

PROGRESS ON THE RESEARCH OF SOLID STATE PHENOMENA AND MATERIALS

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Introduction

The field of molecular electronics will, without doubt, tax the technical abilities of both scientists and engineers in an effort to relate the multitude of solid state phenomena with the many necessary circuit functions. To clarify any misinterpretation of the words "Molecular Electronics" let the following serve as a definition for the purpose of this paper: The molecular electronics concept implies a composite electronic circuit which utilizes the intrinsic properties of atoms and molecules in the solid state (both individually and in combination) for the performance of complete circuit functions.

Before utilization of solid state phenomena for the performance of circuit functions can be realized, it will be necessary to satisfy certain fundamental requirements. To state these requirements involves only some logical thinking; the fulfillment will come only after much future effort. These requirements are considered to be the following; (1) the available solid state phenomena must be well understood, (2) a classification scheme permitting rapid reference must be developed, (3) mathematical techniques must be developed which will permit synthesizing molecular circuits, and (4) relationships between phenomena and function must be obtained.

The Electronic Technology Laboratory at the Aeronautical Systems Division, formerly the Wright Air Development Division, has a dual purpose basic research program in progress to spearhead realization of the concept of molecular electronics. The first goal is to understand and classify solid state phenomena; the second is to mathematically relate phenomena to circuit functions. This basic research program is directed by the Advanced Techniques Branch of the Electronic Technology Laboratory in such a manner that the contractual efforts are designed to complement in-the-house research tasks. The Georgia Institute of Technology, under contract to the Electronic Technology Laboratory, is assisting in a survey and study of the known solid state phenomena. Two reports (1,2) on this survey, currently being printed at the Aeronautical Systems Division, will provide a first attempt at compiling a partial handbook of solid state phenomena. Related studies sponsored by Electronic Technology Laboratory at the University of Pennsylvania and the University of Michigan are also in support of the molecular electronics program. Another program sponsored by Electronic Technology Laboratory at the Catholic University of America will also be briefly mentioned because of some very significant results recently attained by Prof. C. F. Pulvari of that University. Progress on these programs as well as related in-house efforts will be discussed in this paper.

Although desirable, it is not to be implied that these efforts provide a panacea for all the problems encountered, or to be encountered, in the molecular electronics program. Rather they are designed to provide the basic research that will permit us to take that gaint step down the road to truly new, effective, and efficient electronic systems.

Classification

The program at the Georgia Institute of Technology is designed to provide a summary of physical phenomena related to the solid state of materials. One of the goals of the study

is to gather together into a single source the physical phenomena pertinent to the solid state field. The second and concurrent goal is to devise a classification system which will focus attention on possible undiscovered phenomena and which will enable a design engineer to obtain the phenomena information he needs in a useful form, one in which he is not required to conduct literature surveys each time a circuit function problem arises. To date, only a general classification scheme has been formulated from this program. The approach has been the division of phenomena into three broad groups and then the subdivision of these groups into subgroups containing specific phenomena.

Group I includes those effects which depend upon the transport of electrons and holes and those which are intimately associated with band structure. Examples of subgroups in Group I would be (a) Galvanomagnetic and Thermomagnetic effects, (b) Semiconductor effects, (c) Electron Emission Phenomena, and (d) Energy Band Phenomena. Typical phenomena under these subgroups would be, for (a) Hall Effect, for (b) Conductivity Modulation, for (c) Photoelectric Emission and, for (d) Cyclotron Resonance. Group II concerns those effects primarily related to the dielectric properties of materials and transport phenomena for particles other than electrons and holes. Some examples of Group II subgroups would be (a) Mechanical Effects, (b) Optical Effects, and (c) Transport Phenomena. Typical phenomena that would be discussed under these subgroups would be; under (a) Magnetostriction, under (b) Faraday Effect, and under (c) Exciton Transport. Group III includes resonance effects, that is, effects which can be described in terms of discrete energy levels rather than energy bands. Possible subgroups of Group III would be (a) Resonance Effects and (b) Special Devices. Typical phenomena listings under these subgroups would be, for (a) Nuclear magnetic resonance and, for (b) Maser action. The reports soon to be released will contain 63 solid state phenomena in a format which includes a definition, a qualitative explanation, a mathematical description where possible, an indication of the magnitude of the effect, special interesting features, and an annotated bibliography. It is hoped that the wide dissemination of these reports will spur others in the field to investigate possible classification systems.

Another approach to the classification problem was developed within the Electronic Technology Laboratory by R. D. Larson and J. M. Blasingame (3) who indexed some 147 phenomena using a rectangular coordinate system. This system labels the positive portion of the X, Y, and Z axes with appropriate input or output information. The X and Y axes were inputs and the Z axis outputs. For a particular circuit problem an engineer would look on the X-Y axes for the available inputs and compare these with possible output information obtained from the Z coordinate. The intersection would be a cube containing a listing of phenomena having the features originally compared. The engineer then would use appropriate texts for detailed phenomena information.

A third approach being considered at Electronic Technology Laboratory by the author is the development of a "slide-rule of phenomena" which would facilitate finding rapidly certain information about known phenomena and possible relationships between phenomena. This approach requires a logical and sensible use of symbols so that related effects such as the Nernst and Ettinghausen - Nernst Effect will be clearly evident. Much work remains to be done since it is uncertain at the moment if sufficient information can be displayed in a "slide-rule" manner.

There are definite differences between the two classification systems previously mentioned and both have certain inherent short comings. These will be mentioned not to criticize but to point out some of the problems involved in devising a usable system. First of all under the Group-Subgroup System, effects such as the Hall effect, and the Righi-Leduc effect would be grouped together since they fall in the category of Galvanomagnetic and

Thermomagnetic effects. In the rectangular coordinate system they would not be grouped together since their outputs are different (one is electric, the other thermal) and in this system it is the form of the output which determines the phenomena grouping. In addition, neither system currently contains provision for including such effects as those caused by chemical adsorption and nuclear radiation both of which could constitute inputs to a particular system. For example, surface effects on certain junction devices can account for a considerable change in electronic properties (4,5). Chemical adsorption, nuclear radiation phenomena and other presently unclassified phenomena create problems because their effects on a completed system or when used in materials processing may change the nature of the output of an existing phenomena or they may create new phenomena. It would be possible, of course, to keep adding new categories to both of these systems so that eventually all possibilities would be included. The shortcomings of the existing systems are fully realized by personnel in the field. The important point is that the ultimate goal is to devise a classification system which is more basic and more accurate than any existing now. The present systems provide some idea, at least, of the information which must be available from any finalized classification scheme.

Past successes on in-house programs as well as on contractual studies indicate that a good classification system must be based on such fundamental considerations as, the types of chemical bond involved, the interaction of electrons with the periodic lattice of the solid, the quantum mechanics and classical mechanics involved in dielectric polarization, and the fundamental relationships of magnetization in all its various forms, to mention just a few.

The extensive literature survey which so far has resulted in the classification (by one system or the other) of approximately 147 solid state phenomena is only the beginning of the job yet to be accomplished. There are several reasons for this. First of all, many of the phenomena applicable to the solid state were discovered at times when the scientific community was either unable or unready to utilize them. For example, the Peltier Effect was known long before there were suitable materials available for extensive application. The Seebeck Effect was known and used for some time, but lack of the proper materials kept efficiencies lower than desirable. The Nernst Effect is a reasonably familiar phenomena but it has yet to be put to any great use such as in the generation of electrical power.

There are many so-called lesser known phenomena about which comparatively little is known, that is, the specific phenomena is observable but the basic physical explanation is still lacking.

There are still many solid state phenomena which have never been extensively investigated but which show some particular promise for molecular electronics.

More intriguing still, is the possibility of discovering either new phenomena or new materials or both as the result of the intensive study of, and comparison between, various existing phenomena.

Phenomena and Materials

There have been some promising results even this early in our program. At Georgia Tech., Dr. Schiebner has uncovered the possibility of a new effect, the modulation of magnetic susceptibility by an electronic field. Evidence to date indicates that the effect should be observable in thin films of the transition metals and compounds. Some preliminary experiments are in progress to actually observe the effect. These experiments

involve the measurement of the change in frequency of an oscillator operating at about 9 megacycles when a nickel film is inserted into the coil of the tank circuit.

New materials have also been discovered as a result of the phenomena approach. Prof. C. F. Pulvari, mentioned above, has found a new group of materials exhibiting ferroelectric behavior (6). These materials are composed of two antiferroelectric materials and have been discovered in the mixed crystal of sodium-vanadate-niobate. These new materials have been named "ferrielectrics" because of their analogy with ferrimagnetic materials. The reader is referred to reference (8) for details. It is interesting to note that chemical analysis of these crystals has not yet been accomplished because no suitable solvent has been found. These crystals were even insoluble in hot hydrofluoric acid. The important point here is that the state of the art was advanced as the result of a specific phenomena investigation.

There is another example worthy of brief mention here because it incorporates the same considerations concerning the chemical bond, that we believe must also be the foundation of a good classification system. During an in-house study, an effort was made to deposit pyrolytically a thin film dielectric which would possess good stability at high temperature, a high breakdown voltage, and low neutron cross-section.

From the viewpoint of dielectric properties only, the materials considered were boron nitride, aluminum nitride and silicon nitride. However, from neutron cross-section data, the boron compound was eliminated from further consideration. The nitrides of aluminum and silicon have covalent bonding, that is, complete electron sharing which links all atoms together in the solid. Greater stability was predicted for these compounds because a larger number of bonds would have to be broken to effect rupture by voltage breakdown. Furthermore, theoretically, there should be no free conduction electrons available, at least until higher temperatures are reached, if the material has sufficient purity. From the values of standard free energy of formation of the compounds from their elements, it was predicted that silicon nitride would be the most stable of the three. Chemical resistance to attack by acids, water, and oxidation also supported the above conclusions. As a result of this preliminary work, Barnes and Geesner (7,8) deposited pyrolytically thin adherent nonporous films of pure silicon nitride from the vapor phase on hot molybdenum substrates. These films maintained satisfactory dielectric properties to temperatures exceeding 600°C. As a protective coating, these films protected metal surfaces from atmospheric oxidation to temperatures exceeding 1000°C.

These are but a few examples of progress to date. They supply proof that the study of solid state phenomena is not only desirable but necessary. More important, they are helping us to pinpoint the most important basic physical considerations which must be used in the formation of a phenomena classification system. In contrast to the Georgia Tech. program mentioned earlier, the Electronic Technology Laboratory's program at the University of Pennsylvania under the direction of Prof. M. E. Caspari, is concerned with more specific phenomena and materials. This program was designed to contribute information necessary to understand more fully some of the basic physics involved in certain phenomena.

A brief discussion of some of the studies being conducted under this program may be of interest here. The immediate objectives of this program were: (1) to study the electrical properties of mercury atom aggregates, (2) to explore the Faraday rotation effect in semiconductor materials, (3) the investigation of new compounds that may have promising semiconductor properties, (4) certain properties of insulators, and (5) the determination of the physical properties of alkali halides, molecular crystals and magnetic

materials. The initial technical report (9) contained some very interesting preliminary results which are summarized in the following paragraphs.

The electrical behavior of gases such as mercury was expected to be of theoretical interest because the conduction process is closely related to that of impurity band conduction in semiconductors with the obvious exception that atoms in the gaseous state are more mobile. Experiments to date have not been successful because the conductivity of the quartz vessel containing the gas was found to be too large at the temperatures required to obtain a sufficient high density gas and this obscured the conduction in the gas. Suitable containers are presently being sought.

The Faraday rotation studies were performed to determine the effectiveness of using this technique to obtain information about the effective masses, relaxation times, and mobilities of the charge carriers in semiconductors. However, extremely pure crystals maintained at very low temperatures (e.g., liquid hydrogen, liquid helium, etc) are necessary because of the requirement that the mean free path of the carrier be sufficiently large to permit the observance of cyclotron resonance. Since it is not possible in all cases to prepare samples of sufficient purity for cyclotron resonance studies, it would be of value to know how much information could be obtained using a more convenient technique, such as Faraday rotation. Experiments conducted under this program demonstrate that specific information can be obtained about the effective masses, relaxation times and Hall mobility using the Faraday rotation technique. There are also indications that this technique can be applied to powdered samples.

Under the subject of new compounds, this program has yielded some very interesting data concerning the dissolution of alkali metals into the lattice of tungsten trioxide. In particular it was reported that silver tungsten trioxide is a semiconductor possessing a rather complex resistivity vs. temperature function. The aluminum borides which belong to the binary defect system, were found to have very high resistivities but behaved like impurity semiconductors.

The electrostrictive properties of oriented single crystals of rutile (TiO_2) were investigated. It was shown that rutile possesses one of the largest electrostrictive effects ever observed ($\approx 10^{-8} \frac{\text{cm}^2}{\text{Statvolt}^2}$) although it is not a piezoelectric crystal because of its centrosymmetric structure.

A new technical report (10) currently being printed will detail progress to date on the alkali-halides, molecular crystals and magnetic materials. This report will describe experiments on the alkali halides designed to yield information as to whether the ionization of excited F-centers by electric fields can be considered a Zener type tunneling or an impact ionization process. Of particular interest in the investigation of magnetic properties are the novel features designed into a Foner (10,11) type vibrating sample magnetometer. The revised design has yielded a device capable of controlling temperatures between 10°K and 600°K , yet is only 1/4-in. thick and 2-in. wide. This instrument is currently under test at the University of Pennsylvania. A torsion anisotropy apparatus will also be described in that report. Measurements of magnetocrystalline anisotropy are of interest since theoretical considerations permit the prediction of the relationship between anisotropy and magnetization as a function of temperature. Since there is little reliable data at low temperature, these studies are expected to add to a better understanding of low temperature-magnetic anisotropy.

Earlier in this paper, it was stated that mathematical techniques must be developed which will permit synthesizing molecular circuits. This is the ultimate goal of the work being sponsored at the University of Michigan under the direction of Dr. W. M. Brown. Although no reports on the project are available yet (12), there have been a few individual papers published (13,14). This program is intended to provide the mathematical foundations for the future utilization of physical phenomena for the performance of electronic circuit functions. It is the study of nonclassical circuit analysis and synthesis to describe the role of general circuit blocks in sensor and communication systems, and to mathematically characterize important classes of circuits which fall outside the scope of very restricted classical theory. Under consideration is the possibility of developing an operational theory for certain linear time invariant systems. Special problems of interest here are the application of operational methods to non-linear problems and the possibility of a general classification of the equivalence of certain non-linear problems to problems with time varying parameters. Since this program is relatively new, it will be sometime before any detailed reports are circulated. However, at the present time it appears that these mathematical studies will eventually help us in relating solid state phenomena with electronic circuit functions.

In-House Research

Because of the nature and goals of the molecular electronics program, the study of materials in thin film form is intimately related to all solid state phenomena studies. The Advanced Solid State Section, Advanced Techniques Branch of the Electronic Technology Laboratory has an energetic internal research program designed to add new knowledge to the field of thin film growth by the sputtering, vacuum evaporation, and pyrolytic deposition techniques.

Some mention has already been made of the pyrolytic deposition of silicon nitride (7,8). The ideal goal of our pyrolytic work under the direction of Dr. Barnes is eventually to be able to deposit any material desired on any substrate desired and to study the interface problems of multiple layer deposition. Several hundred materials have been deposited in thin film form and much of the information gained has enabled a less empirical approach to this technique. For example, the deposition of boron nitride films at relatively low temperatures (500°C). Previously, deposition of boron nitride thin films was accomplished at temperatures of the order of 1400°-1600°C which made it impossible to use certain substrates. The low temperature technique permits the use of many more substrate materials.

Sputtering and vacuum evaporation studies are under the direction of Dr. E. B. Henschke, who has contributed much new information to the interpretation of sputtering phenomena. Most notable has been the "Henschke Theory" which explains many of the sputtering phenomena heretofore not explained by existing theories. Ample references are listed for those interested (15,16,17,18,19).

Studies such as these will eventually enable the growth of new materials designed to display specific solid state phenomena for use in molecular electronics.

Conclusion

It is fully realized that the foregoing information covers a considerable range of interest. However, with the vast number of organizations now working toward the realization of molecular electronics, it is imperative that maximum communication be maintained between researchers in the field. The basic physical explanations of solid state phenomena

have really only been under serious study for approximately the last 15 years. Much work is yet to be accomplished since phenomena must be understood completely before a meaningful classification system can be formulated. If a successful classification system is developed then the last step of tying together phenomena and electric function should enable the realization of the molecular electric concept.

APPENDIX

The following addresses are listed for those who desire to obtain the references listed in the bibliography.

References Nos. 1, 2, 3, 9, and 10 can be obtained from:

Aeronautical Systems Division, ASRNEA,
ATTN: Mr. J. M. Blasingame, Wright-Patterson AFB, Ohio

References Nos. 4 and 5 can be obtained from:

The Institute of Technology, MCLI,
ATTN: Dr. W. C. Lehmann, Wright-Patterson AFB, Ohio

Reference No. 6 can be obtained from:

Prof. C. F. Pulvari, Electrical Engineering Dept.
Catholic University
Washington, D.C.

References Nos. 7 and 8 can be obtained from:

Aeronautical Systems Division, ASRNEA,
ATTN: Dr. C. R. Barnes, Wright-Patterson AFB, Ohio

Reference No. 12: Requests for future distribution of this report should be addressed to:

Aeronautical Systems Division, ASRNEA,
ATTN: Mr. G. R. Branner, Wright-Patterson AFB, Ohio

References Nos. 13 and 14: Submit requests directly to:

University of Michigan, Willow Run Laboratories,
ATTN: Dr. W. R. Brown, Ann Arbor, Michigan

References Nos. 15, 16, 17, 18, and 19 should be requested from:

Aeronautical Systems Division, ASRNEA,
ATTN: Dr. E. B. Henschke, Wright-Patterson AFB, Ohio

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13. Brown, W. M. and Palermo, C. J. - "Theory of Coherent Systems" (to be published in the IRE Transaction on Information Theory)
14. Brown, W. M. - "Area Transforms" - (to be published), Institute of Science and Technology, University of Michigan.
15. Henschke, E. B. - "Dynamics of Sputtering Phenomena" WADC Technical Note 55-474, June 1955, Aeronautical Systems Division, Wright-Patterson AFB, Ohio.

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16. Henschke, E. B. - "Deposit Spot Patterns from Low-Index Planes of Metal Single Crystals in a New Theory of Cathode Sputtering" Journal of Applied Physics, Vol. 28, No. 5, April 1957.
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