. Therefore the introduction into the interpretation of varied phenomena of unidentified defects and impurities as a kind of "supernatural force" charged with responsibility for everything not understandable and undesirable aroused a natural inner protest among those who were striving to develop a logically consistent theory. The appeal to uncontrolled factors sometimes even "frightened them off". This is precisely why Wolfgang Pauli said: "Ich mag diese Physik des festen Körpers nicht . . ." <sup>1)</sup> Peierls <sup>8</sup> tried to classify solids into "absorbers" and "scatterers" (Streuer), <sup>2)</sup> based exclusively on parameters describing the intrinsic properties of the crystals, while Frenkel' wrote <sup>4</sup>:

"This "stickiness" in a semiconductor has usually been explained by the presence in the crystal of certain physical inhomogeneities (small cracks, etc.) or chemical impurities. However, this viewpoint seems to me to be completely unsatisfactory . . ."

It required the work of several generations of physicists, who learned to grow pure and controllably doped crystals, instead of "dirty" ones, so that the "stickiness" of which Ya. I. Frenkel' wrote (autolocalization) could be distinguished against the background of capture by impurities.

The connection between excitons and narrow absorption bands proved considerably more simple and unambiguous. Here the decisive role is played by the criterion (5) that Frenkel' established in Ref. 3. It selects from the entire exciton band a single state in to which an optical transition is allowed. Owing to this selection rule, the exciton absorption spectrum can be very narrow, even when the exciton band has considerable width. On the contrary, an absorption spectrum in which an independently moving electron and hole are created is always broad-band, since the selection rule has the form

$$\mathbf{k}_e + \mathbf{k}_h = \mathbf{K}. \quad (6)$$

Here  $\mathbf{k}_e$  and  $\mathbf{k}_h$  are the quasimomenta of the electron and the hole. The condition (6) fixes only the total quasimomentum of the two particles. Consequently, optical transitions can occur at practically all points of the electron and hole bands. Therefore narrow-band absorption is specific precisely for excitons: the narrowness of an intrinsic absorption band is usually the first sign indicating that it may belong to the exciton spectrum.

### 3. MODELS OF EXCITONS. EXPERIMENTAL DATA

In order to estimate the significance and field of applicability of the Frenkel' model, we must first establish its place in the scientific literature of that time. The band schema of Bloch, which made possible the systematization and

interpretation on a unitary basis of a broad set of phenomena in metals, semiconductors, and dielectrics, rapidly won the dominant position in the quantum theory of crystals. The well-known monograph of Bethe and Sommerfeld, <sup>10</sup> which appeared in its second edition two years after the studies of Ya. I. Frenkel', <sup>2,3</sup> and which was actually an encyclopedia of the quantum electronic theory of crystals, was almost fully devoted to the band schema. And yet the Bloch band schema was based on the Hartree-Fock method, which does not take electron correlation into account, and is practically incompatible with the existence of Frenkel' excitons. Yakov Il'ich clearly acknowledged the existence of this problem and hence chose the Heitler-London method. In the third article he wrote <sup>4</sup>:

"The Bloch method for a crystal is equivalent to the "molecular-orbital" method of Lennard-Jones . . . The fundamental defect of this method consists . . . in allowing the possibility of assigning many . . . electrons to the same nucleus . . . Such a method of description can be to a certain degree justified in the case of . . . weakly bound electrons in a metal. Its application to the bound electrons in a dielectric . . . is, however, an inadmissible abuse of the Bloch method . . . Such an abuse has been practiced recently . . . in studies on the electronic theory of the solid state, sometimes leading to completely erroneous results. One of these misunderstandings . . . consists in the actual exclusion from the treatment of nonconductive excited states of the crystal, i.e., . . . excitons. According to the theory . . . based on the Bloch method, absorption of light by a dielectric crystal unavoidably converts it into a conductor . . ."

Naturally, one cannot simply supplement the Bloch schema with Frenkel' excitons, since the system of Bloch wave functions is complete. Yet a situation is quite real in which the lower excited states of a crystal are described by Frenkel' excitons, and the upper excited states, which correspond to the ionized states of atoms (or molecules), are described by correspondingly modified Bloch functions.

There is also an important limiting case in which the Bloch schema can be naturally supplemented by exciton states. It has been pointed out by Wannier <sup>11</sup> and Mott. <sup>12</sup> The Wannier-Mott exciton model is extremely simple: it is a hydrogenlike atom formed of an electron and a hole bound by Coulomb attraction. Its energy spectrum is

$$E_n = \frac{\mu \epsilon^4}{2\hbar^2 \epsilon^2 n^2}, \quad n \geq 1 \quad (7)$$

Here  $\mu$  is the reduced mass of the electron and hole, and  $\epsilon$  is the dielectric permittivity. Equation (7) is valid if the corresponding Bohr radius satisfies  $\hbar^2 \epsilon / \mu e^2 \gg d$ . This inequality is well satisfied in semiconductors with  $\epsilon \gg 1$ ,  $\mu \ll m$ , where  $m$  is the mass of a free electron.

Finally, a third model of excitons—charge-transfer excitons—occupies an intermediate position between the Frenkel' and the Wannier-Mott excitons. In this model the hole usually lies at the central node, while the electron density is spread throughout the first coordination sphere.

At present excitons have been found in all classes of crystalline dielectrics and semiconductors, and also in a number of polymers. Apparently they were first reliably

<sup>1)</sup>"I do not like this solid-state physics . . ."

<sup>2)</sup>Ya. I. Frenkel' wrote of them: "A somewhat unusual class of objects", whereas he applied the epithet "ordinary" to absorbers.<sup>4</sup>

identified in polymers by Scheibe.<sup>14</sup> They are formed in aqueous solutions of certain cyanine dyes (of the type of  $\psi$ -isocyanine). These objects are remarkable in that narrow bands of exciton absorption and luminescence in resonance coincidence are observed in them at room temperature. Experiments have shown that the aggregation of molecules into a polymer *per se* does not enhance the quenching of luminescence, i.e., the phonon mechanism of dissipation is ineffective here. Yet the addition of molecules of "quenchers" in concentration  $C \sim 10^{-6}$  leads to complete quenching of the luminescence—the polymer is converted from a "scatterer" into an "absorber". This high efficiency of quenching involves the fact that an exciton effects the transport of electronic excitation from its site of origin to the "quencher" molecule.

The Frenkel' model excellently describes the excitons that arise in many organic molecular crystals—molecular excitons. Their identification is considerably facilitated by the fact that usually the unit cell contains several molecules having different spatial orientations (that is, the crystal consists of several sublattices). Therefore the functions of (1) and (2) bear the extra index of the sublattice  $\alpha$ , while the energy spectrum contains several branches  $E_\lambda(\mathbf{k})$ . Since the selection rule (5) remains in force, the absorption spectrum consists of several narrow bands polarized along the crystallographic axes (rather than the axes of the molecules!). This phenomenon, the Davydov splitting,<sup>15</sup> which was discovered experimentally by Prikhotjko<sup>16</sup> in naphthalene and by Broude *et al.*<sup>17</sup> in benzene, is one of the fundamental criteria for identification of exciton bands. Molecular excitons have been studied widely and several monographs have been devoted to them.<sup>18-20</sup> An analogous model describes excitons in magnetic dielectrics.<sup>21</sup>

The Wannier-Mott model describes excitons in most semiconductors of the type of Ge, GaAs, CdS, Cu<sub>2</sub>O, CuCl, etc. In studying them, the outstanding contribution has been made/by experimental (E. F. Gross, B. P. Zakharchenya, A. A. Kaplyanskiĭ, B. S. Razbirin, S. A. Permogorov, and others) and theoretical (G. E. Pikus, G. L. Bir, E. L. Ivchenko, and others) studies conducted in the A. F. Ioffe Leningrad Physicotechnical Institute of the Academy of Sciences of the USSR, with which the name of Ya. I. Frenkel' is indissolubly associated.

There is an extensive literature on the exciton spectra of solid noble gases and alkali-halide crystals. At first glance the Frenkel' model seems specially constructed for describing excitons in crystals of the noble gases, however, actually the first exciton transitions in them apparently are best described by the charge-transfer model and the higher transitions by the Wannier model. The situation is analogous for the alkali-halide crystals.

There is no doubt now that the existence of excitons is a general law for nonmetallic crystals. The manifestation of exciton effects in biological objects<sup>22</sup> has also been shown experimentally. A number of hypotheses has been advanced on the participation of excitons in biological processes (photosynthesis, muscle contraction, etc.). But at present they remain hypotheses that await thorough experimental verification.

#### 4. EXCITON-PHONON INTERACTION

The interaction of excitons with photons amounts to absorption of light and dispersion near exciton resonances, as well as exciton luminescence. Ya. I. Frenkel' formulated the selection rule (5), which is valid in a rigid lattice, i.e., for optical transitions not involving phonons. This condition, now so usual that it seems trivial, was far from evident in 1931: Yakov Il'ich derived it only in his second article,<sup>3</sup> while in the first article<sup>2</sup> he was ready to reject explanation of narrow-band spectra via excitons! In Ref. 3 he also derived the selection rule for one-phonon processes:

$$\mathbf{k} + \mathbf{q} = \mathbf{K}, \quad (8)$$

Here  $\mathbf{q}$  is the quasimomentum of the phonon.

It is convenient here to resort to an analogy between Frenkel's theory of excitons and the Born dynamic theory of crystal lattices,<sup>23</sup> as Yakov Il'ich stressed.<sup>3</sup> In crystals made of weakly interacting molecules, the intramolecular vibrations are transformed into crystal modes that can be treated as vibrational excitons and are a prototype of the Frenkel' electronic exciton. In a consistent theory of polar lattices, even if constructed on a classical basis, the interaction of light with the lattice vibrations is not considered weak. The result of interaction in the system of light wave + harmonic polar lattice is not absorption nor light scattering, but the formation of new non-decaying normal vibrations—optomechanical waves.<sup>24,25</sup> They have been termed polaritons. The absorption of the light wave (more exactly—attenuation) arises only from lattice anharmonicity or the presence of defects that give rise to scattering (attenuation) of the polaritons.

A similar consistent approach, but now on a quantum basis, has been developed for electronic excitons by Pekar<sup>26</sup> and Hopfield,<sup>27</sup> and by Agranovich<sup>28</sup> as applied to the Frenkel' model. The nontriviality of the results obtained by such a generalization has been elucidated in Ref. 26: owing to the strong dispersion of electronic excitons, in Eq. (3) one must take consistent account of the dependence of  $E$  on the quasimomentum  $\mathbf{k}$ , even in the region of small quasimomenta of the exciton  $k = K \ll \pi/d$ . This is because it leads to the appearance of additional light waves near the exciton resonances. A diagram of the energy spectrum of the system that explains these statements is shown in Fig. 2, which demonstrates the rearrangement of the exciton-photon interaction. In order to compare Fig. 2b with the usual course of a dispersion curve near a region of anomalous dispersion, one must recall that  $E = \hbar\omega$ , while  $k(\omega) = \omega n(\omega)/c$ , and  $n$  is the refractive index, and examine Fig. 2 after turning it through 90°. Then one easily notes that an undamped wave arises in the classical region of "total reflection". One can also understand that the Kramers-Kronig relationship breaks down—dispersion exists in the absence of absorption.

The pattern shown in Fig. 2b has been confirmed by numerous experiments and has been described in special monographs.<sup>29,30</sup> The simple schema of exciton absorption obtained by Ya. I. Frenkel'—a narrow phononless band and phonon satellites—is derived from it in the limiting case of narrow exciton bands and weak exciton absorption (the region of total reflection approaches zero). Up to now this

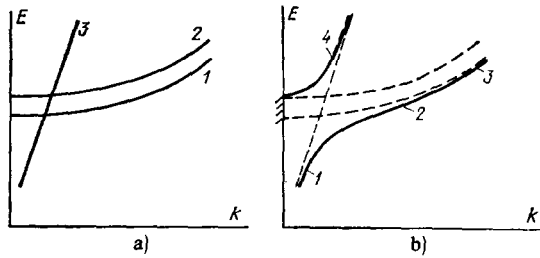


FIG. 2. Spectrum of an exciton-photon system is the absence (a) and the presence (b) of interaction of excitons with photons. a) 1—transverse excitons, 2—longitudinal exciton, 3—photons; b) the lower excitonic polariton in region 1 is an ordinary light wave, while in region 2 it passes through a region of “total reflection”, and in region 3 it is an additional wave; 4—upper polariton. Dashed lines—unperturbed spectrum. The cross-hatched region on the  $E$  axis is the region of total reflection in “ordinary” crystal optics.

schema has proved sufficient for describing a broad set of experiments,

### 5. STRONG EXCITON-PHONON INTERACTION

We have pointed out in Sec. 2 that Ya. I. Frenkel' introduced excitons primarily in order to explain the experimental data on conversion of light energy absorbed by a crystal into heat, i.e., to elucidate the mechanisms of radiationless transitions in perfect crystals.

Owing to the presence in dielectrics of a gap in the electronic spectrum, in the act of radiationless transition the energy of electronic excitation must be converted into about 100 Debye phonons. This number arises in the theory as the reciprocal adiabatic parameter  $E_{el}/\hbar\omega_{vib} \sim \sqrt{M/m} \sim 10^2$ , where  $m$  is the mass of an electron, and  $M$  is the mass of the nuclei. This simple estimate agrees with the experimental data.

Yakov Il'ich stated that the weak lattice anharmonicity cannot be responsible for such transitions: it would arise in the 100th order of perturbation theory. Therefore he proposed<sup>2</sup> another mechanism that was the basis of the subsequent studies on radiationless transitions<sup>31,32</sup>: the difference in positions of equilibrium and of vibrational frequencies of the lattice oscillators in the ground and excited electronic states of the crystal. Here the lattice in each state is described in the harmonic approximation. This means that, while the oscillator function associated with the generalized coordinate  $\xi_s$  in the ground electronic state has the form  $f_{l_s}(\xi_s)$ , where  $l_s$  is the quantum number, in the  $r$ th excited state it has the form  $f_{l'_s}(\xi_s) = f_{l_s} \sqrt{\omega_{sr}/\omega_s} \xi_{sr}$ , where  $\omega_s$  and  $\omega_{sr}$  are the vibrational frequencies in the ground and excited electronic states, while  $\xi_{sr}$  differs from  $\xi_s$  in the position of equilibrium. A multiphonon transition is made possible by the nonorthogonality of  $f_{l_s}(\xi_s)$  and  $f_{l'_s}(\xi_s)$  when  $l_s \neq l'_s$ . A significant step was taken in Ref. 2 in calculating the complex combinatorial sums that arise from the possible participation in the transition of different sets of lattice oscillators.<sup>31</sup>

The weak spot of Ref. 2 consisted in the assumption that the deformation arising in the crystal in the presence of an

<sup>31</sup>Such a summation has subsequently been carried out completely in another problem by Lamb.<sup>33</sup>

exciton is homogeneous. Although such a general expansion (or compression) of the crystal upon electronic excitation certainly must occur, it is not this change in the dimensions of the specimen that affects the quantum properties of the exciton, but the local (strongly inhomogeneous) deformation of the lattice arising near the exciton. This important situation was elucidated by Peierls<sup>8</sup> and was taken into account in the final variant<sup>4</sup> of Frenkel's theory. In it the electronic-vibrational wave function of the exciton is written in the form

$$\Psi_{\mathbf{k}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{m}} \Phi_{\mathbf{m}} \prod_s \tilde{f}_{l_s}(\xi_s^{(\mathbf{m})}) e^{i\mathbf{k}\cdot\mathbf{m}}, \quad (9)$$

Here the index  $\mathbf{m}$  in  $\xi_s^{(\mathbf{m})}$  indicates that the displacement of the equilibrium position of the oscillator corresponds to localization of the exciton at the node  $\mathbf{m}$ . Thus  $\Psi_{\mathbf{k}}$  corresponds to a concerted motion of the electronic-excitation wave and the lattice deformation. The accompanying lattice deformation, which “clothes” the exciton in phonons, can make the band considerably narrower, since in the dispersion law the matrix elements  $J_{\mathbf{m}-\mathbf{m}_1}$  (Eq. (3)) will be multiplied by the non-orthogonality integral of the oscillator functions centered at the nodes  $\mathbf{m}$  and  $\mathbf{m}_1$ . Therefore Frenkel' treated the excitons in (2) as free and those in (9) as “trapped”. In the current literature one most often uses the term *autolocalized* (in the foreign literature—*self-trapped*).

The problem of autolocalization is complicated. It includes the problems of the criteria for existence of free and autolocalized particles, of the possibility of their coexistence, and of the mechanism of transport of autolocalized particles. This problem exists not only for excitons, but also for charge carriers—electrons and holes. Therefore many problems for all these particles can be treated in parallel. We shall briefly summarize the current state of the problem.<sup>34</sup>

The theory contains three fundamental quantities with the dimensions of energy:  $\omega$ —the frequency of the photons,  $J$ —the half-width of the exciton band in a rigid lattice, and  $E_{FC}$ —the relaxation energy of the lattice around an autolocalized exciton, which is a measure of the exciton-phonon coupling; it is often called the Franck-Condon energy.

If  $J \ll \omega$ , then the “slow” particle is the exciton, while the phonons constitute the “fast” subsystem. Under these conditions only the excitons “clothed” by the deformation are real quasiparticles. The initial free states disappear in the spectrum of the interacting system, and hence are not manifested in any way experimentally.<sup>41</sup> An example is Frenkel' excitons in organic crystals of the type of benzene interacting with high-frequency phonons, which genetically arise from the intramolecular vibrations. The “clothing” shifts the band and diminishes its width by a factor  $\sim 2$ . Here the bands maintain a width  $\sim 100 \text{ cm}^{-1}$ . It is precisely these “renormalized” excitons, which maintain a high mobility, that are manifested in all optical experiments.

If  $J \gg \omega$ , the the slow subsystem is the phonons, and the pattern as a whole is considerably more complex. Autolocalization arises only if  $E_{FC} \gtrsim J$ . Actually these two inequal-

<sup>41</sup>The conversion of the initial state into the “clothed” state occurs in a time  $\sim \omega^{-1}$ . The barrier-free mechanism of autolocalization that Frenkel' postulated in Ref. 4 is possible only in this case.

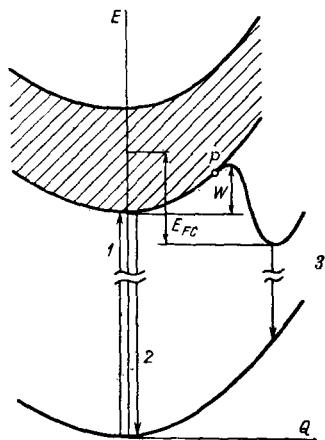


FIG. 3. Schematic dependence of the energy  $E$  of the system on the configurational coordinate  $Q$ . Below—energy of the unperturbed crystal; the cross-hatched region is the exciton band. The level of an autolocalized exciton splits off at point  $P$  from the bottom of the exciton band.  $W$ —height of the autolocalized barrier. 1—absorption with excitation of free excitons; 2, 3—luminescence of free and autolocalized excitons.

ities are the criteria for autolocalization according to Landau,<sup>35</sup> although they were not formulated<sup>35</sup> in this form. The existence of autolocalization does not rule out the preservation of the free-exciton states—both types of states coexist. This is possible because, when  $J \gg \omega$ , the properties of free and autolocalized states are controlled by the two dimensionless parameters:  $\lambda$  and  $\Lambda$  respectively. We have the parameter  $\Lambda \approx E_{FC}/J$ ; if we express all the quantities in terms of world constants, then we have  $\Lambda \sim 1$ . The parameter  $\lambda$ , which determines the scattering of free band excitons, is of the order of  $\lambda \sim \sqrt{m/M} \Lambda$ . That is, it is small with respect to the adiabatic parameter. The free and autolocalized states are separated by the autolocalization barrier. The bound exciton-phonon system must overcome it by tunneling or by activation. The energy diagram is presented schematically in Fig. 3.

The diagram of Fig. 3 gives a good description of excitons in crystals of the noble gases<sup>36</sup> and in alkali-halide crystals.<sup>37</sup> Both these classes of materials contain autolocalized states of an atomic scale and also free states that are manifested in the form of narrow-band absorption and luminescence spectra. In particular, polariton effects are observed in them (Sec. 4).

In connection with autolocalized states in these systems, in closing we turn again to the problem of dissipation of the absorbed light energy. In alkali-halide crystals, processes of radiative and radiationless decay of the autolocalized excitons compete. However, the effective radiationless channels usually correspond not to “trading” of the electronic energy for a large number of weakly anharmonic phonons, but to creation of lattice defects (e. g., Frenkel’ pairs), i.e., a strongly anharmonic process involving the displacement of ions by distances of one or several lattice constants.

In the solid noble gases the defect formation apparently occurs at the stage of autolocalization and is also an effective

mechanism of transfer of the electronic energy to the lattice. Defect formation is accompanied by formation of a cavity (bubble) in which the exciton is localized. These are the intrinsic mechanisms of dissipation of electronic energy that can impart to a crystal the properties of an absorber. At present they are especially topical in connection with the problem of radiation stability of materials. The mechanisms of dissipation at impurities lie outside the scope of this article.

There is also the problem of the transport of autolocalized excitons, which is associated with the migration of electronic energy. To the extent that the wave function of the autolocalized state can be described by the function (9), this problem is analogous to the transport of polarons of small radius.<sup>38</sup> At low enough temperatures in perfect specimens, a band of autolocalized excitons exists, and there the transport is of band type. However, with increasing temperature the transport becomes activation: it corresponds to successive diffusional hops between adjacent nodes.

One would hope that this note will help the readers to form a picture of how fruitful the hypothesis of the existence of excitons and the associated problems of strong coupling and radiationless transitions formulated by Yakov Il’ich Frenkel’ about 50 years ago have been for the subsequent development of solid-state physics.

<sup>1</sup>Ya. I. Frenkel’, *Sobranie izbrannykh trudov* (Collection of Selected Studies), Vol. 2, Izd-vo AN SSSR, M., L., 1958.

<sup>2</sup>J. Frenkel, *Phys. Rev.* **37**, 17 (1931) (Russ. Transl., Ref. 1, article 7).

<sup>3</sup>J. Frenkel, *ibid.*, p. 1276 (Russ. Transl., Ref. 1, article 8).

<sup>4</sup>Ya. I. Frenkel’, *Zh. Eksp. Teor. Fiz.* **6**, 647 (1936); also: *Phys. Z. Sowjetunion* **9**, 158 (1936) (see also Ref. 1, article 10).

<sup>5</sup>E. I. Rashba and M. D. Sturge, eds., *Excitons*, North-Holland, Amsterdam 1982; V. M. Agranovich and A. A. Maradudin, gen. eds., *Modern Problems in Condensed Matter Sciences*, Vol. 2.

<sup>6</sup>J. Becquerel, *Phys. Z.* **8**, 929 (1907).

<sup>7</sup>J. W. Obreimov and W. J. de Haas, *Proc. Amst. Acad.* **32**, 1324 (1929); *Comm. Leiden*, No. 191a (1928).

<sup>8</sup>R. Peierls, *Ann. Phys. (Leipzig)* **13**, 59 (1932).

<sup>9</sup>H. Casimir, in: *Theoretical Physics in the Twentieth Century*, eds. M. Fierz and V. F. Weisskopf, Cambridge, USA, 1960 (Russ. Transl., II, M., 1962).

<sup>10</sup>A. Sommerfeld and H. Bethe, *Elektronentheorie der Metalle: Handbuch der Physik*, 2nd edn., Vol. 24, Springer-Verlag, 1933 (Russ. Transl., ONTI, L., M., 1938).

<sup>11</sup>G. H. Wannier, *Phys. Rev.* **52**, 191 (1937).

<sup>12</sup>N. F. Mott, *Trans. Faraday Soc.* **34**, 500 (1938).

<sup>13</sup>J. Franck and E. Teller, *J. Chem. Phys.* **6**, 861 (1938).

<sup>14</sup>G. Scheibe, *Z. Elektrochem.* **47**, 73 (1941).

<sup>15</sup>A. S. Davydov, *Zh. Eksp. Teor. Fiz.* **18**, 210 (1948).

<sup>16</sup>A. F. Prikhotjko, *J. Phys. USSR* **8**, 257 (1944).

<sup>17</sup>V. L. Broude, V. S. Medvedev, and A. F. Prikhot’ko, *Zh. Eksp. Teor. Fiz.* **21**, 665 (1951).

<sup>18</sup>A. S. Davydov, *Teoriya molekulyarnykh éksitonov* Nauka, M., 1968 [Engl. Transl., (Theory of Molecular Excitons), Plenum Press, N.Y., 1971].

<sup>19</sup>V. M. Agranovich, *Teoriya éksitonov* (Theory of Excitons), Nauka, M., 1968.

<sup>20</sup>V. L. Broude, É. I. Rashba, and E. F. Sheka, *Spektroskopiya molekulyarnykh éksitonov* (Spectroscopy of Molecular Excitons), Énergoatomizdat, M., 1981.

<sup>21</sup>V. V. Eremenko, *Vvedenie v opticheskuyu spektroskopiyu magnetikov* (Introduction of the Optical Spectroscopy of Magnetic Materials), Naukova dumka, Kiev, 1975.

<sup>22</sup>R. M. Pearlstein, see Ref. 5, p. 735.

<sup>23</sup>M. Born, *Dynamik der kristallgitter*, Berlin, 1915; *Atomtheorie des festen Zustandes*, Berlin, 1923.

- <sup>24</sup>K. B. Tolpygo, Zh. Eksp. Teor. Fiz. **20**, 497 (1950).
- <sup>25</sup>M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Clarendon Press, Oxford, 1954 (Russ. Transl., IL, M., 1958).
- <sup>26</sup>S. I. Pekar, Zh. Eksp. Teor. Fiz. **33**, 1022 (1957) [Sov. Phys. JETP **6**, 785 (1958)].
- <sup>27</sup>J. J. Hopfield, Phys. Rev. **112**, 1555 (1958).
- <sup>28</sup>V. M. Agranovich, Zh. Eksp. Teor. Fiz. **37**, 430 (1959) [Sov. Phys. JETP **10**, 307 (1960)].
- <sup>29</sup>V. M. Agranovich and V. L. Ginzberg, Kristallooptika s uchetom prostanstvennoy dispersii i teoriya eksitonov (Crystal Optics with Account Taken of Spatial Dispersion and the Theory of Excitons), Nauka, M., 1979. [Engl. Transl. of 1965 edition: Spatial Dispersion in Crystal Optics and the Theory of Excitons, Wiley, N.Y. 1967].
- <sup>30</sup>S. I. Pekar, Kristallooptika i dobavochnye svetovye volny (Crystal Optics and Additional Light Waves), Naukova dumka, Kiev, 1982.
- <sup>31</sup>K. Huang and A. Rhys, Proc. R. Soc. London **204**, 406 (1950).
- <sup>32</sup>M. A. Krivoglaz, Zh. Eksp. Teor. Fiz. **25**, 191 (1953); R. Kubo and Y. Toyozawa, Prog. Theor. Phys. **13**, 160 (1955).
- <sup>33</sup>W. Lamb, Phys. Rev. **55**, 190 (1939).
- <sup>34</sup>L. D. Landau, Phys. Z. Sowjetunion **3**, 664 (1933).
- <sup>35</sup>E. I. Rashba, see Ref. 5, p. 543.
- <sup>36</sup>I. Ya. Fugol', Adv. Phys. **27**, 1 (1978).
- <sup>37</sup>Ch. B. Lushchik, see Ref. 5, p. 505.
- <sup>38</sup>T. Holstein, Ann. Phys. (N.Y.) **8**, 325, 343 (1959).

Translated by M. V. King