SECOND-ORDER PHASE TRANSITION ASSOCIATED WITH BOSE-EINSTEIN CONDENSATION OF EXCITONS IN A DEFORMED LATTICE

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The jump in specific heat associated with a second-order phase transition due to Bose-Einstein condensation of dipole-inactive excitons in a deformed crystal is calculated. Depending on the parameters of the exciton-phonon system, this jump may be positive or negative. Other phenomena related to exciton degeneracy are also discussed.

1. The possibility of the realization of new semiconductor properties, in connection with the accumulation of large concentrations of metastable excitons forming a nonideal Bose gas inside the crystal, was expressed and discussed earlier.[1,2]

The collective properties of excitons, connected with their Bose-Einstein condensation, are of particular interest. The latter may occur at temperatures $\sim 1°K$ for exciton concentrations from $\sim 10^{16}$ to 10^{17} cm^{-3}, owing to the small translational mass of the exciton which, in a number of semiconductors, does not exceed the mass of a free electron. Excitons are created by the absorption of light in the crystal.

The behavior of excitons depends on their interaction among themselves and with phonons and electron-hole pairs; for dipole-active states, account of retardation and of the long-range Coulomb interaction is important. The finite lifetime and the various dispersion laws of excitons, determined by symmetry properties, also introduce their own specific characteristics. Therefore, one might expect in a medium consisting of excitons the properties discovered in the study of liquid helium, such as superfluidity, thermal superconductivity, first and second sound, the scattering of light by density fluctuations, quantized vortices, phase transition of the second kind, and so on. In addition to the analogous optical-hydrodynamical phenomena in crystals, one can expect changes in the absorption bands and in the crystal optics,[1] and in the case of two intersecting exciton currents one can expect nonlinear optical effects of the polarization type and splitting of the corresponding absorption bands. Exciton degeneracy may be a new method for the storage, transport, and induced radiation of energy in crystals.[3] The possibilities of excitons in this respect were already studied in the article by Basov, Krokhin, and Popov,[4] but without account of Bose-Einstein condensation.

Recently Blatt, Böer, and Brandt[5] and Casella[6] also reached a conclusion about the possibility of observing a number of effects related to the degeneracy of excitons, and they stressed the necessity of studying the establishment of thermodynamic quasi-equilibrium and the accumulation of large concentrations of excitons.

2. Apparently the collective properties of excitons will be different, depending on whether we have to deal with dipole-inactive, metastable exciton states with nondegenerate bands or with dipole-active light-exciton states. In [2] we considered the Hamiltonian for excitons of the first type, interacting with phonons under different dispersion laws for the individual exciton. In this connection, we confined our attention to the case when the frequency of collisions between excitons is considerably greater than the frequency of exciton collisions with phonons. According to [2], this occurs at sufficiently low temperatures, less than T_0. One can estimate T_0 for a quadratic dispersion law from the formula

$$T_0 = 4\sqrt{2}\,\pi^2 r_{ex}^2 \mu^2 D\hbar^4 n/m^2 k\,(C_e - C_h)^2, \qquad (1)$$

where r_{ex} is the exciton radius, u is the velocity of sound in the crystal, D is its density, n is the concentration of excitons, m is the translational mass of the exciton, and C_e and C_h are the coupling constants for the interaction of electron and hole, respectively, with acoustic lattice vibrations.

In this case, quasi-equilibrium is established in the exciton medium before the exciton is scattered by a phonon.

At temperatures below critical, the condensate of excitons, whose effect on the lattice vibrations is similar to that of an external field, alters the

phonon spectrum of the lattice and leads to a "phonon-hydron" spectrum of elementary excitations.[2] Since the exciton collisions are very frequent, the question of the formation of bi-excitons arises. This does not occur if repulsion between excitons is dominant.[2] In the opposite case, following[1], it is necessary to consider a gas of bi-excitons. For larger concentrations of excitons, it is also necessary to take electron-hole pairs, formed during collisions, into account.

3. The dependence of the translational energy of the exciton on its wave vector, in the simplest case of nondegenerate quadratic electron and hole bands with extrema at the point $\mathbf{k} = 0$ and nondegenerate relative motion of the electron-hole, has a quadratic dispersion law with an extremum at the point $\mathbf{k} = 0$. According to Rashba and Sheka,[7] in crystals of the CdS type the bands of type Γ_7 and Γ_8 with account of the spin-orbit interaction have a dispersion law of the form $ak_{\parallel}^2 + bk_{\perp}^2 \pm \alpha k_{\perp}$ in the neighborhood of the point $\mathbf{k} = 0$, where $k_{\perp} = \sqrt{k_x^2 + k_y^2}$. The Schrödinger matrix equation, determining the energy spectrum and dispersion law of the exciton, depends, according to [1], on the matrices defining the structure of the electron and hole bands. Therefore, in the dispersion law for one of the exciton states, one should also expect terms of the form

$$\hbar^2 k_{\parallel}^2/2m_{\parallel} + \hbar^2 k_{\perp}^2/2m_{\perp} + m_{i\perp}|\alpha|k_{\perp}/m_{\perp},$$

where $m_{i\perp}$ and $m_{\perp}$ are the transverse masses of one of the current carriers, for which a loop of extrema and an exciton is possible. For the other excitons, the linear term can be present with a minus sign. The range of values of $k_{\perp}$ in which the linear term dominates over the quadratic is determined by the condition

$$k_{\perp} < k_{\perp 0} = 2m_{i\perp}|\alpha|\hbar^{-2}.$$

The range of actual values of $k_{\perp}$ depends on the temperature. For $m_{i\perp}|\alpha|k_{\perp 0}/m_{\perp} > kT$, the exciton thermodynamics will essentially depend on the linear term. The condition, when for simplicity one can keep only the linear term in the dispersion law, is

$$T < T_1 = 2m_{i\perp}^2\alpha^2/m_{\perp}\hbar^2 k. \qquad (2)$$

According to the data given by Hopfield,[8] in a CdSe crystal $\alpha = 9 \times 10^{-10}$ eV-cm, $m_{h\perp} = 0.5\,m_0$, $m_{\perp} = 0.63\,m_0$; in a crystal of CdS $\alpha = 6 \times 10^{-10}$ eV-cm, $m_{h\perp} = 0.7\,m_0$, $m_{\perp} = 0.9\,m_0$. In this connection, $T_1 \cong 10°K$ for CdSe and $T_1 \cong 7°K$ for CdS.

A detailed calculation of this case leads to more definite criteria about its existence. However the estimates made forced us to examine the thermohydrodynamics of excitons possessing a sufficiently general dispersion law

$$T_{\mathbf{p}} = p_{\parallel}^2/2m_{\parallel} + Cp_{\perp}^s, \qquad (3)$$

where $p_{\perp} = \sqrt{p_x^2 + p_y^2}$; $C > 0$; $s = 1, 2, 3$.

The critical temperature for an ideal Bose gas is here equal to (see [2])

$$kT_{cr} = \left[\frac{2^{5/2}\pi^{3/2}\hbar^3 C^{2/s}}{\zeta_{(s+4)/2s}(1)\,\Gamma(1+2/s)\,m_{\parallel}^{1/2}}\right]^{2s/(s+4)}, \qquad (4)$$

where $\zeta_{\nu}(1)$ is the Riemann zeta function. For $s = 2$ and $C = (2m_{\perp})^{-1}$ we have $T_{cr} \sim (m_{\parallel}m_{\perp}^2)^{-1/3} \times n^{2/3}$. $s = 1$ and $C = |\alpha|m_{i\perp}/m_{\perp}\hbar$ will give $T_{cr} \sim m_{\parallel}^{-1/5} C^{4/5} n^{2/5}$.

In the quadratic isotropic case with $m = m_0$, $r_{ex} = 20$ Å,

$$u = 5 \cdot 10^5\,\text{cm/sec}^{-1}, D = 5\,\text{g/cm}^3,$$

$$n = 10^{16}\,\text{cm}^{-3}, |C_e - C_h| = 3\,\text{eV},$$

using formulas (1) and (4) we find that $T_0 = 8°K$ and $T_{cr} \cong 1.1°K$. $s = 1$, $C = 4 \times 10^5$ cm/sec, $m_{\parallel} = m_0$, $n = 10^{16}$ cm^{-3} will give $T_{cr} \cong 1.2°K$.

Below we confine our attention to temperatures $\sim 1°K$, where our assumptions $T \sim T_{cr} < T_0$ are fulfilled, and we consider the phase transition at the point of Bose-Einstein condensation of excitons which are interacting with phonons.

4. The elementary excitations of the exciton-phonon system in the presence of the consensate of excitons are called "phonon-hydrons" and have an energy

$$E_{1,2}(\mathbf{p}, x) = \left[\frac{T_{\mathbf{p}}^2 + 2T_{\mathbf{p}}L_{\mathbf{p}} + B_{\mathbf{p}}^2}{2}\right.$$
$$\left. \pm \frac{1}{2}\sqrt{(T_{\mathbf{p}}^2 + 2T_{\mathbf{p}}L_{\mathbf{p}} - B_{\mathbf{p}}^2)^2 + \frac{16Nx}{N_a}B_{\mathbf{p}}T_{\mathbf{p}}\theta_{\mathbf{p}}^2}\right]^{1/2}, \qquad (5)$$

where x denotes the fraction of excitons in the condensate, $B_{\mathbf{p}}$ gives the dispersion law for the phonons, $\theta_{\mathbf{p}}$ is the Fourier transform of the exciton-phonon interaction energy, $\nu(\mathbf{p})$ is the analogous quantity for the interaction of excitons with one another, $L_{\mathbf{p}} = V^{-1}N \times \nu(\mathbf{p})$, N is the total number of excitons, N_a is the number of atoms in the lattice. For a quadratic dispersion law, the solution of (5) is stable, if (see [2])

$$\nu(0) \geqslant {}^4/_9|C_e - C_h|^2/Du^2. \qquad (6)$$

In order to check this condition, a calculation of the interaction energy of two excitons of large radius is presently being carried out. The average energy of the assembly of excitons and lattice vibrations is equal to

$$E = E_0 + \sum_{\mathbf{p}\neq 0} E_1(\mathbf{p})\bar{n}_p + \sum_{\mathbf{p}} E_2(\mathbf{p})\bar{\nu}_{\mathbf{p}}, \quad (7)$$

where

$$\bar{n}_{\mathbf{p}} = \left[\frac{1}{z}e^{\beta E_1(\mathbf{p},x)} - 1\right]^{-1}; \quad \bar{\nu}_{\mathbf{p}} = [e^{\beta E_2(\mathbf{p},x)} - 1]^{-1}. \quad (8)$$

We shall take the parameters x and z to be approximately the same as for ideal gases of excitons (the number of excitons being determined by experimental conditions) and phonons (the number of phonons vanishes as the temperature decreases). Thus for $T < T_{cr}$, $z = 1$ and $x = 1 - (T/T_{cr})^{(S+4)/2S}$; for $T > T_{cr}$, the quantity $x = 0$, and z is determined from the equation

$$n = \frac{\Gamma(1+2/s)(kT)^{(s+4)/2s}(\pi m_{\parallel}/2)^{1/2}}{4\pi^2\hbar^3 C^{2/s}}\zeta_{(s+4)/2s}(z). \quad (9)$$

It is easy to see that the average energy of the system (7), and also the thermodynamic potential and the entropy remain continuous at the phase transition point. In order to calculate the specific heat, first we find the derivative with respect to temperature of expression (7) for both $T > T_{cr}$ as well as for $T < T_{cr}$, taking the dependence of the parameters x and z on temperature into account, and we take the limits $x \to 0$; $z \to 1$, i.e., $T \to T_{cr}$. After this, it is possible to carry out the summation over momentum appearing in (7).

As the result, we find that the jump in the specific heat of the crystal is

$$\frac{\Delta C_V}{V} = \nu(0)n^2\left(\frac{s+4}{2s}\right)^2\frac{1}{T_{cr}} + \left(\frac{s+4}{2s}\right)^2 kn\frac{\zeta_{(s+4)/2s}(1)}{\zeta_{(4-s)/2s}(1)}$$
$$+ \left(\frac{s+4}{s}\right)\frac{n}{kT_{cr}^2}\frac{v_0}{(2\pi\hbar)^3}\int d\mathbf{p}\,\frac{B_{\mathbf{p}}T_{\mathbf{p}}\theta_{\mathbf{p}}^2}{T_{\mathbf{p}}^2 - B_{\mathbf{p}}^2}[\bar{n}_{\mathbf{p}}^2 e^{\beta T_{\mathbf{p}}} - \bar{\nu}_{\mathbf{p}}^2 e^{\beta B_{\mathbf{p}}}]. \quad (10)$$

Here the quantities $\bar{n}_{\mathbf{p}}$, $\bar{\nu}_{\mathbf{p}}$ are the limiting values of expressions (8), corresponding to $z = 1$, $E_1 = T_{\mathbf{p}}$, $E_2 = B_{\mathbf{p}}$, $\beta = (kT_{cr})^{-1}$; v_0 is the volume of the elementary cell. The first two terms in (10) were already discussed earlier.[2]

The last term in (10) determines the jump in the specific heat due to participation of the lattice in the phase transition, owing to the intermixing of the spectrum of lattice vibrations (phonons) with the collective exciton spectrum (with "hydrons"). It is easy to see that this term is negative. For parameters $T_{cr} \cong 1.1°K$, $u = 5 \times 10^5$ cm/sec, $n = 10^{16}$ cm^{-3}, $r_{ex} = 20$ Å, for a quadratic isotropic dispersion law, when $s = 2$, with $m = m_0$ and $B_{\mathbf{p}} = pu$, which corresponds to acoustic lattice vibrations, the last term is equal to -3.8×10^{-3} erg/cm^3 deg. The second term vanishes for $s = 2$, and the first term with condition (6) $\nu(0) \geq 0.8 \times 10^{-35}$ erg cm^3 exceeds the value 1.6×10^{-3} erg/cm^3 deg.

Thus, in an exciton-phonon system, the jump in the specific heat associated with a second-order phase transition connected with Bose-Einstein condensation of excitons, may be positive or negative. For the minimum value of $\nu(0)$ compatible with the condition of stability with respect to the formation of bi-excitons, the jump in the heat capacity of the entire crystal as a whole, with account of acoustic phonons only, equals -2.2×10^{-3} erg/cm^3 deg. Bose-Einstein condensation of excitons leads to a change in the mechanical properties of the crystal, for example, it leads to a change in the velocity of sound.[2] It is to be hoped that the application of new light sources and refinements of experimental techniques will permit the observation of the predicted phenomena.

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