INVESTIGATION OF DIELECTRICS AND SEMICONDUCTORS IN THE USSR*

ACADEMICIAN A. F. JOFFE

Institute of Semiconductors, USSR Academy of Sciences, Leningrad

I. Dielectrics

At the beginning of this century all the electrotechnical materials were divided into two groups: conductors and insulators or dielectrics. True, it was known that not all the dielectrics were perfect insulators and that electric currents passed even through dielectrics; these currents were made an object of investigation by the French physicists, Foussereau and Jacques Curie at the close of the nineteenth century. At the beginning of the present century, the investigation of dielectrics was highly developed in Germany and Russia. The peculiarity of currents in dielectric crystals, discovered during the very first investigations, gave rise to the supposition that currents are no more than dielectric anomalies (slow displacements of ions and electron shells within the same crystal cell), similar to the phenomena which characterize the anomalies of elastic and magnetic properties.

V. R. Roentgen and A. F. Joffe proved in a number of researches published during the period 1905-29, that this hypothesis was wrong and that in dielectric crystals we deal with actual, real currents, that is, with a directed movement of charges; as to the seeming anomalies, they can be accounted for by the accumulation of space charges near the electrodes.

The research work of A. F. Joffe, A. A. Shaposhnikov, P. I. Loukirsky, M. V. Kirpicheva, B. M. Gohberg, V. A. Joffe and others has thrown light on the nature of space charges, their origin and their distribution within the crystal, the nature of current carriers (ions or admixtures of ions, of the crystal substance itself in some cases and electrons in others, particularly when connected with photoconductivity) quantitative laws, controlling the passage of the current in dielectric crystals, have been found.

These problems have acquired still greater importance in proportion with the growing requirements with regard to dielectrics, which are used in alternating current circuits and, particularly, in high frequency radiotechniques. Accordingly, the twenties and thirties were characterized by a large-scale development of physical investigations dealing with the phenomena occurring in dielectrics.

In connection with the growing application of different plastic materials as insulators in the USSR, the electrical properties of amorphous dielectrics and polymers have come to be the object of research since the late twenties. P. P. Kobeko, E. V. Kuvshinsky, G. P. Michailov, A. P. Alexandrov, S. N. Gurkov, G. I. Skanavy and others have proved that the electrical properties are closely connected with the viscosity of these substances. The abovementioned scientists have succeeded in giving a detailed description of the processes occurring in amorphous substances, and in revealing the physical nature of the hardening temperature as well as of the influence of plastifiers on this temperature. The nature of the polymer relaxation elasticity has been studied. It is to this group of investigators belongs the discovery of the principal laws in the field of the physics of amorphous state.

In the thirties, B. M. Vul, B. M. Gohberg and their assistants investigated the electrical properties and the breakdown of gases, particularly of those under high pressure. A. F. Walter and L. D. Inge investigated during the same period of time the breakdown of fluid dielectrics.

Owing to the progress of high voltage techniques, particular attention was devoted to the problem of electrical strength and the breakdown of dielectrics. N. N. Semenov, V. A. Fok and A. F. Walter found the laws governing the breakdown, caused by the heating of a dielectric by the electric current. A great number of investigations were devoted to the study of the "electrical" breakdown. In the course of investigating the breakdown of dielectrics were found insulators of the highest quality (polystyrene) and the most stable gases (SF_6). The hypothesis of the ionization breakdown put forward by A. F. Joffe found further confirmation. It was found that not only in electron conductors, but also in electrolytically conducting solid dielectrics, the breakdown is caused by electrons. Since that time, several theories of electrical breakdown have been put forward (Fröhlich, Hippel and others); this problem, however, cannot be regarded as solved as yet.

The rapid development of radio techniques requires a thorough investigation of energy

* This review essentially deals with the developments in the USSR. Similar work done elsewhere is not discussed in detail.

losses in dielectrics, placed in an alternating electric field. Apart from Joule heat produced by the current, there occur also other phenomena in the electric field: both the electric dipoles that form part of many dielectrics, and the dipoles created by the field itself, turn in the direction of the field; not only the electrons in atoms and molecules are displaced, but also the positive and negative ions, forming the crystal lattice of ionic crystals. Each of these phenomena influences both the value of the dielectric constant of the dielectric and the quantity of the losses occurring in it.

At the beginning of the thirties, I. V. Kurchatov and P. P. Kobeko discovered a new phenomenon that proved to be of great practical importance. In crystals of Rochelle salt (Seignette salt), as well as in other similar crystals, the electric field creates polarization, which exceeds by many hundred and thousand times what had been observed in dielectrics up to that time. The dielectric constant of Rochelle salt is measured in terms of thousands of units. Kurchatov and Kobeko proved that the electrical polarization of Rochelle salt resembles the magnetic polarization of ferromagnetic materials (in particular: saturation, residual electrification, hysteresis, the temperature at which these properties disappear, similar to the Curie point for ferromagnetics, etc.).

I. V. Kurchatov and L. D. Landau have also proved that, as in the case with ferromagnetics, there are domains in Rochelle salt composed of thousands of molecules with similarly oriented electric dipoles, which turn simultaneously in the electric field. By analogy with the ferromagnetics, such substances have been named "seignettoelectrics". In foreign literature they have been given the less characteristic name of ferroelectrics.

In the forties, B. M. Vul discovered a new group of seignettoelectrics—barium titanates with a lattice of the perovskite type. The Curie point for this group lies above 100° C., whereas for the Rochelle salt it is 24°, which limited the use of the material for technical purposes.

The barium titanates, like Rochelle salt, possess piezoelectric qualities—mechanical deformation produces electric dipoles in them and conversely, the electric field causes deformation. Unlike Rochelle salt, the barium titanates become piezoelectrics as a result of preliminary electrification, which directs the electric dipoles of most of the domains along the field. Owing to this, it is possible to impart piezoelectric properties not only to a separate monocrystal, but also to a polycrystalline aggregate obtained as a result of ceramic treatment. This discovery, made by B. M. Vul, aroused great interest, and many articles and papers were devoted to it in the USA, England and Germany.

In the fifties, G. A. Smolensky and his assistants still further enlarged the group of seignettoelectrics.

G. I. Skanavi synthesized and studied such dielectrics which possess high dielectric constants amounting to hundreds of units, not as a result of their grouping into domains, but due to the easy displacement of ions that form part of them, as for instance titania, tungsten trioxide, molybdenum trioxide, and other crystals with the structure of rutile and perovskite. Ceramics containing similar crystalline substances have found wide application in condensers.

II. Electron Semiconductors

The investigation and wide practical application of semiconductors is a matter of the recent twenty-five years.

The electron semiconductors fill in a tremendous area of electrotechnical materials that lie between the insulators with specific resistance above 10^{10} ohm cm. and metals with resistance below 10^{-5} ohm cm. From the point of view of chemical composition, certain elements (graphite, silicon, germanium, selenium, tellurium, boron, arsenic, phosphorus) are also semiconductors, as well as oxides, sulfides, selenides, tellurides, certain alloys and the like.

More than 10,000 papers have already been devoted to the investigation of semiconductors; their application in engineering and in national economy has been growing yearly and daily; in proportion with this has grown the variety of materials that are being used for technical purposes.

In the history of semiconductors, short in time but rich in events, the interconnection of science and technique has clearly revealed itself.

The first technical items were rectifiers and photoelectric cells of cuprous oxide and selenium; it is these materials and these phenomena that had been the object of careful and close investigation in the succeeding years. Thallous sulphide and cadmium sulfide have been thoroughly studied in connection with photo-resistance; lead sulfide, lead selenide and lead telluride were investigated in the war and post-war years. Thorium dioxide, ceasium stibide and calcium oxide have been investigated in connection with the requirements of vacuum techniques.

The protection of high voltage lines from thunder storm discharges has drawn the attention of scientists to carborundum and to the investigation of the contact between its separate grains. The use of semiconductors for measuring temperature, for automatic regulation and for switching on electric systems has resulted in a systematic investigation of the temperature dependence of electrical conductivity of such materials as uranium dioxide, vanadium pentoxide, and a number of sulphurous compounds. The so-called electrolytic condensers, formed by layers of aluminium oxide, have given rise to literature devoted to the properties of similar oxides. The variety of semiconductors investigated began to grow considerably when their role in luminescence and catalysis was appreciated.

During the war, germanium and silicon were applied in the USA for radio location purposes. Since that time, these materials have become the main objects of investigation. They have found still wider application in radio techniques, by replacing vacuum detectors, amplifiers and generators of high frequency oscillation. Thousands of investigations in the USA, England, USSR, Germany, France, Holland and Switzerland have revealed all the details in the properties of germanium and silicon. It is on these data that the general quantum theory of semiconductors has been based. The properties of germanium and silicon are known better than those of any other semiconductors, even better than those of such classic materials as cuprous oxide, which were the main objects of investigation in pre-war physics.

In connection with the possibility of applying semiconducting thermocouples to convert thermal power into electrical power, to produce cold and for other purposes, semiconductors of low resistance are being studied in the USSR ; their theory is being developed and their electric, thermal and mechanical properties investigated. In this connection, the attention of Soviet scientists was drawn to the investigation of the mechanism of thermal conductivity and the laws that control it. The research work of A. V. Joffe, E. D. Devyatkova, P. V. Gultyaev and others have proved the connection of thermal conductivity with atomic weight, with the nature of chemical bonds, the influence of admixtures and the correlation of thermal conductivity with the mechanism of the passage of electric current.

With the help of a sealing layer (barrier layer), it is possible to produce electric power not only during the illumination of the photoelectric cell but also under the action of radioactive radiation, which, similar to light, increases considerably the concentration of electrons in the semiconductor.

In the field of magnetism, semiconductors also reveal new possibilities. Semiconductors, constructed after the spinel type, possess as high ferromagnetic properties as iron. But their electrical resistance is high—in this respect they differ from iron. As a result of this, the electromotive force induced in them by the alternating magnetic field excites comparatively weak currents, and accordingly does not lose much energy. Energy losses limit the utilization of metal ferromagnetics with a high frequency alternating current. The use of iron, even with the usual 50-cycle current, requires special conditions. The iron has to be divided into thin isolated layers or it has to be used in powder form, placed in an insulating medium. The semiconducting ferromagnetic materials, called ferrites, may be successfully applied in alternating magnetic fields, up to a frequency of 10^6 hertz.

We may also mention here some of the results of the investigation of semiconductors in the USSR.

Among theoretical problems, the theory of excitons—excitation state of electrons, which have not passed into a free state—put forward by J. I. Frenkel in 1931 is of great interest. The exciton can diffuse in the crystal lattice and give its energy to the lattice or to the electron when encountering admixture atoms of crystal anhomogenetics. The existence of excitons accounted for the possibility of light absorption without the appearance of free electrons. Some time later, E. F. Gross proved experimentally the appearance of the exciton during light absorption by cuprous oxide crystals, by crystals of cadmium sulfide and the like. He studied their spectra, the influence of electric and magnetic fields and revealed the mechanism of the appearance of certain spectral lines.

The theory of the photoelectric cell with a sealing layer was worked out by V. E. Lashkarev, who proved the possibility of obtaining considerable efficiency when converting light power into electric power. U. P. Maslakovetz and B. T. Kolomietz have made a photoelectric cell out of thallous sulfide with a sensitivity 20 times greater than that of selenium and with an efficiency for sunlight up to one per cent.

Recently they have been working at the photoelectric cell on the basis of silicon and germanium with a higher efficiency, amounting to 5 per cent. and more.

I. K. Kikoin and M. M. Noskov have discovered the photomagnetic effect. When a cuprous oxide plate placed in a magnetic field at the temperature of liquid air is illuminated, great electromotive forces arise in it amounting approximately to 15 volts, and in liquid helium even reaching 100 volts.

The behaviour of semiconductors in strong electric fields, where Ohm's law proves to be inapplicable, has been investigated by A. V. Joffe. It has been proved that the concentration of free electrons greatly increases in such fields, whereas the mobility of electrons changes but little. The theory of this phenomenon has been further developed by J. I. Frenkel. U. K. Pojela has found conditions under which a rise in the concentration of free charges, created by the strong field or light in a certain section of the semiconductor, may be used for amplifying purposes.

The most important problem of pre-war engineering—the rectification of the alternating current—has been the object of detailed investigation in the USSR. The theory of this phenomenon has been worked out by B. I. Davidov, and later by Schottky in Germany and Mott in England. A. V. Joffe has proved by experiments the connection between the properties of the sealing layer, which forms in the place where the semiconductor borders on the metal, with the difference of contact potential between them. In spite of Schottky's theory, she showed, even before the war of 1941-45, that the strong current asymmetry (thousands and tens of thousands times stronger in one direction than that in the opposite one, while the difference of potential applied to the rectifier is the same), that is observed in technical rectifiers, arises not on the borderline of the metal, but between two semiconductors, with different conduction mechanisms (usually denoted as conduction mechanism of the P or N type). The theory of rectification on the boundary of two semiconductors was developed on this basis by A. I. Gubanov. The transfer of this boundary into monocrystals of germanium and silicon, which has been achieved during the war years in the USA, has called to life new techniques for radio-instruments, making use of semiconductors (diodes, triodes, generators of radio waves).

As to theoretical investigations, the polaron theory of S. I. Pekar is of great interest. Pekar gives the name of polaron to an electron, whose field has polarized the ambient medium. In ionic crystals, the displacement of ions around the charge reduces its power by several tenths of electron volts, which leads to the prevalence of polarons over free electrons in such crystals. Proceeding from his theory, Pekar has also accounted for the properties of the so-called F-centres, which colour transparent crystals of rock-salt and other ionic crystals when they are lighted by X-rays or when the crystals are heated in sodium or potassium vapour.

The investigations of A. R. Regel have proved to be of considerable importance for the understanding and utilization of semiconductors. These investigations showed that the specific properties of semiconductors are inherent not only in the solid crystal state, but are also preserved after the crystals melt and pass into a fluid amorphous state. A. F. Joffe, V. P. Youze and their assistants have proved that a number of metal alloys such as $MgSb_2$, Cs_3Sb, ZnSb, Mg_2Sn are typical semiconductors. Of no less significance are V. P. Youze's investigations dealing with the problem of the physical properties of semiconductors in relation with their crystal-chemical structure and bond energy.

In conclusion, we should like to point out a number of experimental investigations of A. F. Joffe, U. R. Maslakovitz, E. D. Devyatkova, L. S. Stilbans, A. N. Voronin and the theoretical investigations of T. A. Kontorova, that formed the basis for thermoelectric generators and refrigerators. A generator of that kind, which utilizes the heat emerging from the glass of a kerosene lamp as a source of electricity for a radio set, is produced by the Soviet industry for use in distant regions and places where they do not yet use electric power.

Thermocouples made of semiconductors as well as photoelectric cells with a sealing layer may be utilized in order to convert solar energy into electric power with an efficiency that at present amounts to 5-6 per cent. With the help of semiconducting thermocouples, house refrigerators and other cooling apparatuses are being made.

A considerable number of Soviet physicists persistently work at the problem of semiconductors, their theory and technical application. There are laboratories where the investigation of semiconductors is being carried on, both at the Institutes of the Academy of Sciences and Universities, and industrial institutions.