SOLID STATE PHYSICS

Advances in
Research and Applications

Editors

HENRY EHRENREICH

FREDERICK SEITZ

DAVID TURNBULL

VOLUME 32

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HENRY EHRENREICH

Division of Applied Sciences
Harvard University, Cambridge, Massachusetts

FREDERICK SEITZ

The Rockefeller University, New York, New York

DAVID TURNBULL

Division of Applied Sciences
Harvard University, Cambridge, Massachusetts

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Preface

This volume deals comprehensively with a single topic: the electron-hole liquid in semiconductors. This topic is addressed in companion articles presenting the theoretical and experimental points of view by a group of scientists at Bell Laboratories who have collaborated extensively in their own contributions to this field. The articles are designed to appeal to a readership transcending specialists. In their arrangement of subject matter, the authors have been cognizant of the needs of both those wishing an entry to a field with a very substantial literature, and others, such as students, who have an intrinsic interest in learning about a very rich and exciting aspect of the physics of condensed matter.

HENRY EHRENREICH
FREDERICK SEITZ
DAVID TURNBULL

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Contributors to Volume 32

Numbers in parentheses indicate the pages on which the authors' contributions begin.

J. C. HENSEL, *Bell Laboratories, Murray Hill, New Jersey* (87)

T. G. PHILLIPS, *Bell Laboratories, Murray Hill, New Jersey* (87)

T. M. RICE, *Bell Laboratories, Murray Hill, New Jersey* (1)

G. A. THOMAS, *Bell Laboratories, Murray Hill, New Jersey* (87)

The Electron–Hole Liquid in Semiconductors: Theoretical Aspects

T. M. RICE

Bell Laboratories, Murray Hill, New Jersey

I. Introduction

In an intrinsic semiconductor such as germanium or silicon there are essentially no free carriers at very low temperatures. However, high densities of positive (hole) and negative (electron) charge carriers can be generated in these crystals by photoexcitation with a photon energy greater than the forbidden gap. In recent years, experiments in Ge and Si have revealed that optically pumped electrons and holes at high

densities can undergo a phase transition at liquid helium temperatures into a metallic, liquid state. This condensate represents a state of matter particularly unique in nature because the electrons and holes, by reason of their small masses, are simultaneously in the quantum limit. This collective behavior of electrons and holes at low temperatures and high densities is the topic of this review.

Photoexcited carriers relax rapidly in energy to the band extrema by the emission of phonons. These thermalized carriers can, in the spirit of the effective mass approximation, be regarded as *free* particles with an altered ''effective'' mass determined by the local curvature of the energy bands, with an effective charge reduced by the square root of the static dielectric constant, and interacting with a simple Coulomb force law. A single electron and hole can bind to form an exciton which is directly analogous to a hydrogen atom or, more accurately, to a positronium atom. Eventually the electron and hole recombine, but in the indirect semiconductors Ge and Si this is a slow process since optical recombination is allowed only with the simultaneous participation of a phonon to conserve crystal momentum. As a result it is possible to create relatively high densities of excitons at a low temperature and to study their interaction.

The first systematic study of such effects was a photoluminescence experiment in Si done by Haynes[1] in 1966. Pumping strongly at 3 K he observed in the photoluminescence spectrum a new and unexpected set of lines, each lying slightly lower in energy than the well-known exciton lines. Haynes[1] attributed the new lines to the formation of excitonic molecules, the existence of which had been postulated earlier by Lampert.[2] At the time, Haynes's conclusion seemed reasonable in light of his data. Later developments, however, showed it to be mistaken; instead the new lines represented something of even more profound significance, the condensation of electrons and holes.

Two years later Asnin and Rogachev[3] observed a discontinuity in the photoconductivity with excitation power which led them to suggest that they had achieved a sufficiently high density of excitons to cause a metallization of the excitons. Later that year Keldysh[4] in his summary talk at the Moscow conference discussed these results and went on to propose that the most stable phase of electrons and holes might be a

[1] J. R. Haynes, *Phys. Rev. Lett.* **17**, 860 (1966).

[2] M. A. Lampert, *Phys. Rev. Lett.* **1**, 450 (1958).

[3] V. M. Asnin and A. A. Rogachev, *Zh. Eksp. Teor. Fiz., Pis'ma Red.* **7**, 464 (1968) [*JETP Lett.* **7**, 360 (1968)].

[4] L. V. Keldysh, *Proc. Int. Conf. Phys. Semicond., 9th, Moscow* p. 1303 (1968).

high-density metallic liquid rather than any type of molecular phase. He argued that one should view excitons as analogous to the monovalent atoms. Such atoms condense in two different ways: either as a molecular phase, in the case of hydrogen, or as a metallic phase, in the case of alkali atoms. The molecular state of excitons is only very weakly bound, because the light masses of all the constituents greatly increase the kinetic energy of localization; and this suggested to Keldysh that the better analogy is to the alkali atoms rather than to hydrogen.

Keldysh's remarks acted as a catalyst to a series of Russian experimentalists. In 1969 Pokrovskii and Svistunova[5] demonstrated that the new luminescence lines existed in Ge also and showed that there was a sharp onset of these lines as the temperature was lowered at constant excitation power. They concluded that the new lines arose from a condensed phase and interpreted their results as evidence of a phase transition to a state that was possibly metallic. At the same time Asnin and Rogachev[6] reported some rather more indirect evidence in optical absorption experiments which also supported the idea of a condensation phase transition as the temperature was lowered. Later that year (1969), Vavilov et al.[7] found that a resonance appeared in the far infrared absorption in Ge under similar excitation conditions. They interpreted this resonance as an absorption at the reduced plasma frequency of small metallic droplets. In this way they made the first microscopic measurement of the density of the metallic phase. Their value of 2×10^{17} electron–hole (e–h) pairs per cm^{-3} compares very favorably with the more recent measurements discussed below. At the same time Bagaev et al.[8] demonstrated that the new luminescence line was sensitive to strain and that the position of the emission in a sample could be moved in a strain gradient. They interpreted this as evidence for mobile droplets of the metallic condensate in agreement with Keldysh's original speculation.[4]

Since that time there has been an explosive growth of experiments in this field. The many beautiful experiments will be reviewed in the companion article by J. C. Hensel, T. G. Phillips, and G. A. Thomas. In this historical introduction we mention only a few of the important early

[5] Y. E. Pokrovskii and K. I. Svistunova, Zh. Eksp. Teor. Fiz., Pis'ma Red. 9, 435 (1969) [JETP Lett. 9, 261 (1969)].

[6] V. M. Asnin and A. A. Rogachev, Zh. Eksp. Teor. Fiz., Pis'ma Red. 9, 415 (1969) [JETP Lett. 9, 248 (1969)].

[7] V. S. Vavilov, V. A. Zayats, and V. N. Murzin, Zh. Eksp. Teor. Fiz., Pis'ma Red. 10, 304 (1969) [JETP Lett. 10, 192 (1969)].

[8] V. S. Bagaev, T. I. Galkina, O. V. Gogolin, and L. V. Keldysh, Zh. Eksp. Teor. Fiz., Pis'ma Red. 10, 309 (1969) [JETP Lett. 10, 195 (1969)].

experiments performed by Pokrovskii and co-workers[9a,b] and others.[10a,b] In 1970, Kaminskii, Pokrovskii, and Alkeev showed that the lineshape of the new line could be accurately fit by a simple convolution of the density of occupied states of the electrons and holes. This work clearly established the metallic nature of the condensed phase and led to a determination of the density and binding energy of the metallic phase. The demonstration that the metallic liquid was in the form of droplets came from two different sets of experiments. Two groups, Asnin *et al.* and Benôit à la Guillaume *et al.* showed that large pulses of charge were liberated when the droplets were dissociated by the strong electric fields of a reverse biased p–n junction.[10a,b] In 1971, Pokrovskii and Svistunova performed an elegant light scattering experiment to show that the metallic liquid was in the form of droplets whose radius was of the order of microns, in agreement with estimates from the p–n junction experiments. An excellent review of the early work in this field was published by Pokrovskii in 1972.[11]

Since the beginning there has existed some controversy over the nature of the new phase and the role of excitonic molecules. Haynes[1] had originally interpreted the new luminescence line as arising from molecules and this interpretation has been kept alive in the work of Asnin, Rogachev, and co-workers.[12] They argue that the initial condensation is of molecules and that it is only at high densities that the transition to a metallic phase occurs. Their suggestion has been commented on elsewhere,[13] and we will not discuss it in detail here. In our view the experimental fact that the lineshape of the new luminescence lines never changes and is always (including the original Haynes data[1]) fit excellently by the metallic lineshape is very persuasive evidence against two separate condensations and the molecular point of view.

An excellent review of the qualitative aspects of the theory was given in 1971 by Keldysh.[14] At that time he was pessimistic about the

[9a] A. S. Kaminskii, Y. E. Pokrovskii, and N. V. Alkeev, *Zh. Eksp. Teor. Fiz.* **59**, 1937 (1970) [*Sov. Phys.—JETP* **32**, 1048 (1971)].

[9b] Y. E. Pokrovskii and K. I. Svistunova, *Zh. Eksp. Teor. Fiz., Pis'ma Red.* **13**, 297 (1971) [*JETP Lett.* **13**, 212 (1971)].

[10a] V. M. Asnin, A. A. Rogachev, and N. I. Sablina, *Zh. Eksp. Teor. Fiz., Pis'ma Red.* **11**, 162 (1970) [*JETP Lett.* **11**, 99 (1970)].

[10b] C. Benôit à la Guillaume, M. Voos, F. Salvan, J.-M. Laurant, and A. Bonnot, *C. R. Acad. Sci.* **272**, 236 (1971).

[11] Y. E. Pokrovskii, *Phys. Status Solidi A* **11**, 385 (1972).

[12] A. A. Rogachev, *Springer Tracts Mod. Phys.* No. 73, 127 (1974), and references therein.

[13] T. M. Rice and W. F. Brinkman, *Comments Solid State Phys.* **5**, 151 (1973).

[14] L. V. Keldysh, *in* "Eksitony v Poluprovodnikakh" [Excitons in Semiconductors], p. 5, Nauka, Moscow, 1971.

possibilities of making a good calculation of the properties of the metallic phase. Subsequently the work of several groups[15-19] has shown that such a detailed theory can be made and that good agreement can be reached with experiment. Indeed it now appears that this system is one of the best numerical tests of many-body theory at present. The comparison of theory and experiment will be one of the major themes of this review and the companion review by Hensel *et al.* which follows.

II. Semiconductor Systems

1. BAND STRUCTURE

The basic property of a semiconductor is that it has an energy gap which separates the filled valence band from the empty conduction band. The energy bands are now known in detail for most simple semiconductors by a combination of semiempirical band structure calculations and optical and other experiments.[20] In this review we will be concerned with the properties of electrons near the minimum in the conduction band and holes near the maximum in the valence band.

It has long been known that such electrons and holes can be described accurately by the effective mass theory.[21] In a pure crystal there are no states available into which an electron at the energy minimum can decay. Such an electron can be described as a particle with negative charge and a mass determined by the local curvature of the energy band at the minimum. Similar considerations apply to a hole at the maximum in the valence band. It can be described as a particle with positive charge and a positive mass whose value is determined by the local curvature of the valence band.

Semiconductors can be divided into two classes. Those in which the conduction band minimum and valence band maximum occur at the same value of the wavevector are known as direct gap semiconductors, while those in which they are separated in **k** space are known as indirect gap semiconductors. We shall be concerned with the latter. In indirect

[15] W. F. Brinkman, T. M. Rice, P. W. Anderson, and S.-T. Chui, *Phys. Rev. Lett.* **28**, 961 (1972).

[16] M. Combescot and P. Noziéres, *J. Phys. C* **5**, 2369 (1972).

[17] W. F. Brinkman and T. M. Rice, *Phys. Rev.* **B7**, 1508 (1973).

[18] P. Vashishta, P. Bhattacharyya, and K. S. Singwi, *Phys. Rev. Lett.* **30**, 1248 (1973).

[19] P. Vashishta, S. G. Das, and K. S. Singwi, *Phys. Rev. Lett.* **33**, 911 (1974).

[20] C. Kittel, "Quantum Theory of Solids." Wiley, New York, 1963.

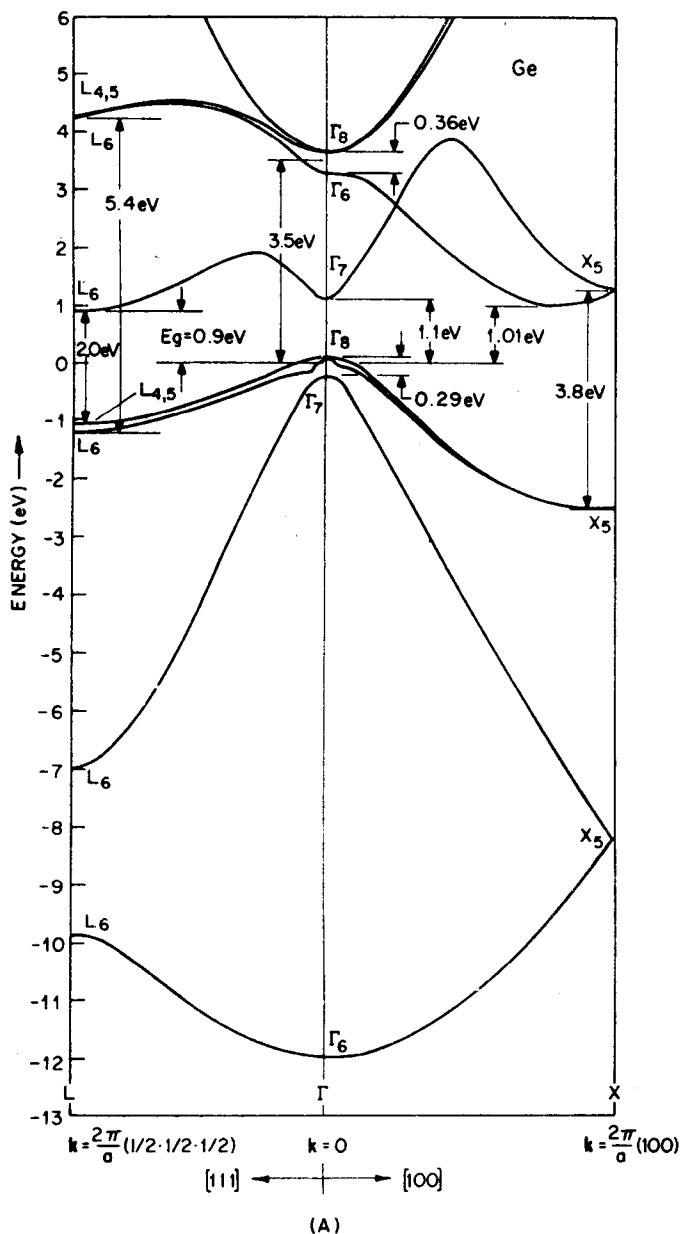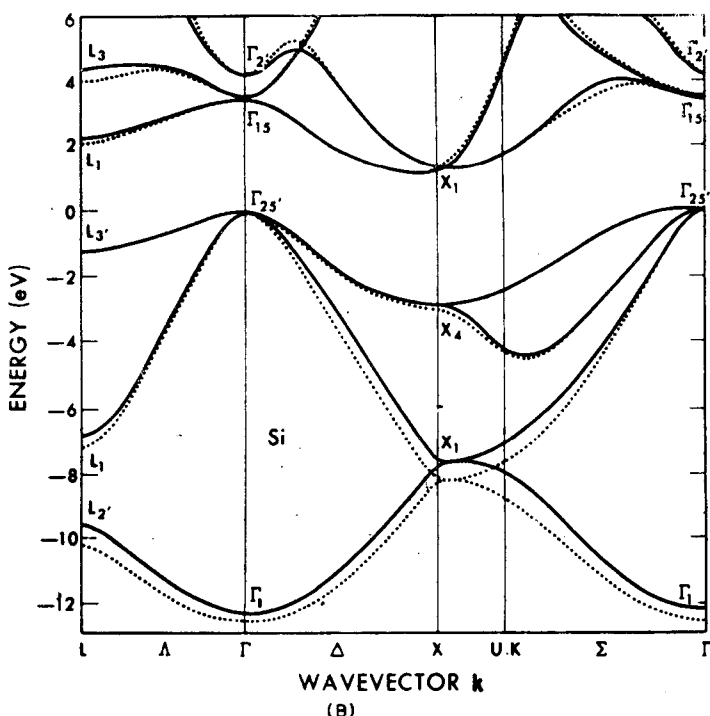[21] W. Kohn, *Solid State Phys.* **5**, 257 (1965).

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FIG. 1. The calculated band structures of (A) Ge and (B) Si. The general features of these band structures are in good agreement with experiment. The calculation for Ge

WAVEVECTOR **k**

(B)

includes the effect of spin-orbit coupling. However, in Si this effect is much weaker and for clarity it has been omitted. The dashed and solid lines were obtained using a local and nonlocal pseudopotential, respectively. Note the experimental value of indirect energy gap at $T = 0$ K is 0.745 eV in Ge and 1.170 eV in Si. [(A) From C. Y. Fong, unpublished calculations; (B) From J. R. Chelikowsky and M. L. Cohen, *Phys. Rev. B* **10**, 5095 (1974).]

gap semiconductors optical recombination is allowed only with the emission or absorption of a phonon to conserve crystal momentum and is a much slower process than in direct gap materials.

The band structure of Ge and Si is shown in Fig. 1. In Ge the electron minima are located at the L point of the zone which is at the zone boundary in the [111] direction.[20] There are, thus, four equivalent electron minima. Cyclotron resonance studies have led to very accurate values of the masses.[22] In Table I we quote the values for Ge. The electron energy surfaces are highly ellipsoidal with a value of 20 for the ratio of longitudinal (m_{el}) to transverse (m_{et}) mass. In Si the energy

[22] B. W. Levinger and D. R. Frankl, *J. Phys. Chem. Solids* **20**, 281 (1961).

TABLE I. ENERGY BAND PARAMETERS[a]

Electrons	m_{el}	m_{et}	m_{de}	m_{oe}	μ_0
Ge	1.58	0.082	0.22	0.12	0.046
Si	0.9163	0.1905	0.3216	0.2588	0.123

Holes	A	B	C	m_{hH}	m_{hL}
Ge	13.38	8.48	13.15	0.347	0.042
Si	4.28	0.75	4.85	0.523	0.154

Holes	m_{hl}	m_{ht}	m_{dh}	m_{oh}
Ge [111]	0.04	0.13	0.088	0.075
Si [100]	0.198	0.256	0.235	0.234

[a] The electrons have ellipsoidal energy surfaces with transverse and longitudinal masses m_{et} and m_{el}, respectively. The density of states is proportional to the geometric average, $m_{\mathrm{de}}^3 = m_{\mathrm{el}} m_{\mathrm{et}}^2$, rather than the optical mass average defined by $3 m_{\mathrm{oe}}^{-1} = m_{\mathrm{el}}^{-1} + 2 m_{\mathrm{et}}^{-1}$. The hole energy bands are given by Eq. (1.1) and have density-of-state masses m_{hl} and m_{hH} as defined in Eq. (1.2). In the high-strain limit the hole bands are ellipsoidal also with longitudinal and transverse masses given by $m^{-1}_{\mathrm{hl}} = A + \frac{1}{3}(3C^2 + 9B^2)^{1/2}$ and $m^{-1}_{\mathrm{ht}} = A - \frac{1}{3}(3C^2 + 9B^2)^{1/2}$ in Ge[111] and $m^{-1}_{\mathrm{he}} = A + B$, $m^{-1}_{\mathrm{ht}} = A - \frac{1}{2}B$ in Si[100].

minima are located along the [100] directions at a point $2\pi/a$ [0.86, 0, 0].[20] There are six equivalent electron minima which are ellipsoidal.[23] The parameters are also given in Table I.

In both Ge and Si the valence band maximum is at Γ (see Fig. 1). In the absence of spin-orbit coupling, the hole level at Γ would be a Γ'_{25} level with a sixfold degeneracy. However, spin-orbit coupling has the effect of splitting the level into a fourfold degenerate Γ_8^+ level and a twofold Γ_7^+ level. This latter level is usually ignored since the energy splitting between the Γ_8^+ and Γ_7^+ levels is large. (In Ge it is 0.29 eV, whereas in Si it is only 0.04 eV[20]). The Γ_8^+ level splits as $\mathbf{k}$ moves away from the zone center into a heavy (H) and light (L) hole band. These bands have a warped energy surface of the form[20,21]

$$E_{\pm}(\mathbf{k}) = Ak^2 \pm [B^2k^4 + C^2(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)]^{1/2}. \qquad (1.1)$$

The values of the parameters A, B, and C, as determined by cyclotron resonance,[24,25] are listed in Table I. Also listed there are the density-of-states masses m_{hL}, m_{hH} obtained by taking the average

$$\frac{m_{\mathrm{hL,H}}^{3/2} E^{1/2}}{\sqrt{2}\pi^2 \hbar^3} = \sum_{\mathbf{k}} \delta[E - E_{\pm}(\mathbf{k})], \qquad (1.2)$$

[23] J. C. Hensel, H. Hasegawa, and M. Nakayama, *Phys. Rev. A* **138**, 225 (1965).
[24] J. C. Hensel and K. Suzuki, *Phys. Rev. B* **9**, 4219 (1974).
[25] J. C. Hensel and G. Feher, *Phys. Rev.* **129**, 1041 (1963).