Exciton and Plasma Phase Transitions in Semiconductors of the Ge Type

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We analyze the experimental data for the densities of exciton vapor and liquid in Ge and Si. Attention is called to the degeneracy and appreciable dissociation of the excitons in the gas phase. It is suggested that the phase transition in Ge and Si has a plasma behavior, i.e., it is due to the interaction between free charged particles (electrons and holes).

At low temperatures (~10°K) one observes in a system of nonequilibrium carriers (electrons and holes) in a semiconductor phenomena that can be interpreted as first-order phase transitions of the vapor-liquid type. This phase transition was investigated both theoretically[1] and experimentally for Ge by a number of workers[2-4] (and also by Glicksman and Gurney, who reported their results in a discussion on the conference on plasma theory in Kiev in 1971) and for Si[5,6]. It was assumed that at such temperatures the electrons and the holes practically do not exist in the free state, but are bound into neutral particles (excitons), so that the phase transition proceeds in the exciton system in the same way as vapor condenses into liquid in a system of atoms or molecules[1].

In the present study, we have plotted coexistence curves for the exciton vapor and liquid densities in Ge and Si, using the experimental data obtained by various workers. An analysis of these curves and estimates of the characteristic parameters for the gas phase show that the mechanism of ordinary condensation is not always suitable for the description of a phase transition in a system of excitons. Attention is called to (a) the probable overlap of ordinary condensation and Bose condensation of excitons and (b) the noticeable dissociation of the excitons in the critical region and the ensuring possibility that the discussed phase transition has a plasma behavior[7]. We confine ourselves to an examination of the nature of the condensation; possible phase transitions in the condensed state have been investigated in[1,8].

TEMPERATURE-DENSITY DIAGRAMS FOR Ge AND Si

Figure 1 shows the results of the measurements of the coexistence curve of the exciton phases in germanium. Vavilov, Zayats, and Murzin[3] give one value each for the liquid and vapor density. Glicksman and Gurney measured the densities of the liquid and the vapor, and also the parameters of the critical point. Asnin, Rogachev, and Sablina[2] believe that they measured the vapor density and liquid density, but their data for the liquid contradict the results of[3], and also the results of Glicksman and Gurney. Glicksman assumes that both points obtained in[2] should be assigned to the gas branch of the coexistence curve. When this circumstance is taken into account, the results of[2-4], as well as those of Glicksman and Gurney, are in good agreement with each other and make it possible to draw a smooth curve describing the parameters of the two phases in Ge. The estimated value ~6°K for the critical temperature[2,4] also agrees with curve 4.

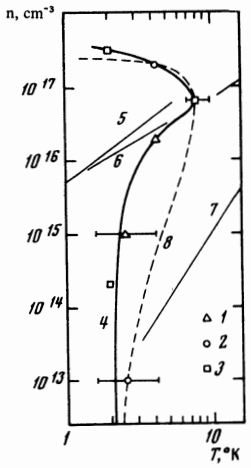

FIG. 1. Density-temperature diagram for Ge. Results of measurements of the coexistence curve: 1–[2], 2–[3], 3–Glicksman and Gurney, 4–smooth curve joining the experimental points. Lines of equal values of the characteristic parameters: 5–$\lambda_{ex}^3 n = 2.6$, 6–an/kT = 1, 7–$\gamma = 1$. 8–liquid-vapor coexistence curve in alkali metals, expressed in terms of the parameters of the critical point for excitons.

The authors of[2-4], and also Glicksman and Gurney, determined the exciton density n_{ex} at which drop formation sets in. These points were used indeed to plot the gas branch of curve 4. In principle, these values of the density exceed somewhat the saturated vapor density n_T of the excitons. The difference can be estimated from the formula[1]

$$n_{ex} - n_T = n_0 R / 3 v_T \tau_0, \qquad (1)$$

where n_0 is the density of the liquid phase in the drop, R is the average stationary radius of the drop, v_T of the thermal velocity of the excitons, and τ_0 is the lifetime of the excitons in the drop. Substituting in (1), in accordance with[3], $n_0 = 2 \times 10^{17}$ cm^{-3}, $R = 10^{-4}$ cm, $\tau_0 = 10^{-5}$ sec, and $v_T = 10^6$ cm/sec, we obtain $n_{ex} - n_T \sim 10^{12}$ cm^{-3}.

Thus, for temperatures at which $n_T \gg 10^{12}$ cm^{-3}, the densities n_{ex} and n_T practically coincide; these are precisely the conditions corresponding to the data of Fig. 1. For lower temperatures, when $n_T < 10^{12}$ cm^{-3}, the experiment would have yielded the temperature-independent value $n_{ex} \sim 10^{12}$ cm^{-3}.

Let us compare the vapor-liquid coexistence curve obtained for the excitons with the curves known for He^3[9], He^4[9,10], H_2[9], Ar[9] and alkali metals[11]. In Fig. 2, all these curves have been recalculated in such a way that the parameters of the critical points are equal to the parameters of the critical point of He^4. We see that in the region of the liquid phase the curve for the excitons is in fair agreement with the curve for

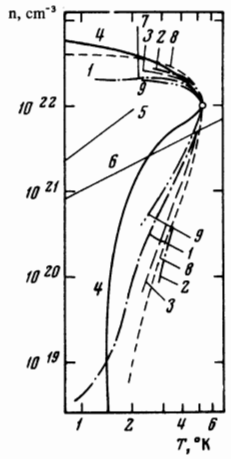

FIG. 2

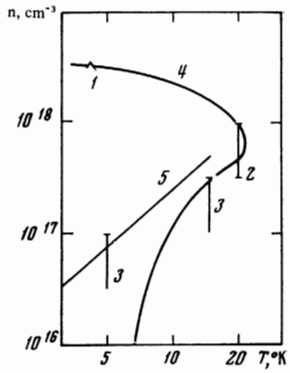

FIG. 3

FIG. 2. Density-temperature diagram for He^4. 1—coexistence curve for He^4. Coexistence curves of different substances, refer red to the values of the critical point of He^4: 2—Ar, 3—H_2, 4—excitons (curve 4 of Fig. 1), 8—alkali metals, 9—He^3. 5—line of equal values $\lambda_{He^3} n = 2.6$; 6—an/kT = 1, 7—λ-transition point.

FIG. 3. Density-temperature diagram for Si. Results of measurements of the coexistence curve: 1—[6], 2—[5], 3—[5] (only the upper density limit was measured for points 3); 4—coexistence curve for Ge (curve 4 of Fig. 1), recalculated for Si; 5—line of equal values $\lambda_{ex^3} n = 2.6$.

alkali metals and differs greatly from all the other curves. This apparently indicates that the liquid phase of the excitons, as predicted in[1], is reminescent of a liquid crystal. The curve for the excitons on Fig. 2 differs appreciably from all the curves in the gas phase. The greatest density near the critical point is possessed by exciton vapor. To explain the specific features of the curve obtained for Ge, we discuss below the role of Bose condensation and dissociation of the excitons.

We first discuss briefly the experimental results for Si (Fig. 3). These results are more limited than those for Ge, and cannot be used to draw a coexistence curve in a wide interval of n. The available data do not allow us to state that the phase transitions of the excitons in Ge and Si obey the law of corresponding states. Curve 4 on Fig. 3 was drawn to pass through the points obtained in[6] for the liquid phase, and had a critical temperature 22°K (this value was measured for the excitons in Si[5]).

EXCITON PHASE TRANSITION

Assuming that the gas phase consists of excitons, let us estimate the values of the characteristic parameters in this region. Line 6 on Fig. 1 separates the regions where the interaction between excitons is larger and smaller than the energy of their thermal motion. The exciton interaction energy U was calculated from the formula U = na, corresponding to Van der Waals equation[12]; the value of the constant a was obtained from the expression

$$a = (16\pi/9)\varepsilon\sigma^3,$$

where ϵ is the depth of the potential well, for the interaction of two particles, and σ is the effective diameter. In the estimates we assumed $\epsilon \sim 0.1I$[1] and $\sigma^3 \sim n_0^{-1}$, where I is the binding energy of the exciton. The analogous line 6 on Fig. 2 characterizes the interaction of the helium atoms. It is seen that lines 6 in Figs. 1 and 2 are approximately similarly located relative to the critical points (but still somewhat higher in Fig. 1 than in Fig. 2).

The role of the quantum corrections to the classical thermodynamic quantities is estimated with the aid of expansions in powers of $\hbar$[12]. For systems of the inert-gas type, the expansion in powers of h reduces to expansion in the de Boer parameter[13]

$$\Lambda = \hbar/\sigma(M\varepsilon)^{1/2}.$$

For the excitons in Ge and Si we have $\Lambda \cong 1$. This indicates that the quantum effects play an important role and that it is impossible to use an expansion in powers of Λ. We note that Λ = 0.49 for He^3, 0.42 for He^4, 0.28 for H_2, 0.03 for Ar, and 10^{-2}--10^{-3} for alkali-metal vapors (the parameter Λ becomes meaningless for liquid metals). The relative locations of the curves for Ar, H_2, He^4, and He^3 on Fig. 2, both in the gas and in the liquid phase, correspond to the variation in the value of Λ: the density of the gas phase increases and that of the liquid phase decreases with increasing Λ. Curve 4 for the excitons agrees with this behavior only in the gas phase. The disparity between the position of the liquid branch of curve 4 and the value of Λ, and its agreement with curve 8, confirm the assumption[1] that the excitons break up upon condensation into electrons and holes and form a dense phase reminiscent of a liquid metal.

The parameter Λ can be useful in the case of small quantum corrections. Under conditions of strong degeneracy, new effects are possible. Lines 5 in Figs. 1—3 correspond to the condition of Bose condensation of non-interacting particles[14]:

$$\lambda^3 n = 2.6, \qquad (2)$$

where $\lambda = (2\pi\hbar^2/MkT)^{1/2}$, M is the particle mass, and the values of M for the excitons were taken with allowance for the multi-valley factor[15]. Lines 5 on Figs. 1 and 3 intersect the coexistence curve near the critical point. In this respect, the excitons differ from He^4, for which line 5 is far from the gas phase (Fig. 2).

Taking into account the errors in the experimental data, and also the probable deformation of line 5 under the influence of the non-ideal conditions, one could admit of the possibility of a variant in which the excitons undergo first a Bose condensation in the gas phase, and condensation into a liquid occurs with further contraction. More probable, however, is a variant in which the Bose condensation leads to simultaneous condensation into the liquid state. The point is that the degeneracy of a Bose gas leads to the appearance of an effective "attraction" between the particles[12]. This attraction can be balanced only by repulsion forces, but the repulsion forces are short-range and come into play only at high densities (in liquids). Thus, Bose condensation leads to a first-order phase transition. Such a situation was considered in[16] as applied to a hard-sphere Bose gas. The presence of long-range attraction between the excitons makes the coalescence of Bose con-

densation and ordinary condensation even more mandatory[1].

Taking the foregoing into account, we can write an approximate equation of state for the interacting bosons

$$P = \frac{nkT}{1-nb} - an^2 - \frac{\pi^{3/2}\hbar^3}{2M^{3/2}(kT)^{1/2}}n^2, \quad (3)$$

which differs from the Van der Waals equation in that account is taken of the degeneracy. Putting $b = n_{cr}/3$ and using the experimental values of n_{cr}, we obtain from (3) $T_{cr} = 10.3°K$ for Ge and 25.5°K for Si. We note that if we neglect degeneracy in (3) we obtain $T_{cr} = 5.4°K$ for Ge and 16°K for Si; on the other hand, if we put A = 0 in (3), we obtain 6.2 and 12°K respectively.

In spite of the arguments presented above, the use of Bose condensation to explain the nature of the phase transition in Ge or Si is hardly sufficient. First, lines 5 on Figs. 1 and 3 still lie above the experimental points for the vapor density. Deviation from ideal behavior is more likely to move line 5 still higher, as seen from Fig. 2, where line 5 should go over into line 7. Second, the dense phase is not an exciton liquid but an electron-hole liquid, so that equation (3) does not hold for it. Nor is it clear how the Bose condensation would take place at $T > T_{cr}$. Finally, at such high densities one must take into account the non-Bose character of the excitons, which leads to an effective "repulsion," and its effect with respect to density is of the same order as the non-ideal character of the excitons, so that the use of the Bose-condensation condition for ideal particles that are "exactly" bosons is incorrect[8].

PLASMA PHASE TRANSITION

It was assumed above that the gas phase consists only of excitons. The experimental data of Glicksman and Gurney indicate that the gas phase has good conductivity along the saturation line. Thus, the gas phase consists not only of excitons but also of electrons and the holes, i.e., it is suited to the partially-ionized non-ideal plasma considered in[7,17]. For a rough estimate of the degree of dissociation of the excitons, we use an equation that is the corresponding modification of the ionization-equilibrium equation

$$n_{ex} = n_e n_h (2\pi\hbar^2\beta M / m_e m_h)^{3/2} (\Sigma_0/4) \exp(\beta I - \varphi(n_e, T) + n_{ex}\beta(2a - a_{ex.e} - a_{ex.h}) + \beta(\Delta\mu_{ex} + \Delta\mu_e + \Delta\mu_h)], \quad (4)$$

where n_{ex}, n_e, and n_h are the concentrations of the excitons, electrons, and holes ($n_e = n_h$), m_e and m_h are the masses of the electron (with allowance for the multi-valley behavior) and hole; $\beta = 1/kT$; Σ_0 is the partition function of the exciton and takes into account the contributions of the excited states; $\Sigma_0 \to g_0 = 1$ as $T \to 0$; the statistical weights of the electron and of the hole are equal to 2; $I = 3 \times 10^{-3}$ eV for Ge[3] and 8×10^{-3} eV for Si[18]; $\varphi(n_e, T)$ takes into account the interaction of the charged particles with one another[7]; $a_{ex.e}$ and $a_{ex.h}$ are coefficients characterizing the exciton-electron and exciton-hole interaction: $\Delta\mu_{ex}$, $\Delta\mu_e$, and $\Delta\mu_h$ are corrections for the degeneracy of the particles. In writing down (4) it was assumed that the repulsion between the excitons can still be neglected.

Estimates based on formula (4) show that in the region of the critical point the degree of dissociation of the excitons in the gas phase amounts to not less than several per cent. More accurate estimates are difficult, since the electron-hole subsystem is strongly non-ideal, and the function φ can be estimated only very roughly. Estimates of the other terms in the argument of the exponential in (4) are also difficult. It is possible that the role of the exciton-charge interaction is also appreciable.

The non-ideality of the electron-hole subsystem can be characterized by the parameter

$$\gamma = e^2\beta(n_e + n_h)^{1/3}D^{-1},$$

where D is the dielectric constant (D = 16 and 11 for Ge and Si, respectively[19]).

Line 7 of Fig. 1, with $\gamma = 1$, is drawn under the assumption that all the excitons are dissociated. Allowance for the actual degree of dissociation would cause the line $\gamma = 1$ not to be straight and pass only slightly below the critical point. The electron-hole subsystem in the region of the critical point is still non-degenerate, so that this region corresponds precisely to the conditions under which, according to[7], there can occur a plasma phase transition due to the Coulomb interaction of the free charges. The critical temperature of such a plasma transition can be estimated from the formula

$$kT_{cr} \simeq 0.06\, me^4/\hbar^2D^2, \quad (5)$$

where m is the reduced mass of the electron and hole. From (5) we get $T_{cr} \sim 6°K$ for Ge and 36°K for Si, which is in satisfactory agreement with the experimental data discussed above.

As already noted above, in the gas phase on the saturation line the parameter γ exceeds unity somewhat. A similar result was obtained in[20] by the Monte Carlo method and for the gas phase of a plasma phase transition. This agreement also favors the plasma nature of the phase transitions in Ge and Si. We note that an estimate of the density of the gas phase by means of the formula from[1]

$$n = g_0(MkT/2\pi\hbar^2)^{3/2}\exp[\beta(\mu_{0e} + \mu_{0h} + I)], \quad (6)$$

which was derived under the assumption that the gas phase consists only of excitons, leads to values of n that are smaller by four orders of magnitude than the experimental ones. μ_{0e} and μ_{0h} in (6) are the chemical potentials of the electrons and holes in the liquid phase, and are known from experiment[4].

We can thus conclude that when T is of the order of T_{cr} the phase transition in Ge and Si is a plasma phase transition[2]. When the temperature is lowered, the degree of dissociation of the excitons decreases and the phase transition can turn into exciton condensation. In the case of Ge this can be revealed, e.g., by the approach of lines 4 and 8 in Fig. 1 at T = 2–3°K. For a final explanation of the nature of the phase transition, it is very important to have more exact measurements of the coexistence curve of the exciton phases.

[1] We note that the kinetics of such a phase transition would be an interesting problem.

[2] We note that the estimate of the supersaturation (1) remains in force also for a plasma phase transition.

In addition to Ge and Si, phase transitions in a system of non-equilibrium carriers can be observed in principle also in other semiconductors. It is possible that some of the mechanisms discussed above and rejected for Ge and Si are realized in other substances. We point out also a paper[21] dealing with the plasma of strongly-doped semiconductors and where the possibility of a phase-transition is likewise analyzed in analogy with[7].

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