Excitons and instability of the dielectric state in quasi-one-dimensional and quasi-two-dimensional structures

A. M. Agranovich and B. P. Antonyuk

Institute of Spectroscopy, USSR Academy of Sciences
(Submitted July 18, 1974)
Zh. Eksp. Teor. Fiz. **67**, 2352–2356 (December 1974)

We consider quasi-one-dimensional structures with a strongly anisotropic dielectric constant ($\epsilon_\parallel/\epsilon_\perp \gg 1$). In such structures the interaction between electrons and holes located at different filaments gives rise to an abundant and unusual spectrum of large-radius excitons. The spectrum is shown to contain either one or two oscillatory series with frequencies of the order of tens of reciprocal centimeters. For the lowest exciton level the electron-hole binding energy turns out to be of the order of $\epsilon_\parallel^{-1/2}$. As a consequence, the forbidden band width Δ is sufficiently small, and the dielectric state with $\epsilon_\parallel \sim 1/\Delta$ is unstable against transitions to the excitonic insulator phase. We also discuss the stability conditions for the dielectric state that results from the Peierls rearrangement of the metallic state of filaments, as well as those for the dielectric state of quasi-two-dimensional structures.

The physical properties of systems which comprise weakly interacting (in a definite sense) filaments are being extensively studied at the present time (for a review of these properties see[1]). In the numerous theoretical works of this type the largest effort has been concentrated around the following questions: what is the structure of the metallic state of the filaments, and what causes the instability (the Peierls rearrangement, etc.). However, it is also of interest to further analyze the properties of the dielectric state. In this case, as is shown below, the interaction between electrons and holes located at different filaments gives rise to a spectrum of large-radius excitons which differs dramatically in structure from the corresponding spectrum in ordinary semiconductors. A distinctive feature of this spectrum, which is of particular importance regarding the stability conditions for the dielectric state of filaments with a narrow forbidden band, is that it depends on various components of the dielectric constant tensor of the medium.

The peculiarity of the situation in hand is associated with the quasi-one-dimensionality of the collectivized electron motion as well as with the sharp anisotropy of the dielectric tensor in the low-frequency region ($\epsilon_{xx} = \epsilon_\parallel \gg \epsilon_\perp \equiv \epsilon_{yy} = \epsilon_{zz}$; the filaments are assumed oriented along the x axis). In a uniaxial crystal of the type under consideration the interaction between an electron and a hole is of the following form[7];

$$V(x,y,z) = -\frac{e^2}{\varepsilon_\perp \sqrt{\varepsilon_\parallel}}\left(\frac{x^2}{\varepsilon_\parallel}+\frac{y^2+z^2}{\varepsilon_\perp}\right)^{-1/2}. \tag{1}$$

If both the electron and the hole are located on the same filament (i.e., $y = z = 0$), then the electron-hole interaction does not continue $\epsilon_\parallel$, in other words $V(x) = -e^2/\epsilon_\perp x$. Inasmuch as $\epsilon_\perp \approx 3$–5 for the media involved, we cannot use (1) to calculate the total spectrum of the excitons localized on the same filament, since this expression is not suitable for small-radius excitons.

On the other hand, if the electron and the hole are localized on different filaments, then

$$V(x) = -\frac{e^2}{\varepsilon_\perp \sqrt{\varepsilon_\parallel}}\left(\frac{d^2}{\varepsilon_\perp}+\frac{x^2}{\varepsilon_\parallel}\right)^{-1/2},$$

where d is the distance between filaments, $x = x_e - x_h$, and e is the electron charge. Consequently, the Hamiltonian for the system electron + hole, describing a state with a large (along the x axis) "radius," can be represented in the form

$$\hat{H} = -\frac{\hbar^2}{2M}\frac{d^2}{dX^2} - \frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + V(x),$$

where X denotes the x-coordinate of the center of mass, $M = m_e + m_h$ is the translational mass of the electron, and μ is its reduced mass. For states with the "radius"

$$x_0 \ll d(\varepsilon_\parallel/\varepsilon_\perp)^{1/2} \tag{2}$$

the function V(x) can be represented in the form of a power series

$$V(x) = -V_0 + \frac{\mu\omega_0^2 x^2}{2}, \quad V_0 = \frac{e^2}{d(\varepsilon_\perp\varepsilon_\parallel)^{1/2}}, \quad \omega_0^2 = \frac{e^2\varepsilon_\perp^{1/2}}{\mu d^3 \varepsilon_\parallel^{3/2}},$$

so that the Schrödinger equation reduces to that for a harmonic oscillator with the frequency ω_0. In this approximation the exciton energy E_n is given by

$$E_n = \Delta - V_0 + \hbar\omega_0(n+1/2) + P^2/2M, \tag{3}$$

where Δ is the dielectric gap, n is the oscillator quantum number ($n = 0, 1, \ldots$), and P is the momentum of the exciton.

At $n = 0$, the wave function of the exciton relative motion along the x axis extends over the distance $x_0 \approx (\hbar/\mu\omega_0)^{1/2}$. Hence, the condition (2) is satisfied for these states if

$$\hbar^2/\mu d e^2 \ll (\varepsilon_\parallel/\varepsilon_\perp^3)^{1/2}.$$

For d = 10 Å and for μ of the order of the electron mass in vacuum m_0, the left-hand side of the inequality is $\approx 1/20$. The right-hand side for substances of the type under consideration is greater than or of the order of unity (see[1]; $\epsilon_\parallel \approx 10^2$–$10^3$, $\epsilon_\perp \approx 5$). This means that the above expansion of V(x) can be used to find several states with $n > 0$ as well. Regardless of whether the expansion of V(x) in powers of x^2 is justified, the use of the initial phenomenological expression for V(x) requires that the inequality $x_0 \gg d_0$ (i.e., $\hbar^2\epsilon_\parallel^{3/2}/\mu e^2\sqrt{\epsilon_\perp} \gg d_0$; see above) also be satisfied, where d_0 is the distance between neighboring filaments. Clearly, at sufficiently large $\epsilon_\parallel$ and $\epsilon_\parallel/\epsilon_\perp$, this inequality is satisfied as well.

Since $\omega_0 \sim \epsilon_\parallel^{-3/4}$, we have $\Delta \gg \hbar\omega_0$ for large $\epsilon_\parallel$. Therefore, in the expression (1) for the interaction we must use for the dielectric constants static values, which are precisely those that have large anisotropy.

Due to its quasi-one-dimensionality, the system under consideration may also contain more complex collective excitated states (biexcitons, polyexcitons, electron + exciton, etc.). Moreover, because of the large "radius" of the excitons, many other effects of the exciton-exciton interaction can, in principle, become significant even at comparatively low exciton concentrations. Without discussing the very interesting questions that arise here, we consider the spectrum of a single exciton.

In the case when $V_0 < \Delta$ even for the nearest filaments, the entire spectral picture can be regarded as a superposition of shifted oscillatory series due to electron and hole formation on more and more distant filaments. The number of levels of a series that fall into the forbidden band equals $V_0/\hbar\omega_0$ and is by no means small. For the nearest filaments with, say, $d_0 = 10^{-7}$ cm, $\epsilon_\parallel = 100$, and $\epsilon_\perp = 4$ this number is equal to five. It should be borne in mind, however, that the oscillatory series can only exist if the exciton line widths are small compared to the exciton vibrational quanta $\hbar\omega_0$. For example, if the exciton is formed between filaments which are nearest neighbors with $d_0 = 10$ Å, $\epsilon_\parallel = 100$ and $\epsilon_\perp = 5$, then $\hbar\omega_0 \approx 30$—50 cm^{-1}. For $d = 20$ Å (next series), $\hbar\omega_0 \approx 10$—15 cm^{-1} and so forth. Since at low temperatures the exciton line widths can be as large as 5—10 cm^{-1}, these estimates suggest that only one or, at most, two exciton series remain stable against scattering of electrons and holes by phonons and lattice defects. It is clear, however, that a spectroscopic observation of these series would furnish a new means for studying the properties of the systems involved.

According to (3), the excitation energy of the lowest large-radius exciton state (exciton on neighboring filaments) is given by

$$E_0(\Delta) = \Delta - V_0 + \frac{\hbar\omega_0}{2} = \Delta - \frac{e^2}{d_0(\varepsilon_\parallel\varepsilon_\perp)^{1/2}} + \frac{\hbar e\varepsilon_\perp^{1/4}}{2d_0^{3/2}\mu^{1/2}\varepsilon_\parallel^{1/4}}. \quad (4)$$

For sufficiently small Δ, the value of V_0 can exceed Δ, and the energy E_0 may become negative. In this case, at low temperatures, the dielectric state becomes unstable against the formation of bound electron-hole pairs. It is precisely this type of instability that has been discussed by Knox[8] (see also[9,10]). An investigation of this instability may prove useful specifically in connection with a number of experimental data (see, e.g.,[11]), which are usually interpreted on the basis of the assumption that the dielectric gap is small.

The difference between the situation at hand and the case of an isotropic semiconductor lies in the peculiar dependence of the lowest exciton energy on the dielectric constant, which, at small Δ, favors the onset of instability. Indeed, for an isotropic semiconductor the electron-hole binding energy in the lowest exciton energy state is proportional to ϵ^{-2}, where ϵ is the dielectric constant. Inasmuch as $\epsilon \sim 1/\Delta$ for small Δ, the lowest exciton energy is equal to $\Delta - \alpha\Delta^2$, where $\alpha > 0$, and therefore, for sufficiently small Δ, it is always positive. In our situation, only $\epsilon_\parallel$ depends on the gap width Δ at small Δ, and one has to know this dependence in order to find the critical gap width Δ_0 at which the dielectric state becomes unstable ($E_0(\Delta_0) = 0$).

If we assume that $\epsilon_\parallel = \hbar\omega_p/\Delta$, where ω_p is some frequency of the order of the plasma frequency (see also[11]), then $V_0 \sim \sqrt{\Delta}$ and the instability always arises if $\Delta < \Delta_0$, where $\Delta_0 \approx 10^{-2}$ eV. If, however, the dielectric state itself results from the Peierls instability of quasi-one-dimensional metallic filaments, then, as was shown by Rice and Strässler[6], the dependence of $\epsilon_\parallel$ on Δ is essentially different in various temperature regions ($\epsilon_\parallel \sim 1/\Delta$ for $\Delta < T$, and $\epsilon_\parallel = \hbar^2\omega_p^2/\Delta^2$ for $\Delta \gg T$)[1)]. Therefore, as can be seen from (4), in the limit of low temperatures and small Δ, the instability can arise only if the condition $e^2/d_0\sqrt{\epsilon_\perp} > \hbar\omega_p$ is satisfied.

For ordinary three-dimensional superconductors, the instability of the dielectric state against formation of bound electron-hole pairs has been analyzed in[9,10]. It has been shown there that the proper allowance for the electron-hole interaction leads to a renormalization of the ground state, which leads in turn to formation of a dielectric state with a wider forbidden band. These results are rather general and remain valid in our case of quasi-one-dimensional structures as well. For structures of this type, the elementary excitation energies after rearrangement can be again assumed to depend only upon the longitudinal component of the wave vector P_x, and, therefore, the equation derived in[9,10], which determines the new value of the gap width, becomes one-dimensional. On transforming to the coordinate representation, we can subject this equation to an analysis similar to that given by Kozlov and Maksimov[9] for ordinary semiconductors. From this analysis it is inferred that the electron-hole interaction changes (enlarges) the gap width at for parameters values for which the initial excitation energy of a lowest-energy exciton is nonpositive.

In conclusion, we note that similar excitons and instabilities can occur in quasi-two-dimensional systems as well. In this case again a macroscopic description of the electron-hole interaction in the spirit of (1) proves possible only if the dielectric constant in the direction along the flat layers greatly exceeds the transverse dielectric constant. If the z axis is perpendicular to the layers and $\epsilon_{xx} = \epsilon_{yy} \equiv \epsilon_\parallel \gg \epsilon_\perp \equiv \epsilon_{zz}$, then, for an electron and a hole localized on the same layer[7] we have $V(\rho) = -e^2/\epsilon_\perp\epsilon_\parallel\rho$.

Two-dimensional excitons with this type of interaction have often been considered in literature. It has been shown (cf., e.g.,[12]) that they correspond to a spectrum of the form

$$E_n = \Delta - \frac{R\mu}{\varepsilon_\parallel\varepsilon_\perp m_0}\left(n + \frac{1}{2}\right)^{-2},$$

where R is the Rydberg constant for hydrogen, μ is the effective mass, and n = 0, 1, ... It is essential that in the presence of a small (straight) gap, when $\epsilon_\parallel = \hbar\omega_p/\Delta \gg 1$, the energy E_0 can become negative only if $\gamma = 4R\mu/m_0\epsilon_\perp\hbar\omega_p > 1$. This suggests that, in contrast to the case of ordinary semiconductors, for quasi-two-dimensional structures with small values of the dielectric gap and $\gamma > 1$, there must again exist a limiting value of the gap Δ_0 below which the dielectric state is impossible.

The above considerations may prove useful in a discussion of the ever increasing number of works on the properties of quasi-one-dimensional and quasi-two-dimensional structures.

The authors are grateful to V. L. Ginzburg and the members of his seminar for discussions.

[1)]The fact that the contribution of the above-considered excitons was ignored in [6] in the evaluation of $\epsilon_{\parallel}$, can hardly be significant, since these states correspond to relatively small oscillator strengths (because of the small overlap of the wave functions of electrons at different filaments).

[1] I. F. Shchegolev, Phys. Status Solidi A12, 9 (1972).
[2] A. A. Ovchinnikov, N. N. Ukrainskiĭ, and G. F. Kventsel', Usp. Fiz. Nauk 108, 81 (1972) [Sov. Phys.-Usp. 15, 575 (1973)].
[3] L. P. Gor'kov and I. E. Dzyaloshinskiĭ, Zh. Eksp. Teor. Fiz. 67, 397 (1974) [Sov. Phys.-JETP 40, 198 (1975)]; ZhETF Pis. Red. 20, 37 (1974) [JETP Lett. 20, 16 (1964)].
[4] L. B. Coleman, M. J. Cohen, D. J. Sendom, F. G. Yamagashi, A. F. Garito, and A. J. Heeger, Solid State Commun. 12, 1125 (1973).
[5] M. J. Rice and S. Strässler, Solid State Commun. 13, 125 (1973).
[6] M. J. Rice and S. Strässler, Solid State Commun. 13, 1931 (1973).
[7] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), GITTL, M. 1957 [Pergamon, 1959].
[8] R. S. Knox, Theory of Excitons, Acad. Press, N. Y.-London, 1963.
[9] A. N. Kozlov and L. A. Maksimov, Zh. Eksp. Teor. Fiz. 48, 1184 (1965) [Sov. Phys.-JETP 21, 790 (1965)].
[10] J. Zittartz, Phys. Rev. 162, 752 (1967).
[11] F. F. Igoshin, O. N. Eremenko, A. P. Kir'yanov, and I. F. Shchegolev, ZhETF Pis. Red. 19, 644 (1974). [JETP Lett. 19, 333 (1974)].
[12] H. J. Ralph, Solid State Commun. 3, 303 (1965).

Translated by S. Luryi
249