THERMOELECTRIC PROCESSES AND MATERIALS

by

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1.0 Introduction

This report covers the period from January 1, 1963 to July 1, 1964. A bibliography was submitted in lieu of a progress report in July 1963. No progress report was submitted in January of 1964 since several major pieces of work were very near completion and technical reports have been prepared on these projects.

The theme of the research reported here is the investigation of basic properties of semiconductor materials which are of importance in energy conversion applications, and the study of physical mechanisms involved in energy conversion. Much of our recent effort has been directed toward a theoretical understanding of a particular semiconductor (PbTe). The theoretical calculations reported here have suggested several experimental investigations which are now being pursued. The theoretical work has been done in conjunction with Professor Pratt's Materials Theory group; this collaboration has been a fruitful one and we expect to continue it in the future.

Section 2 of this report deals with investigations which have been completed. These are described fully elsewhere (in Technical Reports and Theses) and the abstracts are reproduced here for information.

Section 3 presents the status of continuing investigations, and Section 4 gives some information about projects which have been discontinued as unprofitable at this time.

A list of publications for the period covered by this report is attached.

2.0 Summary of Completed Investigations

The research reported in this section has reached a stage where a formal report has been made. In most cases, this is in the form of a distributed technical report; occasionally, the report is in the form of a thesis. Abstracts of these investigations are given below.

2.1 Mechanical Energy Flow in Crystal Lattices, L. M. Magid, Phys. Rev. 134, A158 (1964).

(The material in this article and the following one is based on Technical Report No. 3, May 12, 1962. It has been rewritten and somewhat extended. Reprints of these two articles will be distributed as Technical Reports when available.)

A detailed study of the mechanical energy transported through a completely general crystal lattice in the classical temperature range is presented. Both a mechanical "Poynting" vector and the corresponding mechanical "Poynting" theorem are established for an arbitrary, 3-dimensional, anisotropic, anharmonic crystal lattice, containing many atoms per cell, inclusive of substitutional impurities, and possessing an arbitrary range of atomic interactions. The extension of the energy-flow procedures to a quantum treatment is discussed, and the resulting quantum-mechanical form of the relation of mechanical energy flow to the group velocity for the restricted case of a perfectly periodic and harmonic, but otherwise completely general, crystal is derived for the classical temperature range.

2.2 Attenuating Wave Analysis of Heat Flow in Crystal Lattices, L. M. Magid, Phys. Rev. 134, A163 (1964).

A direct approach to the detailed analysis of the thermal relaxation and conduction processes in crystal lattices in the classical-temperature range is presented in terms of the mechanical

energy transported by attenuating lattice waves. A second-order classical perturbation procedure, formulated in terms of time- and space-dependent normal coordinates, is used to solve for the dynamics of a slightly imperfect, nonlinear general crystal lattice model under the influence of an applied temperature gradient. Only the use of a random-phase assumption for initial wave amplitudes at $t = 0$ and statistical averaging of the subsequent dynamical response are required for the direct determination of the accepted lattice relaxation times from the time dependence of the stored mechanical-energy density (for first- and second-order perturbation terms). In addition, the well-known anharmonic, mass-fluctuation, and force-fluctuation components of the high-temperature thermal conductivity are found directly from the steady-state mechanical-power density within the lattice. No use is made of the Boltzmann transport equation or standard phonon scattering theory, although the results obtained are wholly consistent with their use. Finally, a brief discussion is given on the extension of this attenuating-wave technique to the corresponding quantum treatment of low-temperature heat flow in crystal lattices.

2.3 Relativistic Effects in Lead Telluride, J. B. Conklin, Jr., Technical Report No. 8, Nonr 1841(51), June 1964. (Also submitted to the Department of Electrical Engineering in partial fulfillment of the requirements for the degree of Doctor of Science at the Massachusetts Institute of Technology.)

The Augmented Plane Wave Method for calculating the band structure of a solid has been extended to include the relativistic terms of the two-component Hamiltonian which is obtained by two successive applications of the Foldy-Wouthuysen transformation to the Dirac Hamiltonian. The order of the secular equation is reduced by using basis functions which are basis partners for the

irreducible representations of the double group. These functions are constructed from the solutions of the non-relativistic Hamiltonian for lead telluride. The forms of the relativistic matrix elements between them are found, with full use of group-theoretical techniques to simplify the calculation. These matrix elements are evaluated numerically, and the resulting Hamiltonian matrix is diagonalized to give the energy levels of lead telluride. The resulting band structure appears to be reconcilable with the available experimental information about lead telluride and, it is hoped, will be of value in correctly interpreting the experimental data for the material.

2.4 Calculation of Electronic Properties of Strained Lead Telluride, L. G. Ferreira, Technical Report No. 7, Nonr 1841(51), April 1964. (Also submitted to the Department of Electrical Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology.)

The present work is a study of the electronic properties of Lead Telluride under strain. The results from the band structure calculation for this material are the starting point for a numerical calculation of the deformation potentials for the important electron states. The method is based on Slater's APW scheme. An expression for the matrix element of the strain Hamiltonian between two general augmented plane waves is found. Group Theory is extensively used in connection with the reduction of the cubic group of Lead Telluride by a uniaxial strain, and in relating different deformation potential coefficients. The effects of the spin-orbit interaction are discussed and the machine program for the calculation is explained.

The work ends by comparing the calculated deformation potentials with those obtained from experimental data on the

conduction properties of the material. The magnitude of the calculated values seems to confirm the order of the energy levels given by the band structure calculation.

2.5 Temperature Dependence of the Electron-Voltaic Effect in Silicon P-N Junctions, Carl E. Rieck, Jr., submitted to the Physics Department in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology.

This thesis presents a theoretical foundation for the electron-voltaic effect, beginning with the mechanism of excitation of atomic electrons by fast beta particles and ending with the temperature dependence of the behavior of the carrier pairs so formed. Experimental results are also presented which are substantially in agreement with the theory. From the experiments it appears that correct conclusions are reached if it is assumed that the collections of electrons and holes are created in quasi-equilibrium, even though it seems certain on other grounds that this is not the case. It is concluded that quasi-equilibrium conditions are reached in times which are short in comparison to the recombination time.

In the study of the excitation mechanism, soft, midrange, and very hard collisions are, under certain conditions, governed primarily by resonance scattering. The relative importance of this effect depends mainly on the off-diagonal elements of the linear momentum operator. Reliable numerical results could be obtained only if these elements were known. For this reason it is suggested that the electron-voltaic effect might be a useful tool in the study of semiconductor properties.

In the treatment of carrier-pair behavior it is predicted that the maximum output voltage over the saturation range will be nearly linear, decreasing function of temperature. On the

basis of the elementary theory, the predicted extrapolated limit at absolute zero is the gap energy divided by the electron charge, but the need for a multiplicative correction is indicated. These predictions are confirmed by the experimental results.

The efficiency of an electron-voltaic cell is limited by the imperfect utilization of bombarding energy in carrier pair production, by the imperfect collection of carrier pairs, and by a factor which closely resembles a Carnot efficiency at low temperatures. For these reasons it appears that the electron-voltaic effect probably cannot be made to provide an efficient means of converting radioactive source power, especially at room temperature.

3.0 Current Research

3.1 Energy Bands and Properties of Lead Telluride

The calculated electronic energy bands reported in Section 2.3 provide a model which may be useful in explaining various experimentally determined properties of lead telluride. There is a great deal of experimental information available and it should be possible to check some of the major predictions of the model. In some cases, further calculations are required and in others, more specific experiments need to be carried out. Some of the possibilities are discussed in this section.

One of the predictions of the calculation is the size of the energy gap for PbTe. However, as pointed out in Technical Report No. 8, the gap is small (≈ 0.3 ev) compared to the total energies calculated (≈ 8 ev) and the calculation is not sufficiently accurate to make a definite prediction. Instead, the energy gap has been taken as a parameter to be adjusted to the experimental value.

Other energy differences, which could be detected in optical reflection studies, are much larger and one would expect to be able to check the theory here. However, there are many possible transitions and the available reflection data are not sufficiently precise to allow an unambiguous interpretation.

Using the calculated energies and wavefunctions (with the energy gap adjusted to the experimental value), Ferreira and Pratt have calculated the effective masses for the valence and conduction bands using the k·p approximation. They obtain very good agreement with experimental values. Using similar techniques, they have calculated g-factors for the electrons and holes. These factors are quite different from the free-electron value and it may be possible to determine the values experimentally. Such experiments are being considered.

Another check on the theoretical model would be a measurement of the work function or electron affinity of the material. With this in mind, we are attempting to grow epitaxial films of PbTe and perform photoelectric and contact potential measurements on these films without removing them from the vacuum chamber in which they are grown.

One may obtain some information about the symmetry of the wave functions associated with the conduction and valence band edges by looking for the Knight shift in nuclear resonance. Published data[1] show that such an effect exists in p-type PbTe and supports the theoretical predictions. Further investigation using this technique is planned.

In order to use the model to interpret transport phenomena, it will be necessary to study the scattering processes in more

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[1] I. Weinberg and J. Callaway, Nuovo Cimento 24, 190 (1962).

detail. In particular, we are investigating the electron-phonon interaction theoretically. Once this analysis is completed, it should be possible to make comparison with the wealth of experimental data on transport processes.

3.2 Heat Flow and Attenuating Wave Analysis

The extension of the analysis reported in Sections 2.1 and 2.2 to the low temperature region where quantum effects are expected to be important is nearing completion. The results obtained so far are for the most part in agreement with conventional analyses, but the present method gives some additional insight. It is expected that a complete report on this work will be published in the near future.

4.0 Discontinued Investigations

4.1 Energy Bands in Bi_2Te_3

We have considered a variety of experimental techniques which might be useful in determining in more detail the energy bands of Bi_2Te_3. In particular, we were interested in the departure of the bands from parabolic in state density, and in the reasons for the temperature dependence of the Hall effect.

After a detailed consideration of magneto-optical effects, it seems that the interpretation of these experiments is not sufficiently precise for us to obtain the desired information. Part of the problem lies in the nature of the material and the available samples; using realistic estimates for these samples, it was clear that the desired information would be obscured by other effects. In some cases, the experiments were so difficult that it does not seem worthwhile to attempt them. We have therefore suspended our efforts in this direction.

4.2 Effects of Strain in PbTe

We have carried out a preliminary investigation of the effects of strain on PbTe tunnel diodes. Several PbTe tunnel diodes were constructed and measurements of the effects of strain were made on the best of these. The diodes were made on material oriented so that the largest effects of strain were anticipated.

These diodes do not have characteristics which follow any of the present theories of tunneling current. At best, if the effects of strain were large, it might be possible to relate the strain qualitatively to a parameter of the diode. However, the effect of strain was a small one and did not occur in a region of the characteristic which could be easily interpreted. Since our major interest is in the material and not in the theories of tunneling, we have abandoned this particular line of investigation of PbTe.

PUBLICATIONS

(January 1, 1963 - July 1, 1964)

Technical Reports

J. B. Conklin, Jr., Relativistic Effects in Lead Telluride, Technical Report No. 8, Nonr 1841(51), June 1964.

L. G. Ferreira, Calculation of Electronic Properties of Strained Lead Telluride, Technical Report No. 7, Nonr 1841(51), April 1964.

Theses

J. B. Conklin, Sc.D., Department of Electrical Engineering, MIT, (see above).

L. G. Ferreira, Ph.D., Department of Electrical Engineering, MIT, (see above).

C. E. Reick, Jr., Temperature Dependence of the Electron-Voltaic Effect in Silicon P-N Junctions, Ph.D., Department of Physics, MIT.

Other Publications

J. B. Conklin, L. E. Johnson, and G. W. Pratt, Jr., "PbTe Band Structure", (submitted to Physical Review).

L. G. Ferreira, "Calculation of Electronic Properties of Strained PbTe", (submitted to Physical Review).

L. E. Johnson, J. B. Conklin, Jr., and G. W. Pratt, Jr., "Relativistic Effects in the Band Structure of PbTe", Phys. Rev. Letters, 12 538 (1963).

L. M. Magid, "Mechanical Energy Flow in Crystal Lattices", Phys. Rev. 134, A158 (1964).

L. M. Magid, "Attenuating Wave Analysis of Heat Flow in Crystal Lattices", Phys. Rev. 134, A163 (1964).

G. W. Pratt, Jr. and L. G. Ferreira, "Effective Mass, g-Factors, and Relativistic Effects in PbTe", presented at the International Conference on Physics of Semiconductors, Paris, July 1964.

DISTRIBUTION LIST

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