Electron-Hole Droplets: A Unique Form of Matter

In the parlance of the scientist working with semiconductors, the vacant energy state that remains when a valence electron is excited to a higher energy state is said to be occupied by a hole. In the treatment of the electrical properties of semiconductors, electrons in excited states (free electrons) and holes are both considered to be current carriers, except that the hole, as the absence of an electron, bears a positive charge. At sufficiently low temperatures, when thermal effects are small, the attraction between a negative free electron and a positive hole causes these two particles to behave as a single, uncharged entity, which is known as an exciton. Recent experimental and theoretical investigations in the U.S.S.R., in France, and in the United States have indicated that, at extremely low temperatures, a new phenomenon appears in some semiconductors. When large numbers of excitons are produced at temperatures only a few degrees above absolute zero, a metallic phase appears within the semiconductor—a phase known as electron-hole droplets. The properties of this new phase, which so far has only been observed in silicon and germanium, are attracting attention among solid state physicists.

The formation of electron-hole droplets has been likened by some investigators to the condensation of fog droplets in a moist atmosphere. When the exciton concentration in the semiconductor is sufficiently high, the metallic droplets condense. The density of electrons and holes (number of particles per unit volume) in the droplet is much greater than that of excitons outside the droplet. But, unlike water, the electron-hole droplet is metallic, possibly because the high density of the droplet causes the excitons to become so squashed together that they lose their individual identities and become a plasma of free electrons and holes.

The first experimental observation of electron-hole droplets is generally attributed to the late J. R. Haynes of the Bell Laboratories, Murray Hill, New Jersey. In 1966, Haynes observed a previously unreported luminescence emission in silicon while exciting his sample with a mercury arc source. In Haynes' experiment, the absorption of photons from the mercury source by the silicon created free electrons and holes, along with excitons. When the excited electron returns to a valence state (recombines with a hole), a photon is given off (luminescence), whose energy roughly corresponds to the energy of the excited state. Haynes' new luminescence, occurring at a slightly lower energy than that resulting when an exciton recombines, is now attributed by most investigators to the recombination of an electron and a hole in the droplet.

Some time later, V. M. Asnin and A. A. Rogachev of the A. F. Joffe Physical-Technical Institute, Moscow, observed a change in the electrical conductivity of germanium samples subjected to high intensity illumination at very low temperatures. This new photoconductivity observation prompted L. V. Keldysh of the P. N. Lebedev Physical Institute, Moscow, to propose the electron-hole droplet model. Most subsequent investigations of the properties of electron-hole droplets have proceeded on the basis of the original Keldysh proposal.

That the entity responsible for the observed luminescence and photoconductivity was a condensed phase of high density droplets coexisting with a low density phase of excitons was demonstrated persuasively by Ya. E. Pokrovsky and K. I. Svistunova of the Institute of Radioengineering and Electronics, Moscow. In addition to being absorbed, light incident on a semiconductor may either pass through unaffected or it may be scattered and emerge in a direction different from that of the incident light. Scattering can occur when the path of the light beam contains opaque particles with dimensions comparable to the wavelength of the light. By analyzing both the angular distribution and the intensity of laser light scattered in a germanium sample containing electron-hole droplets, Pokrovsky and Svistunova deduced that droplets with diameters of the order of 5 micrometers, each containing from 10^7 to 10^8 electrons and holes, were in the sample. Other scientists have since confirmed these results in similar experiments.

A number of investigators have also observed charge pulses passing through *p-n* junctions in germanium samples presumed to contain electron-hole droplets. The pulses, resulting from the breakup of the droplets in the high electric field near the junction, have magnitudes consistent with the droplet size measured by Pokrovsky and Svistunova.

Although the photoconductivity experiments of Asnin and Rogachev, as well as more recent photoconductivity studies by M. Glicksman and co-workers at Brown University are consistent with a model of metallic electron-hole droplets, some scientists remain skeptical that the photoconductivity can be unambiguously interpreted. As a result, observers agree, the behavior of the luminescence due to the recombination of electrons and holes in the droplets gives the most reliable evidence for the metallic character of the droplets.

The success of many different investigators, beginning with Pokrovsky, in analyzing the spectral distribution (number of photons emitted and their energies) of the droplet luminescence tends to confirm the plausibility of models based on a metallic electron-hole plasma. Moreover, additional support for the metallic plasma model has been obtained by G. A. Thomas, T. G. Phillips, T. M. Rice, and J. C. Hensel of the Bell Laboratories. These workers showed that the width of the luminescence (the energy difference between the maximum and minimum energy photons in the emission) decreases in a particular way as the temperature is raised. This temperature dependence is only possible when the droplet is metallic.

Attempts by theorists to understand why electron-hole droplets occur and why, so far, they occur only in silicon and germanium have focused on the details of the electronic energy states of these two semiconductors. These states are arrayed in quasi-continuous groups (or bands) of energies that are separated by intervals (or bandgaps) unavailable to electrons. The bands may be thought of as arising from the discrete electronic energy levels of the isolated atoms that broaden into bands of energy levels as the atoms are brought together to form a solid. As the bands fill up with electrons, the lowest energy bands are occupied first. The occupied band of highest energy

is the valence band, and the next higher (unoccupied) band is the conduction band. Creation of a free electron and a hole corresponds to exciting an electron to the conduction band, leaving a hole in the valence band.

There are three parts to the calculation of the energy of electrons and holes in the droplet: (i) the kinetic energy, which is the average energy of electrons in the conduction band and holes in the valence band; (ii) the exchange energy, which arises from the Pauli principle that no two electrons can occupy the same quantum state; and (iii) the correlation energy, which comes about because electrons tend to avoid other electrons, holes avoid other holes, and electrons and holes attract each other, so that the motions of electrons and holes are not independent of other electrons and holes, but are correlated. The stable state of this electron-hole system occurs when the sum of these three energies is a minimum. Since the most quoted value of the energy of an exciton in germanium is -3.6×10^{-3} electron volt, relative to a free electron-hole pair, the minimized droplet energy must be more negative for the droplet to be formed.

Pokrovsky's group was one of the earliest to attempt such calculations. And, although they used only a very approximate model, their results showed that the energy per electron-hole pair in the droplet was at least 2×10^{-3} ev less than the exciton energy in germanium. More recently, theoretical treatments of the binding energy of electron-hole pairs in droplets (absolute value of the droplet energy) have been given by M. Combescot and P. Nozières of the Ecole Normale Supérieure, Université de Paris, and by W. F. Brinkman and Rice of the Bell Laboratories. These investigators found binding energies of 5.7×10^{-3} and 5.3×10^{-3} ev per pair, respectively, and a density of 2.0×10^{17} pairs per cubic centimeter in germanium. Calculations were also made for silicon.

All these investigators have emphasized that it is the details of the electronic energy structure of germanium and silicon which permit the formation of electron-hole droplets in these materials. For example, in germanium, the kinetic energy contribution to the total energy is reduced by spreading the electrons over germanium's four conduction bands. Many semiconductors have only one conduction band. The kinetic energy can be further reduced because of the anisotropy of the energy structure. Anisotropy corresponds to the somewhat unobvious notion that, in a semiconductor, the energy depends not only on how fast the electron is traveling, but also on the direction of its motion. This effect is more pronounced in germanium and silicon than it is in many other semiconductors.

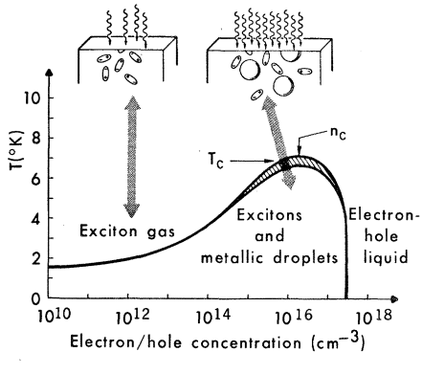

Fig. 1. The phase diagram indicating the distribution of electron-hole pairs between the exciton phase and the electron-hole droplet phase in germanium. The temperature and the density of electron-hole pairs at the critical point is indicated by T_c and n_c. The shaded area represents what is still under investigation. Thus, for example, at 2°K when the density of electron-hole pairs is less than about 10^{12} cm^{-3}, germanium is filled with excitons. At average densities greater than this, electron-hole droplets with a density of 2×10^{17} cm^{-3} electron-hole pairs coexist with 10^{12} cm^{-3} excitons. When the average density exceeds 2×10^{17} cm^{-3}, the entire sample is filled with droplets. [Courtesy of G. A. Thomas, Bell Laboratories]

The correlation energy is by far the most difficult of the three contributions to the binding energy to calculate; the principal difference in the details of the treatments by theorists is in choosing a suitable approximation for calculating the correlation energy. P. Vashishta of the Argonne National Laboratory, together with P. Bhattacharyya and K. S. Singwi of Argonne and Northwestern University, have calculated the correlation energy in germanium and silicon when a higher order approximation of the electron-hole correlations was taken into account. They found that the binding energy increased about 5 percent when this extra correlation was included.

Early experimental determinations of the binding energy were made with the use of the spectral distribution of the electron-hole luminescence by Pokrovsky's group and by C. Benoît à la Guillaume and M. Voos of the Ecole Normale Supérieure in Paris in collaboration with F. Salvan of the Centre Universitaire de Luminy, Marseille. These early measurements resulted in values of the binding energy that were much higher than the theoretical values. More recently, however, careful analyses of the droplet and of the exciton luminescence emissions by Benoît à la Guillaume's group, by Thomas and coworkers at the Bell Laboratories, and by T. K. Lo, working in C. D. Jeffries' group at the University of California, Berkeley, have yielded values of the binding energy near 5.6×10^{-3} ev per pair, more in agreement with the theoretical values.

Just as water molecules can evaporate from the liquid surface into the atmosphere, electron-hole pairs may "evaporate" from the droplet phase into the exciton "gas." Since the evaporation rate varies rapidly with temperature and depends on the binding energy, under the proper conditions, measurement of the temperature dependence of some characteristic feature of the droplet phase could yield values of the binding energy. This method was first applied by Pokrovsky and Svistunova when they found binding energies by analyzing the intensity of luminescence resulting from recombination in the droplet as the optical excitation power was increased.

Subsequently, others have used similar methods to find a binding energy consistently in the neighborhood of 5.1×10^{-3} ev per pair. For example, Hensel, Phillips, and Rice observed the onset of cyclotron resonance resulting from free electrons evaporating from the droplets. Jeffries and his co-workers repeated Pokrovsky's luminescence experiments. And J. C. McGroddy, working with Voos and O. Christensen at IBM's Thomas J. Watson Research Center, Yorktown Heights, New York, measured the onset of charge pulses collected in *p-n* junctions on the back of his samples. The lower binding energy found from these experiments as compared to those from analysis of the luminescence spectrum is thought by some scientists to be due to the still poorly understood nature of the droplet surface.

Because of the much shorter time of droplet formation in comparison to the time it takes electrons and holes to recombine, the electron-hole droplet is in a kind of quasi-thermal equilibrium. Thus it is possible to construct a phase diagram for the equilibrium between the excitons and the electron-hole droplets

—much like the phase diagram for a gas-liquid system. Such a phase diagram can be constructed from luminescence measurements at different temperatures (Fig. 1).

Calculation of any part of the phase diagram at finite temperatures is difficult, because the theory is tractable only at $T = 0$°K. By ignoring the details of germanium's band structure and omitting treatment of the correlation energy, R. N. Silver of the California Institute of Technology was able to derive the equivalent of a van der Waals equation of state for the electron-hole system, from which such a phase diagram may be calculated.

As in all gas-liquid systems, there should be a critical value of the temperature and the density at which the exciton phase and droplet phase become indistinguishable. This critical point is of some interest because scientists are unsure of the nature of the fluid there. For example, some believe that, near the critical point, the excitons are largely dissociated into free electrons and holes and the droplet has lost its distinctly metallic character. Thus, near the critical point, both the gas and the liquid phases are like a classical (not high density) electron-hole plasma.

So far, no published data exist for germanium concerning the critical point. A rough approximation has enabled Combescot to extend the binding energy calculation to finite temperatures, and she estimated the critical temperature to be about 8°K and the density of electron-hole pairs at the critical point to be about 7×10^{16} cm^{-3}.

All of the experiments reported above have used fluxes of photons or electrons to produce high densities of electrons and holes. However, R. B. Hammond, T. F. Lee, V. Marello, J. W. Mayer, T. C. McGill, and Silver at Caltech have recently demonstrated that droplets can be produced in both silicon and germanium by direct injection of electrons and holes through electrical contacts on the ends of a sample. This method may prove advantageous in measuring the properties of electron-hole droplets under somewhat different conditions from those of previous experiments. Such electrical injection would also be preferable if the condensation of electron-hole droplets should ever become important in making useful opto-electronic devices.

Still to be answered are a number of questions concerning the properties of droplet surfaces, the nature of the nucleation process when droplets condense, and possible practical applications. As work continues on the nature of electron-hole droplets, it will doubtless become clear how much new knowledge of lasting significance emerges from the study of this phase. So far, the observation of a well-known process (gas-liquid transition) in a totally new environment (multicomponent quantum plasma) has afforded the solid state theorist an opportunity to test his hypotheses of electron behavior in a unique form of matter.

—ARTHUR L. ROBINSON

Combinatorics: Steps toward a Unified Theory

The classical mathematical treatment of continuous phenomena has proved indispensable to the other sciences. However, a different type of mathematics is required to describe the discontinuous processes that occur in such areas as network analysis, molecular evolution, and computer science. These processes can best be described with combinatorics, the mathematics of discrete phenomena.

According to Gian-Carlo Rota of the Massachusetts Institute of Technology, combinatorics is one of the least developed fields of mathematics. He attributes this lack of development to the extreme difficulty of combinatorial problems and to the lack of a unified theory that would give direction to those who attempt to solve such problems. Now some mathematicians are optimistic that a unified approach to combinatorics may be forthcoming. Recently, two outstanding problems have been solved and techniques for solving them are being generalized. Research on a third major problem is also leading to new methods that appear to have extensive applications.

The proof by Richard Wilson of Ohio State University of an important conjecture that involves the existence of various block designs has aroused considerable interest among combinatorial mathematicians. Block designs are arrangements of a set of distinct objects (points) into a collection of subsets (blocks). The arrangement is restricted by the requirement that various groups of points occur specific numbers of times in the blocks. Of considerable practical importance in the design of statistical experiments, block designs are used to reduce the number of experiments necessary to prove a hypothesis.

One class of block designs consists of Latin squares—a type of design introduced by Euler who, in 1782, made a famous conjecture about such designs. Euler was asked to arrange 36 army officers from 6 ranks and 6 regiments in a square array so that each rank and each regiment was represented in each row and each column of the array. This led to the more general problem of deciding when such arrangements are possible. Euler convinced himself that it is impossible to arrange the 36 officers in the desired array and then conjectured that no such arrangement exists for any array of n^2 objects when n minus 2 is divisible by 4. This conjecture was finally shown to be incorrect by R. C. Bose of Colorado State University in Fort Collins, S. S. Shrikhande of Bombay University in India, and E. T. Parker of the University of Illinois. While resolving Euler's problem, these mathematicians developed two new research techniques (which were also independently developed by H. Hanani at the University of Nagev in Israel). Wilson then used similar techniques in his proof of a conjecture that certain designs can exist if the designs are permitted to consist of sufficiently many points.

The first technique of Bose, Shrikhande, and Parker, and Hanani is recursive and allows the construction of large block designs from smaller designs. The second technique is applied to the direct construction of designs from finite algebraic structures which are used to specify the points of the blocks. According to Wilson, these two techniques provide a systematic method to prove the existence of various block designs.

Coloring problems are another class of combinatorial problems which, like block designs, are now being approached with unified theories. One coloring problem is that of assigning various "colors" or symbols to regions of a surface. A general statement about colorings of maps, the Heawood conjecture, has been solved for nonplanar surfaces by Gerhard Ringel and the late J. W. T. Youngs of the University of California in Santa Cruz, together