ADVANCES IN SEMI-CONDUCTOR SCIENCE

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INTRODUCTION

M. H. HEBB

General Electric Research Laboratory, Schenectady, N.Y.

THE 1958 International Conference on Semiconductors was held during the week 18–22 August, at the University of Rochester, Rochester, New York. Doubtless, it will become known as the Rochester Conference, just as its predecessors are known by the names Reading, Amsterdam, and Garmisch-Partenkirchen.

The Proceedings of the Conference are published as a single issue of the *Journal of the Physics and Chemistry of Solids*. Great efforts have been made to meet the early deadline for publication. Credit goes to the authors of papers for their promptness in submission of manuscripts, to the editorial committee for their work in preparing the manuscripts for publication and to the staff of Pergamon Press for its accomplishment of a difficult task.

The selection of the papers presented at the Conference from those submitted, as well as their logical arrangement in sessions, was the responsibility of the Program Committee. Its members should be congratulated for their efforts. In addition to the formal program, a valuable part of any conference is the discussion that follows the formal papers. The organizing and editing of these questions and comments to make them available to others is a challenging assignment. The Conference is indebted to the co-chairmen for the discussion reported in these Proceedings.

Special recognition is due to the speakers in the summary session, whose incisive comments set the subject presented at the Conference in perspective. The remarks made at this session were invaluable to the participants of the Conference. They have been recorded in the Proceedings so that even those unable to attend the Conference can benefit from them. Some of the flavor of the talks is inevitably lost in a literary transcription. This loss is particularly regrettable in the case of the introductory remarks made by CONYERS HERRING, who organized the summary session.

For those interested in statistics, the total attendance was officially 500, of whom 412 were from the United States, 18 were from Canada, and the remaining 70 from 14 countries overseas.

There remains the pleasant task of acknowledgment to several organizations for their parts in the success of the Conference.

Foremost is the University of Rochester. The facilities provided by our host were ideal and the arrangements—even including the weather—were excellent.

Without financial support the Conference would not have been possible. Our principal support came from the Atomic Energy Commission, the National Science Foundation, the Office of Naval Research, and the Office of Scientific Research of the Air Research and Development Command. Substantial contributions were made by a number of industrial organizations. Local industry groups in Rochester assumed the burden of many of our extra-Conference activities.

Many of the delegates from overseas were able to attend the Conference only because of the support provided by the Military Air Transport Service, whose help was generously made available to the Conference through the courtesy of the Office of Scientific Research.

Finally, sponsorship of the Conference by the International Union of Pure and Applied Physics formalized its international character and expedited participation by delegates from abroad.

SESSION A:
OPENING SESSION*

A.2

TRENDS IN SEMICONDUCTOR RESEARCH

J. BARDEEN

University of Illinois, Urbana, Ill.

THE rapid expansion of scientific research in recent years has created a real problem in communications. It is a problem which involves mass, time, and distance, but you can't find the answers in a physics text. If for no other reason than the sheer mass of published work, it is impossible to keep up with what's going on by reading journals, as one could do not so long ago. Another important difficulty concerns the speed of research. Work being done now in one laboratory may depend on what's been done in another laboratory in a distant part of the world only months before. Preprints and journal articles help one keep up to date in one's own narrow field, but they have their limitations. Books on special subjects and review articles in periodical or book form help one keep up with related fields.

Conferences on special subjects, such as this one, are becoming of increasing importance in scientific communication. They allow one to meet and talk with co-workers and to have an up-to-date summary of current work presented. The main limitation is that of the human mind to absorb all with which it is confronted. This meeting should provide everyone with a good opportunity to review research programs in the light of what is going on elsewhere, to put current semiconductor research into better perspective, and perhaps, most likely in private conversations, to get hints as to how one might surmount one difficulty or another in his own research.

It may be of interest to spend a few minutes this morning with a brief survey of trends in semiconductor research. What have we accomplished and where are we heading? It was not until the advent of quantum theory, some thirty-odd years ago, that there was an adequate basis for understanding the many properties of solids. Many facts now can be correlated on the basis of the Bloch theory and the corresponding energy-band model, in spite of its limitations. Left out of the Bloch model are interactions between electrons and lattice vibrations, except for scattering processes, and correlations between electrons resulting from Coulomb interactions, which are by no means small. Because of its simplicity, and the mathematical difficulties involved in going beyond it, the Bloch theory has been applied to many problems in metals and semiconductors, and with what must be regarded as remarkable success in view of its basic limitations. It is, in fact, only in recent years that we are beginning to understand why the Bloch model works as well as it does. It is, of course, much more satisfactory for s–p valence electrons than for the more tightly bound d-electrons.

In this afternoon's session on band theory, SLATER will give a general review and ZENER will discuss applications to d-band semiconductors.

There is now considerable interest in many-particle theories which go beyond the Bloch one-particle model to take into account dynamical correlations between the particles. A method which has proved useful in metal theory and is now being applied to semiconductors is to introduce screening of electrons by means of a complex frequency-dependent dielectric constant. This is a rather general method which involves taking pair correlations properly into account. Electrons and holes may be regarded as elementary excitations described by many-particle wave functions. It

* *Chairmen:* J. BARDEEN and D. L. DEXTER.

turns out, as will be discussed by KOHN and others, that some results of the Bloch model, such as introduction of quasi-particle excitations with an effective mass and use of a static dielectric constant in the force between a conduction electron or hole and a charged impurity center, follow from the many-particle treatment.

Most of the basic ideas and concepts used in semiconductors go back to the 'thirties. A. H. WILSON in 1931, was the first to introduce the concept of a hole from the modern point of view and to show how impurities can influence the carrier concentrations. It was recognized that photoconductivity could arise from excitation of electrons from the valence to the conduction band, and that the excess carriers introduced in this way would have a finite lifetime before recombination occurs. Not long after, in 1935, FRENKEL applied the concepts of generation of electron–hole pairs by light, diffusion in a concentration gradient, and flow of carriers in electric and magnetic fields, to account for experimental results of KIKOIN and NOSKOV on the photomagnetoelectric effect in Cu_2O and of DEMBER on the change of contact potential with light.

FRENKEL also suggested the exciton as a localized atomic excitation which could be transferred from atom to atom in the crystal. Another concept of an exciton as a bound state of an electron and a hole was suggested by SLATER and SHOCKLEY, and the theory developed further with the use of effective masses and dielectric constants by WANNIER. It was in the paper of WANNIER that the localized electron functions which now bear his name were introduced. These two different approaches to the exciton have since been developed by many people. Some recent theoretical developments will be discussed at this meeting by HAKEN and by MUTO, the latter work applying particularly to the alkali halides. TOYOZAWA and also GOODMAN and OEN will discuss interactions between excitons and lattice vibrations.

For a long time excitons were regarded as a theoretical possibility, but there was no real experimental demonstration of their existence. The first experimental proof of energy transfer by excitons was obtained several years ago by APKER and TAFT from their studies of photoelectric emission of electrons from alkali halide crystals. Excitons are now coming into their own, as shown by the fact that they are the principal subject of two sessions at this meeting.

Among the most interesting papers at the Garmisch meeting two years ago were those of GROSS on the discrete line absorption spectrum observed near the band edge of Cu_2O, with term values which could be fitted so remarkably well with a hydrogen-like formula, and of BROSER and BALKANSKI, who presented evidence for diffusion of excitons in CdS crystals. There is still controversy about this latter work and related experiments done since. BROSER now takes the view that his experiments can be accounted for by scattering and reabsorption of fluorescent radiation, while BALKANSKI and also DIEMER and his co-workers believe that true exciton diffusion has been observed in certain specimens. You will be able to hear both sides of the story tomorrow afternoon and form your own conclusions.

GROSS has extended his work on line spectra in Cu_2O and CdS to observe the Zeeman splitting, and has found evidence for both the electron–hole-type exciton and the localized-type exciton of FRENKEL. In a long series of experiments, NIKITINE has observed in a large number of different substances line spectra in emission and absorption which can be interpreted in terms of excitons.

Excitons are stable in germanium and silicon only at low temperatures. Evidence for excitons in these materials has come from analysis of the fine structure of the absorption spectrum obtained under high resolution near the band edge by MACFARLANE and his co-workers and from the corresponding emission spectrum of the recombination radiation by HAYNES and his co-workers. These experiments also give detailed information about the phonons involved in the indirect transitions. ZWERDLING and his co-workers have observed the Zeeman effect of the exciton absorption spectrum in germanium. All of this work on germanium and silicon will be discussed on Thursday afternoon. The first paper of this session is an important one by ELLIOT on the theory of the fine structure of the absorption edge.

A distinct trend of semiconductor research in the past few years is that it has become a quantitative science with a close coordination between theory and experiment. This is, of course, due in large part to the availability of very perfect single crystals of germanium, silicon, and now an

increasing number of other substances. These materials are ideal for the theorists because they are at once simple enough to understand and sufficiently complex to yield a rich variety of phenomena. Theory is not only able to account for the gross features, but also in many cases the fine details of complex phenomena. The main basis for the theory is the band model, with modifications in some cases for many-particle aspects or for intereactions between electrons and lattice vibrations. The theory forms a framework for analysis and interpretation of experiments. Parameters of the theory, such as effective masses, dielectric constants, energy gaps, and mobilities, which would be extremely difficult to evaluate theoretically from first principles, usually are obtained from experiment as empirical parameters.

The first experiments to give precise information on effective masses were the cyclotron-resonance experiments of KIP, KITTEL and their co-workers at California, and of LAX and his co-workers at the Lincoln Laboratory. This work was presented at the Amsterdam meeting four years ago. These experiments showed the complex nature of both the conduction and valence bands of germanium and silicon, as had been indicated earlier from magneto-resistance studies. The cyclotron-resonance method is limited to materials with a long relaxation time for collisions of the carriers, so that they can make a number of orbits in a magnetic field between collisions. Shorter relaxation times can be tolerated if the magnetic field is increased, but then direct observation of resonance is not easy because the cyclotron frequencies usually come in the most difficult region of the spectrum in which to work, the far infrared.

Ways out of this difficulty have been shown independently by BURSTEIN and by LAX, who detected the quantitized LANDAU-type levels of the carriers in a magnetic field in the optical absorption spectra near the band edge, either in interband transitions or in transitions from an impurity level to one of the bands. These powerful methods for getting information on band structure will be discussed in a series of papers on Thursday morning.

At one time traps were traps, and that was the end of it. Now we try to understand the energy levels of particular impurity atoms or other imperfections, and the trapping cross-sections of these for electrons and holes. Through careful research by a number of investigators, a large amount of information has been accumulated. Of particular interest and technological importance are the recombination centers. Several interesting papers dealing with these subjects are to be given in one of the sessions this afternoon. The theory of recombination via traps as worked out by SHOCKLEY and READ and by HALL is well confirmed by experiments, although generalizations are required in some cases. An important problem for the future is to get a more detailed and quantitative picture of luminescent centers.

A very ingenious and powerful method for investigating wave functions of electrons at impurity levels is the Electron Nuclear Double Resonance (ENDOR) method of FEHER. This method, which involves saturating the electron resonance and then observing the nuclear resonance lines, will be discussed by him on Friday morning, in a session which includes a number of other interesting papers on spin-resonance phenomena in semiconductors. We can expect an expansion of activity in this very interesting field in the years to come.

There has always been a close connection between semiconductor science and semiconductor technology, and I think this is a good thing for both. In the 'thirties, semiconductors were used mainly as rectifiers, and the important materials were copper oxide and selenium. Theories of rectification were worked out independently by MOTT, SCHOTTKY and DAVYDOV. From SCHOTTKY come most of our ideas concerning space-charge layers in which the space charge comes from uncompensated donor or acceptor ions. He had the concept of an inversion layer in which the conductance changes from n- to p-type as a result of the change in potential in the barrier region, and this came close to the ideas required for transistors. What he failed to recognize is the importance of minority carriers in the current flow. DAVYDOV, as early as 1938, came close to an adequate theory of p–n junctions, but the assumptions he made to get a mathematical solution were such as to mask minority carrier injection, which is of course one of the most important features of modern junctions and is a consequence of SHOCKLEY's theory. No doubt SCHOTTKY and others were thinking of their work in semiconductors such as copper

oxide in which minority carrier flow is unimportant.

Much of the semiconductor research in America and elsewhere during the past ten or fifteen years has been on germanium and silicon. As you know, this work has been greatly stimulated by applications first to radar detectors and then to diodes and transistors. Of great importance to the study is ability to make exceptionally perfect single crystals and to control the impurities present to a very high degree. As we have mentioned, these materials have served and are continuing to serve as a splendid testing ground for theoretical developments.

A large part of this research has been associated with transistor development, a great deal of it pioneered by SHOCKLEY. I will discuss just two of these briefly, the so-called "hot" electron problem, or change in mobility with electric field, as first observed by SHOCKLEY and RYDER, and the semiconductor surface-barrier problem, in which BRATTAIN has played a leading role.

There are several papers devoted to each of these subjects at this meeting. TAUC will discuss the increased quantum yield which occurs when the absorbed photon has so much energy that the excited electron or hole has sufficient energy to create further pairs by impact ionization.

A general review of the hot electron problem will be given by KOENIG. He himself has been investigating the change in ionization of impurities at low temperatures which occurs when the electrons are heated by a pulsed electric field to a higher temperature than the lattice. Such experiments give information about ionization and recombination processes. Several other interesting papers on the same general subject will be given on Wednesday morning.

During the past few years methods have been developed for determining the energy distribution of *surface* traps and capture cross-sections of electrons and holes. A general review will be given by MANY. Of particular theoretical interest is whether or not states exist on a surface free of any oxide layer or other contamination. The possibility of such states was first pointed out by TAMM, and SHOCKLEY later developed a more elaborate theory for valence crystals, in which he showed that surface states in the forbidden gap may be associated with uncompensated or dangling chemical bonds. For example, in germanium an interior atom forms four bonds with its near neighbors, but a surface atom can form only three. The unfilled orbital corresponding to the fourth bond is free to be occupied by electrons.

FARNSWORTH has shown that an apparently clean surface can be formed on germanium or silicon by an ion-bombardment technique. Several investigators have studied the electrical properties of surfaces cleaned in this way. HANDLER found that a germanium surface cleaned by bombardment is strongly p-type with a very high density of surface states. BARNES and BANBURY report different results for a freshly cleaved surface maintained in high vacuum. There should be some interesting discussions at the session on surfaces tomorrow morning.

This meeting reflects the increasing interest in compound semiconductors. Some of this stems from WELKER's pioneer work on the III–V compounds, whose properties are roughly similar to those of germanium and silicon. There is also great interest in compounds useful for thermoelectric elements. Much of the early work in this field was purely empirical. The first real scientific study of electron mobility, thermal conductivity, and other factors important for thermal elements, and the way they depend on composition was made by JOFFÉ and his co-workers. Results they have obtained clearly demonstrate the virtue of the scientific over the purely empirical approach. We are honored to have both JOFFÉ and WELKER on this morning's program.

Research on thermoelectric effects and on thermal conduction in semiconductors has yielded a number of interesting phenomena, involving phonon scattering, phonon drag, and heat transfer by ambipolar diffusion. Much remains to be done in this field. No doubt Professor JOFFÉ will discuss some of the accomplishments and outstanding problems in his talk. More details on thermal conduction will be given by KANAI and others in the session on Thursday morning.

In this brief review I have had time to indicate only a small fraction of the interesting papers to be presented, and many of those I have discussed were picked more or less at random or from personal interest rather than intrinsic importance.

Questions are often asked as to whether any new revolutionary discoveries can be expected in

the semiconductor field. In one sense, I believe the answer is no. Practically all of our basic ideas —energy bands, electrons and holes, phonons, excitons, polarons, dislocations, thermal generation and recombination of carriers, and so forth —date from the 'thirties or earlier. But the application of these ideas to particular situations, making them more precise and quantitative, and the working out of the wide variety of interactions possible among the elementary excitations have provided and will continue to provide many interesting and important problems with unexpected results and new applications. This meeting shows that the semiconductor field is a very live one, and there is no reason to expect interest to decline in the years to come.

PROPERTIES OF VARIOUS SEMICONDUCTORS

A. JOFFÉ

Institute of Semiconductors, Leningrad, U.S.S.R.

A.3

Abstract—The discovery of a p–n transition inside a monocrystal of Ge and of analogous materials (instead of a boundary between two semiconductors with a hole and electron conductivity which we investigated in 1938), the simple crystal structure, and the highest purity of Ge justify the extensive interest in these materials.

A neglect of the immense diversity of semiconductors is however a disadvantage. Contrary to Ge, for a large number of low mobility or of liquid semiconductors even the notion of velocity and effective mass cannot be defined; the scattering time is no longer short compared to the relaxation time. Melting of such semiconductors does not influence their properties, while a radical change appears if the number or the position of the next neighbours becomes involved.

Thus the interest must be directed toward the chemical bond and toward the structure of the electronic cloud inside a unit cell. Professor SAMOILOVICH has succeeded in explaining in this way the appearance of two effective masses for holes in Ge, the right dependence of mobility on temperature $\mu \sim T^{-2.3}$, the influence of a magnetic field, etc. The use of semiconductors for thermoelectric devices raises problems concerning their thermal, electric and mechanical behavior.

A systematic study of a variety of semiconductors, of solid solutions, of phenomena determining the ratio of thermal conductivity to the electron mobility, a favorable choice of the degree of degeneration, a consideration of the anisotropy, and of the anharmonicity of the chemical bond—all those fundamental problems must be taken into account. Some of the results achieved in this direction will illustrate the importance of the problems involved. While many of such problems are still rather obscure, some success has already been achieved. The figure of merit $z = \alpha^2/\varkappa\rho$ (α—thermoelectric power per °C) has increased up to and over $z = 3 \times 10^{-3}$/deg. (some papers use $\sqrt{z}$ instead of z) which means a cooling by one thermocouple from 112°C to 0°C or from +27°C to −45°C.

The problems of thermoelectric cooling, heating and energy production have become a promising field of research.

THIRTY years ago the discovery of rectification in an oxidized copper plate, and shortly afterwards the discovery of copper oxide and selenium photocells, directed the interest of physicists to the field of semiconductors and especially to copper oxide and selenium. A new era arose after the war due to the discovery of phenomena at a p–n boundary inside a monocrystal of germanium or silicon. The modern semiconductors are the germanium-like materials. Thus the

immense diversity of semiconductors became neglected in spite of the fact that they include resistivities from 10^{10} to 10^{-4} Ω-cm, mobilities from 0·1 to 10^5 cm²/V sec, impurities between 10^{-8} and 50 per cent, and all possible types of chemical bond.

We came to the problem of semiconductors from another point of view and therefore investigated somewhat different materials. Allow me to describe some of the results of our work.

The diversity of properties of semiconductors as depending on their structure may be illustrated by the various mechanisms of thermal conductivity we met during our researches in the domain of thermoelectricity.

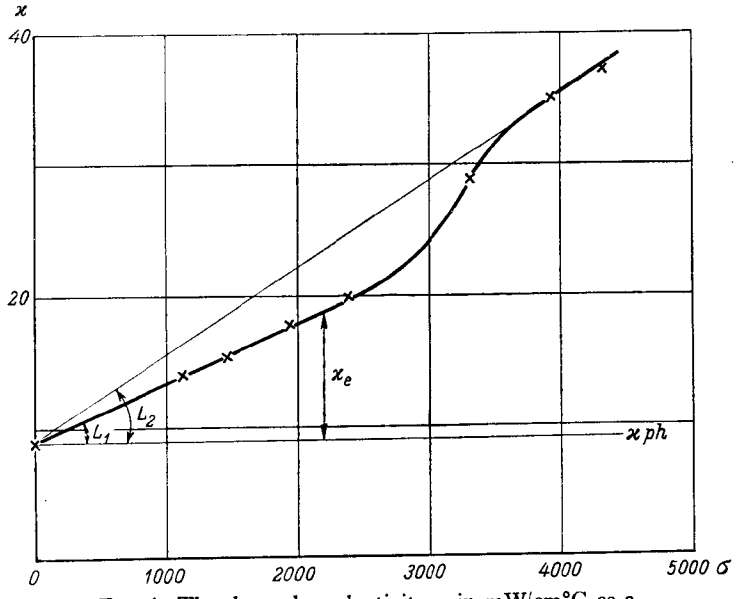

FIG. 1. The thermal conductivity κ in mW/cm°C as a function of the electrical conductivity σ in Ω^{-1}cm^{-1} Bi_2Te_3.

(1) In semiconductors with impurity conduction, the conductivity may be divided into two parts: the phonon term κ_{ph} and the Wiedemann–Franz term κ_{el} due to free charges:

$$\kappa = \kappa_{ph} + \kappa_{el} \tag{1}$$

$$\kappa_{el} = A\frac{k^2}{e^2}T\sigma = L\sigma, \tag{2}$$

where $A = \pi^2/3$ for a degenerate state of charges and $A = (r+2)$ for nondegenerate charges; r denotes the exponent in the expression for the free path l as a function of the kinetic energy

$$l \sim \epsilon^r \tag{3}$$

Increasing the impurity conduction σ of some Bi_2Te_3 materials from 1000 to 4500 Ω^{-1}cm^{-1}, we checked the Wiedemann–Franz ratio L for the nondegenerate state ($\sigma < 2500$ Ω^{-1}cm^{-1}) and found an increase of L for the degenerate state ($\sigma > 3500$ Ω^{-1}cm^{-1}). For r, we found $r = 0$, in good agreement with the value following from other considerations (Fig. 1).

(2) As soon as intrinsic conductivity appears, and charges of both signs begin to take part in the electric conduction, an additional energy transport becomes noticeable. In 1940, DAVYDOV and SHMUSHKEVICH and later Dr. P. J. PRICE and others derived a formula for the additional thermal conductivity $\Delta\kappa_{el}$ due to the ambipolar diffusion of charges in the direction of the temperature gradient:

$$\Delta\kappa = L\frac{\sigma_1\sigma_2}{\sigma_1+\sigma_2}\left(\frac{\Delta E_0}{2kT}+r+2\right)^2, \tag{4}$$