Electronic Properties of Carbons – The Last 25 Years*

S. Mrozowski

Department of Physics and Astronomy
Ball State University, Muncie, Indiana (U.S.A.)

Abstract: The history of the development of ideas and of advancements achieved in knowledge of various electronic properties of chars, carbons and graphites is presented. The subject is discussed by considering four periods: the early years, when carbons were not yet recognized as a separate class of solids (pre-1949), the pioneering period, when organized and planned research was begun at various places (1949–56), the start of international cooperation and the consolidation of carbon science (1957–64) and finally the most recent period of detailed studies and advancements on many fronts (1965–74). The main problems awaiting solution are indicated and the importance of carbon studies for the general understanding of the electronic processes in disordered solids is emphasized.

1. Introduction

Twenty-five years ago, in anticipation of things to come, a small group of Japanese technologists and scientists decided on formation of the first in the world Carbon Society. There was no carbon science then as such; here or there some interest in carbon properties flared up at various times, but it was not yet generally recognized that carbons constitute a distinctive class of solids and no systematic efforts to unravel the secrets of these materials were undertaken. This was especially true in case of the electronic structure and electronic properties of carbons, which are the subject of this historical review. It was only around 1949 that in several parts of the world a number of people realized the opportunities presenting themselves in this field and started broadly planned programs of fundamental research. It so happens also that the year of 1949 was of great importance to me personally, because that was the year when I have left the carbon industry and started unconstrained research at the University of Buffalo. Since at the end of 1974 the Carbon Research Laboratory at the University of Buffalo, after 25 years of existence, will be ceasing its operation in connection with my retirement, this historical review gives me a most welcome opportunity to look back at the laboratory's contributions to understanding of the electronic processes in carbons, and to place them in perspective together with the rich harvest collected by others.

2. The Early Years (pre-1949)

Before starting my recollections of the way the field

has grown in the last 25 years, I like to remind the reader about the general situation as it existed in 1949 and about several of the earlier papers, which played the role of landmarks in setting the stage for the later surge in carbon research. After Hückel and London have shown early in the thirties that π -electrons become delocalized in benzene ring systems by providing the resonating Kékulé bond structures, Ubbelohde was quick in pointing out, that this mobility of π -electrons probably is the reason for the high electrical conductivity of graphite along the graphite planes (1936). The exceptionally high diamagnetic susceptibility of graphite, which was known to be at least by a factor of ten greater than the values calculated by London for small condensed aromatic molecules, attracted Pauling's attention, who made a try to find an explanation, by assuming a superconductive behavior of the π -electrons (1937). Soon after, Ganguli and Krishnan (1940) published the results of a most excellent experimental study of the anisotropy and temperature dependence of the diamagnetic susceptibility of a single graphite crystal. They gave a quantitative interpretation of the results in terms of the band theory assuming a metallic behavior of the π -electrons filling half of the strongly flattened hexagonal Brillouin zone polyhedron. However, several years later Wallace (1947) and, independently, Coulson (1947) have shown, that for a graphite benzene ring plane the π -band is not single, but splits into two touching bands due to the symmetry of the lattice, the lower band being completely filled with electrons and the upper remaining empty. At the point of contact the density $n(E)$ of energy levels being zero for a single plane, and finite for a tridimensional crystal, the graphite has been shown to be in the direction of the graphitic plane a semi-conductor with a zero energy

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band gap. Using this model Wallace has tried to evaluate the electrical resistivity of graphite and its temperature dependence, with some measure of success. The interest of Wallace and Coulson in the electronic structure of graphite was probably aroused by the by then publicly disclosed Fermi's application of graphite as moderator in nuclear reactors and Wigner's prediction of a gradual destruction of the crystalline structure by the neutron bombardment. Measurements of the electric resistivity were one of the ways for following the process of this degradation. Although research on neutron damage of graphite was continued after the end of the Second World War in the U.S. and in England and a large amount of valuable data amassed as well as interesting explanations proposed, this work, carried behind closed doors, had little, if any, influence on the development of the carbon field in its initial stages, until such time when the secrecy was partially lifted and some of the results began to be released for publication in the middle 1950's.

At the other end of the organic compound → carbonization → graphitization process, considerable interest developed soon after the end of the war in electronic structure and properties of condensed aromatic molecules. To avoid lengthy orbital calculations of energy levels, Bailey (1947) proposed a simplified model in quantizing the angular momentum of electrons travelling around the rings, and others expanded and refined it further. On the experimental side Eley (1948) obtained evidence of the intrinsic semiconductive nature of a crystal of one of such organic compounds. This sparked the interest of a number of people, among them of Akamatu and Inokuchi, resulting subsequently in development of a new important field of research, that is on organic semiconductors. The work on graphite on one hand and on condensed aromatic molecules on the other, coming at about the same time, created 25 years ago the proper background for directing the attention of a few researchers to the transition "from benzene to graphite."

3. The Pioneering Period (1949–1956)

Systematic and organized studies to unravel the secrets of the class of intermediary materials were started in several corners of the world. The work was mainly of a pioneering nature; a large number of new and interesting properties of organic materials on their way to carbonization and after they were carbonized was discovered and crude explanations in terms of various models attempted. There was little or no direct interaction between these groups at first, except for

reading each other's publications scattered over various more or less accessible journals. Thus the transfusion of information and of ideas occurred with much delay, the thinking in each group going on independently, although frequently in parallel. Hoping that someday we will hear from Akamatu, Blayden and Pacault their sides of the story, I will describe here the development of the events as we have seen them from Buffalo.

Having come from an industrial laboratory with a good background in carbon technology and applications and being convinced by then that carbons form a distinctive class of materials overlooked by physicists as a worthy field for study, I have tried to formulate a program of research on carbons which could be carried out by a group of physics Ph.D. candidates using the modest equipment available at our University. In the after-the-war period Riley has, with his collaborators Blayden and Gibson, carried out most fundamental X-ray investigations of the structure of carbons, on its changes in heat treatment from chars toward graphite, evaluating the crystallite sizes by means of the Warren's formula. A study of development of various electronic properties as it occurs in parallel with the changes in structure seemed as a very good starting point for our research. Diamagnetic susceptibility (Pinnick 1950–56) and thermoelectric power (Loebner 1950–56) were chosen, the first one because this property does not depend on electron scattering effects, and the second one simply because we did not have at the time a second magnet for Hall effect determinations. Having modified the Ganguli-Krishnan theory, so as to adapt it to the touching band model of Wallace, I was hoping to find an explanation of the changes in the magnetic susceptibility by the variation of Landau-Peierls diamagnetism of free electrons with size of the box (crystallite), and induced my theoretical colleague, H. Nye (1952) to look into this problem (a problem treated about the same time by Dingle, by Osborn and Steele and others, 1952–53).

All through the beginnings of our research we were not aware of the similar work carried out in England and France. In continuation of the work on the changes of structure in the process of carbonization and graphitization, Wynne-Jones and Blayden carried out (and were first to publish) a study of changes in diamagnetic susceptibility occurring in the process of carbonization (1952). In France Pacault, after having investigated the susceptibility of condensed aromatic molecules (while Pullman developed the theory), together with Marchand (1951–56) addressed themselves to an exhaustive study of diamagnetism of graphitic and pre-graphitic materials and to the changes occurring in the process of graphiti-

zation. In considering the electrons as a bi-dimensional degenerate gas, they developed a formula, which fits the experimental data in a wide range of temperature, and from which the degeneracy temperature of the gas can be evaluated. Although in subsequent years the diamagnetic susceptibility of graphite found a rigorous explanation in the work by Adams and McClure, its decrease for incompletely graphitized and more so for pregraphitic carbons from the Landau-Peierls down to the London diamagnetism is still not understood and constitutes one of the major problems awaiting solution. In view of this situation the Pacault-Marchand formula retains even today its empirical usefulness.

Knowing what the electronic band structure of the two terminal states is like, namely, for the organic crystal — an intrinsic semiconductor with a gap (Eley 1948) and for graphite — an intrinsic semiconductor with a zero gap (Wallace 1947), I was pondering on how the transition from one to the other in the process of charring — carbonization — graphitization could be described in terms of a band model. The transition going through highly disordered states, there was even no assurance that anything like a band model could be applicable. However, in absence of any other choice, I have assumed that there are bands and that the band gap gradually closes in the process. We have tried to check this assumption by studying the infrared absorption of a cellophane char, submitted to various degrees of heat-treatment (Kmetko 1951). In fact, a progressive decrease in the gap was found up to the point where the incipient conductivity covered the gap with continuous absorption. Just about that time we became aware of the work by Akamatu and Inokuchi (1950—), who in a beautiful series of studies investigated the semiconductive and photoconductive properties of polynuclear aromatic compounds, and demonstrated the presence of an energy band gap decreasing with increase in molecular size. This we felt was a good evidence that we are on the right track, and greatly boosted our morale.

I was aware however from the beginning, that a decreasing band gap alone is not sufficient to explain the peculiar plateau observed for soft carbons in the electrical resistivity in the heat-treatment range 1200°–2000°C. Much earlier in a very important but little known paper, Corriez (1937) has reported an increase in the resistivity of carbon blacks occurring in about the same range of heat-treatments. This paper had a strong impact on my thinking: how can the resistivity increase, when the mobility of the carriers has to increase with the growth of crystallites? Clearly then this must be due to a decrease in concentration of carriers, formed in abundance in the charring-carbonization range (700–

1000°C) and then gradually disappearing by anneal at higher heat-treatments. Since, for a number of reasons, the corresponding donors or traps could not possibly be due to impurities, they had to originate from some kind of centers in the carbon itself. Thus was the band model born, which I suggested in 1950–52, and which became a stimulus and a guide to our research through the next several years, permitting us to formulate problems and design experiments for their solution. To our delight, as long as we did not insist on details, our results seemed to support the model on broad terms. Let me here recount an amusing incident: we have believed originally the extrinsic carriers to be electrons on basis of the sign of the thermoelectric power. But a slip was made due to a mixup in electric terminals and lack of clarity to the student of the definition of the sign of the power. Actually the carriers are holes and the defects are traps; we published a correction as soon as we realized this, but we were told later that our mistake caused some frustration, delays and checks and rechecks behind closed doors, where at that time the Hall effect of irradiated graphite was being investigated.

In the early fifties the growing interest in the mechanism of electrical conductivity of carbons became evidenced by a number of short publications (Bowen, Okada, Mizushima, Tsuzuku). Bowen and others connected with the reactor research tried hard to interpret electronic properties of partly graphitized and also of neutron damaged polycrystalline graphite strictly in terms of Wallace's theory. Very soon after the final publication of my model, in analyzing experimental data, I realized that the bands in graphite must slightly overlap, and having heard from Polder the results of his theoretical conclusion that interlayer interaction might cause either a gap or an overlap, I went ahead and published this prediction (1953). Most of the people continued, however, to believe in the touching band model of Wallace, some of them as late even as 1956. I know of some theoretical papers in which the overlap was derived in 1954 and which were rejected from publication for insufficient rigor — but finally Slonczewski and Weiss (1955) gave a clear proof of the overlap, and McClure (1956) refined the band theory of the graphite crystal to a point where an experimental check of several parameters could be carried out by others (Soule 1957, Wagoner 1959).

In studying the Hall coefficient as a function of heat-treatment with Chaberski (1955), at various temperatures, we found good evidence that the overlap of bands must already occur for soft carbons at HTT of about 2200°C. Furthermore, we noticed in that range the occurrence of a negative magnetoresistance, which we

could observe even at room temperature. This finding met at the time with general disbelief, some people suggesting contact troubles as an explanation (at an APS meeting in 1956). However, in subsequent years the negative magnetoresistance has been found also in many other materials and became a recognized electronic property deserving detailed experimental and theoretical studies.

In 1951 Hennig published a very important paper on electronic properties of Carbon - Bisulfate lamellar and residual compounds, which was followed soon by more publications on other compounds. At about the same time, Ubbelohde and his coworkers started their long series of researches in this field. Modifications brought about in electronic properties of graphite by neutron irradiation were investigated by the Harwell group in U.K. (Kinchin 1953) and by the Argonne and North American Aviation groups in U.S.A. (Hennig and Hove, 1955). Although the original assumption that the band structure is little affected by neutron damage, by formation of a compound or by doping, can at best only be a very rough approximation, its use requiring great caution, the doping of carbons and graphites by donors and acceptors became a very useful tool in studies of electronic properties of carbon.

Electron spin resonance, becoming rapidly in the late forties a very important tool for investigation of behavior of electrons in solids, Castle has begun assembling an apparatus for such a study at our laboratory in 1951. In the Fall of 1953 Castle finally succeeded in obtaining good signals for cokes and graphites in the heat treatment range 1500°–2800°C first using the ESR apparatus at Yale, and then continuing the work on the Buffalo instrument. Actually the ESR was discovered some weeks earlier by Hennig and Smaller at Argonne Laboratory in polycrystalline graphite as such and after irradiation. At the time Castle was sending out his Letter to the Editor of the *Physical Review*, Hennig and Smaller were presenting a more exhaustive paper at a meeting behind closed doors. Unfortunately the slow workings of the declassification office have prevented Hennig and Smaller from publishing quickly their findings and to become generally recognized as the discoverers of the ESR in graphite.

Events began to roll fast, after Ingram and, independently, Uebelsfeld found a very strong resonance absorption in chars and coals which, in contrast to the carbon resonance, was found to be strongly oxygen sensitive (1954). A number of people started trying their hand on such experiments, but most did not succeed in adding much to what has been established in series of excellent papers by Ingram and by Uebelsfeld.

The exception was the highly precise study by Singer and Spry (1956) which clarified a number of additional points. This last work emerged from an industrial research laboratory (Union Carbide Corp.) which became very active in the middle fifties after having attracted a number of excellent researchers. Thanks to some relaxation in restrictions, a number of very important and interesting papers were released for publication by this laboratory.

The accelerated pace of development of the field in the middle fifties was due not only to formation of new groups interested in the carbon field, but also to breaking down the publication barriers imposed by the reactor secrecy or by the industrial competition. To a great extent this was forced about, I believe, by the advances achieved by those who worked in the free academic atmosphere, convincing everyone that exchange of information will be beneficial to all groups concerned.

4. Great Hopes and Disappointments (1957–1964)

Whereas the first Carbon Conference (1953) was designed purely to acquaint the industrial community of the area about the research work carried at the University of Buffalo, the larger Second Carbon Conference (Buffalo 1955) gave an opportunity to the American groups to get together and exchange information. The still larger Third Conference (Buffalo, 1957) brought about the same on an international level. Those who took part in that Conference will never forget the enthusiastic response of the audience to the presentations in the symposium "From Benzene to Graphite." The rich harvest collected through the previous years was presented at that symposium, as well as in contributed papers, by key people and enhanced by interesting comments from the floor and even more so by lively discussions at informal meetings of the participants. The great strides made in understanding of the electronic processes and properties of carbons, seemed to justify high hopes for early victories.

The several years following the Third Conference were years of consolidation and reappraisal of the advances achieved. The publication of the Proceedings helped to develop a feeling of belonging and created "esprit de corps" among carbon researchers throughout the world. Information was exchanged freely and the pace of carbon research accelerated. In case of electronic properties the availability of new types of carbon materials just developed, such as pyrolytic carbon or glassy carbon created new opportunities for the experimenters. Big advances were achieved in the understand-

ing of electronic band structure and diamagnetic susceptibility of graphite, and of turbostratic systems. Cyclotron resonance was found (Galt 1957), and the startling variation in magnetic susceptibility (and its anisotropy) of pyrolytic carbons resulting from structural changes as the material is heat-treated was investigated and explained by Fischbach and by Pacault and his group (1961). Since the band structure of perfect graphite has been found at the zone edges to be much more complicated than originally anticipated and there were good reasons to expect that these details are strongly modified by perturbing influence of defects, Klein (1961-) has tried to analyze, with considerable degree of success, the various electronic properties of well and incompletely graphitized pyrolytic carbons and their temperature dependence in terms of a simple two band model. However, all efforts to find a detailed two band model to explain the properties of pregraphitic carbons met with failure. Towards the end of this period one gradually came to realize that none of the simple models can give a satisfactory description of all the various electronic properties of a carbon at the same time. This led Pacault to advance the view, that models being derived to explain one or another of the properties, should not be expected to possess any wider applicability than for what they were originally designed, certainly a pessimistic view, which however was hard not to share.

Important advances were achieved in the electron spin resonance. Wagoner (1959) has shown that the ESR in graphite is due solely to conduction electrons, and the same has been shown by Singer and Wagoner (1961) to be the case for well graphitized polycrystalline materials. Studies of the temperature dependence of the ESR absorption in pregraphitic carbons carried out by various people culminated in the realization that the single ESR line in carbons is due to conduction carriers and to localized spins, thus leading to a technique for determination of the relative contribution of the two types of spins (myself and, independently, Marchand and Delhaes, 1963). As far as nuclear resonance is concerned, some preliminary experiments on double resonance were carried out on protons in chars and on C^{13} in graphite (Abragam 1957), and the interaction of paramagnetic centers of the coal with protons from hydrogen containing fluids adsorbed on the surface was studied (Uebelsfeld 1959).

A specific difficulty in exact evaluation (and comparison) of various electronic transport properties for carbons is frequently created by their inhomogeneity on macro- and microscopic scale, such as porosity of various kinds, two component composition, or by their

state of comminution (powders, carbon blacks). Some efforts were made in the fifties and early sixties to work out proper correction factors, with some degree of success. However, it must be noted, that throughout the recent decade this problem disappointingly has been left untouched.

5. Big Strides (1965-1974)

The Tokyo (1964) and the Cleveland (1965) Conferences, and the publication of the two volume book "Les Carbones" by the French can be considered as the end of the consolidation period. Realizing that the actual band structure of carbons must be very different from any of the originally anticipated, one had to reassess critically the situation, and start a sober program of painstaking detailed studies of each of the electronic properties, in as wide temperature range as possible. As a result in these last 9-10 years many remarkable advances were made on various fronts. Since the volume and diversity in the research have greatly increased, it would take much space to discuss it all. Furthermore, it becomes more difficult to evaluate objectively the importance of more recent events, not having advanced knowledge of their subsequent impact on the field. One can obtain a pretty good impression of the developments through this most recent chapter of history by looking through the volumes of the *Carbon* journal and of the *Chemistry and Physics of Carbon* and try to reach a personal evaluation. I will therefore, mention here only those few avenues which, according to my personal view, seem to be most informative or most promising for the future.

Much has been done for graphite crystal in elucidating the fine details of the surprisingly complex π -band edge structure in theory (McClure) and in various experiments; for instance in magneto-optics (Dresselhaus), and in trying to determine the broad structure of the bands through application of modulation spectroscopy. The magnetic properties of rhombohedral graphite were studied by Gasparoux (1966) and the details of band structure clarified by McClure (1969). Striking electronic effects in well graphitized materials were observed and investigated by Mizushima (Esaki kink effect 1972) and by Tsuzuku in magneto-thermoelectricity (1973). The electric conductivity in direction transverse to the graphitic planes was investigated and some advances in clarifying its mechanism were made (mainly by Ubbelohde and his group). The large increase in conductivity (in the plane as well as across) occurring with formation of layer compounds received lately an increasing attention, stemming from a desire to develop

new highly conductive nonmetallic materials for industrial use. Superconductivity at very low temperatures (below 0.5°K) in graphite-alkali metal and other layer compounds was discovered by Bell Telephone people. Recently some efforts are made in Japan and in the U.S.A. to study the details of the band edge structure of such layer compounds.

The technique of introduction of donors or acceptors by way of layer and residual compounds, by substitution (Boron) or by introduction of defects (neutron damage) has been very widely used in the past decade. The influence of various dopings on the magnetic susceptibility of carbons and graphites was investigated by Marchand and Delhaes (1964–67), and on the electric conductivity, on the Hall coefficient and on the magneto-resistivity at Buffalo by a number of people (1965–71). Two effects relating to compounds seem to be quite remarkable and deserving further studies: the reversal in behavior of acceptors when introduced into soft carbons of HTT below 1800°C (Buffalo 1969) and the presence of a phase transition in residual nitrate compounds below room temperature (Tsuzuku 1975, the phase transition having been discovered earlier in ordered layer compounds by Ubbelohde).

The use of decomposition procedure of the ESR absorption into contributions of localized and of conduction spins, the applicability of which was established earlier (Section 4), has permitted to achieve some advances in understanding of the behavior of spins in carbons in absence and in presence of dopants. The variations in *g*-values and widths are no more so mysterious as they used to be. The work of Honda and collaborators on phenolformaldehyde resins (1970), supported by work of others, has shown that the ESR does not disappear in the so-called transition region of heat treatments (1000–1400°C), as was widely believed in the fifties and early sixties. The large broadening of the ESR line occurring in the transition region was recently shown by me to be connected with some changes in the structure of carbons and irradiated graphites, but the exact cause could not be ascertained (1972). The usefulness of the ESR studies has been amply demonstrated in the work of Lewis and Singer (1965–69), who analyzed the process of charring of simple organic compounds. In spite of all these advances the nature of the air sensitive spin centers in chars, and of the air insensitive localized spin centers in carbons and graphites remain as elusive as they always have been, and their relationship to traps removing electrons from the π -band, if any, is still not understood.

Studies of Hall coefficient and of ESR absorption of variously doped carbons led me to the realization that

most probably throughout the whole range above carbonization (when presumably all band gaps have closed) up to the beginning stages of graphitization contrary to earlier conjectures, there is a strong band overlap present (this was shown by experiments only for the higher range of HTT's — from 1600°C up), the overlap going through a minimum at the beginning stages of graphitization (HTT ~ 2100°C). This led me to a reformulation of my old band model for soft carbons (1969). Except for the overlap and for the Fermi level being depressed by the presence of traps, nothing more definite can be claimed for the HTT range 1000–2000°C. Certainly the lack of any reliable theoretical model of electronic level structure for disordered solids represents here a major hurdle. As I have pointed out at that time the presence of strong interaction of conduction electrons with local lattice vibrational modes might be a serious difficulty preventing formulation of a purely electronic band model for disordered solids. But specifically in case of carbons the split of the π -band into two parts caused by the symmetry of the benzene ring plane having two atoms per unit cell, might become less and less meaningful as disorder is introduced. Thus the partial fusion of the two π -sub bands might result from the loss of order.

Negative magnetoresistance has been widely investigated by various people in the last decade and shown to correlate well with the concentration of defects in the lattice. Its presence has been established even for well graphitized materials, however only at very low temperatures and at very low magnetic fields, the negative magnetoresistance saturating at higher fields (Hishiyama 1970). The angular dependence and the question of additivity of both types of magnetoresistance were studied in detail by Delhaes (1972). The negative magnetoresistance was shown not to depend on position of the Fermi level (Toyoda and myself, 1969) and not to be due to interaction with localized spins (Hishiyama, myself and Vagh, 1971). An explanation proposed by Fujita (1968) in spite of some very attractive features misses some essentials. Yazawa has reported remarkable results obtained on pyrolytic carbon materials, and proposed recently a different explanation of the effect (1966–74). However there are still many questions left unanswered and the problem of negative magnetoresistance must be considered as one of the big unsolved problems in the carbon field.

Carbon fibers, having gained a great technological importance, attracted attention of a number of people. Among others, some very informative work was done by Ingram and his collaborators (1970–72). To me personally, however, the new findings in electronic properties

of carbon films seem to be even more promising. Whereas the presence of an infrared band gap (Mizushima and Fujibayashi, 1967) can be interpreted in terms of the probably preferential diatomic or polyatomic (C_4 , C_6) structure of deposited evaporated carbon, the effects reported by Antonowicz and his group (1970–74) are not only most striking, but might open some new possibilities in our quest to unravel the secrets of electronic processes in highly disordered solids. Switching from a high resistance to a low resistance state and reverse switching were observed to occur with application and reversal of sufficiently high potential to a carbon film sandwiched between Aluminum electrodes. Yazawa (1974), using a gold electrode, has recently shown that this switching effect most probably occurs at the contact surfaces between the Al-metal (oxide?) and the carbon. The second effect observed by Antonowicz is a stepwise change in conductivity of such films in a magnetic field (or microwave field) closely reminding the Josephson junction effect observed in superconductors at very low temperature. Antonowicz believes that the effect is due to small superconductive regions existing inside of the carbon material and recently found some quantitative support for this assertion. Clearly if this is a superconductivity occurring at room temperature it must be of a very different nature than the one we are familiar with at low temperature.

Before closing I like to mention a new avenue which opened up recently for a study of interaction between spins in chars, carbons and graphites. It seems pretty certain now, that low temperature specific heat anomalies observed and investigated at Buffalo (1970–) are due to presence of localized spins in these materials, the

large linear term being analogous to the one observed in some metal alloys, whereas the peak (or peaks) below $1^\circ K$ being caused by formation of an antiferromagnetic phase. Detailed studies of these effects might not only contribute to our knowledge of carbons, but become a possibly unique source of information on behavior of and interactions in randomly distributed spin systems.

6. What's ahead?

I have tried to show in this presentation, that studies of electronic properties of carbons present a very wide and promising field for further research. Although a great number of new facts has been collected and some not anticipated relationships found, until now we have not succeeded in resolving any of the major fundamental problems yet. Whereas one can blame partly these failures on the state of the present day physics, which has not yet been able to penetrate the darkness surrounding the mechanism of electronic processes in disordered systems, we have to take heart in the fact that this state of affairs continues to offer the carbon researchers the unusual opportunity for contributing to the clarification of the most fundamental problem of today's solid state physics. After all, this was the main reason why the research on electronic properties of carbons was started 25 years ago by us, oldtimers. Let's hope that our younger colleagues will not miss the opportunity which is still before them, and that in the next decade we will be witnessing most remarkable developments in the carbon field.

要 旨

炭素の電子的性質—最近の25年間の歩み

炭素および黒鉛の種々の電子的性質を理解する過程でなされた着想の発展ならびに達成し得た進歩に関する歴史を紹介する。主題は四つの期間すなわち、炭素が未だ分離された固体として認識されていなかった黎明期(1949年以前)、組織化されかつ計画された研究が種々の研究場所で開始した開拓期(1949–1956年)、研究の

国際協力がはじまり炭素の科学の整理統合がおこなわれた期間(1957–1964年)、多くの先駆的な内容に関する詳細な研究と進歩とがあった最近時(1965–1974年)に分けて論ずる。解決が待たれている問題を提示し、さらに一般の非晶質固体の電子固体を理解する際炭素の研究が非常に重要であることを強調する。