THERMOELECTRICITY

A Conference Report by ***David S. Lieberman***

The NRL-sponsored Conference on Thermoelectricity described below was held last September in Washington, D. C. The author is associate professor of metallurgical engineering at the University of Illinois at Urbana and is a consultant to the Solid-State Sciences Division of the Air Force Office of Scientific Research.

FOLLOWING within two weeks the Rochester International Conference on Semiconductors, the US Naval Research Laboratory conducted a Conference on Thermoelectricity on September 3 and 4, 1958, in the Department of Interior auditorium in Washington, D. C. More than 450 scientists and engineers from university, government, and industrial laboratories attended. The conference had as its primary goal the exploration of "problems in physics, chemistry, and engineering related to the development of thermoelectric materials". Although the conference was "prompted by military interest in thermoelectricity", it was an open technical meeting. As will be seen below, the program was concerned primarily with basic research on materials for both power generation and cooling and only a few papers were devoted in any way to specific applications or the design of devices.

Three papers were given at the opening Wednesday morning "Information Requirements" session which was intended "to bring to focus the scope of the problem". Clarence Zener (Westinghouse), in introducing his paper on the impact of thermoelectricity on science and technology,* mentioned that World War II marked the end of an era when thermoelectricity was merely an interesting phenomenon to physicists. Today it has applications to almost every field of technology, as the Russians, under the leadership of A. Joffe, have known for some time. By using the analogy of the steam engine, Zener showed how the intuitive feeling for its operation could be transferred to the thermoelectric power generator. He discussed the "figure of merit" $Z = S^2\rho K$ (where S is the Seebeck coefficient, ρ is the electrical resistivity, and K is the total thermal conductivity); he agreed with Joffe (see paper delivered at the Rochester conference) that TZ (which is of the order of unity at operating temperatures) is more significant since it is dimensionless. He spent some time discussing the rapidly increasing amount of effort which is being devoted to the search for, preparation of, and research on thermoelectric materials toward the goal of maximizing the "figure of merit" and subsequently the efficiency of a thermoelectric power converter and of a Peltier heating or cooling device. Such materials must have carrier concentrations of 10^{19} to 10^{20} per cc compared with the order of 10^{16} for standard semiconductors and 10^{22} for typical metals. Hence one must (1) dope semiconductors or (2) change the Brillouin zone in a metal by the proper structure choice, in order to achieve the desired carrier concentration. In Zener's opinion an intensive study of the compounds of Mn, Co, and Ni ions with O, S, Se, and Te is warranted by the several advantages of these "narrow band" mixed valency compounds over the "broad band" semiconductor materials: (1) relative abundance of materials, (2) high-temperature operation, (3) lack of susceptibility to traces of impurity, and (4) lack of deterioration by radiation damage. His colleague, R. R. Heikes, developed this approach further in a later talk (see below).

Gerhart Stoll (Whirlpool) described in some detail a thermoelectric refrigerator—a direct application of Peltier cooling. His talk was devoted primarily to the advantages of such a refrigerator over the conven-

* A paper covering essentially the same material presented at the conference has appeared in *Industrial Science and Engineering*, **5**, 26 (October 1958).

tional compressor type model (small, easily controlled, separate location for each shelf temperature, no moving parts) and engineering and fabrication considerations (size of elements, corrosion, machining, cutting, and bonding problems). Some areas where interesting experimental and theoretical work could be done were pointed out. Fred Rosi (RCA) closed the morning session with a discussion of performance factors and research on materials for refrigeration and power generation. He described the phase diagrams of solid solution alloys of such systems as Bi_2Te_3-Sb_2Se_3 with which the metallurgist and physical chemist must now be concerned. Particular attention must be paid to the variation of the band gap with composition and temperature. He touched briefly upon the exciting possibility of making "graded alloys" of these materials which would function better than cascade multistage thermopiles. This topic was also treated by P. Aigrain in the final session (see below).

The Wednesday afternoon session, "Thermoelectric Parameters", was "devoted to the physical phenomena directly involved in thermoelectricity"—a theme which actually permeated all of the sessions. R. R. Heikes (Westinghouse) followed Zener's earlier remarks with a discussion of electron transport properties of mixed valence semiconductors. These materials are usually electron compounds containing an ion in two different valence states and can be formed by substitution (as in $La_xSr_{1-x}MnO_3$ which has Mn^{+++} and Mn^{++++} ions) or by introducing vacancies (as in NiO_{1+x}, which has Ni^{++} and Ni^{+++} ions). It is possible to change the activated conduction process in these materials to metallic conduction (and produce ferromagnetism) by addition (e.g., adding 50% Sr to La_xMnO_3). He described internal friction experiments to determine the activation energy associated with the migration of ions. Using irreversible thermodynamics (since a treatment different from the Boltzmann transport equation seems desirable in mixed valency crystals), he argued that the mechanical, thermal, and electrical properties of these materials can be interpreted on a localized picture. J. A. Krumhansl, Jr., (National Carbon) opened his review of thermal conductivity mechanisms with the remark that the conflicting interests and divergent purposes of physicists, metallurgists, and ceramists had militated against rapid development in this field up to now. First he discussed in some detail the mechanisms of heat conduction in solids (and their interactions): phonons, anharmonic displacements, excitons, electrons. Next he presented some of the experimental problems peculiar to low- and high-temperature studies. The percent errors in the latter measurements can be appreciable, as high as 50%.

Following a short break, Werner Teutsch (General Atomic) discussed some considerations of the basic physics of thermoelectric effects. He showed how one material parameter describes the Peltier, Thomson, and Seebeck effects. This parameter, α, represents the tendency for a potential gradient to exist in a uniform material when a thermal gradient is present. By viewing the phenomenon as "heat pushing electrons", the α is an "entropy of transport". Thermoelectric effects are the result of the mixing of charge and energy carriers. He sketched the following table which indicates the order of magnitude of α and related quantities for different systems.

	C_v/N	$\alpha(V/°K)$	$\alpha\Delta T$ (at 100°C for $\Delta T=10°$)
metal	$k\frac{kT}{E_f}$	10	1
classical gas	k	100	10
"gap"	$k\frac{E_g}{kT}$	1000	100

The talk of Raymond Wolfe (Bell Telephone Laboratories) on the determination of the basic properties of thermoelectric semiconductors was a treatment of the "many valley" energy surface model for semiconductors. This theory was necessitated by recent magnetoresistance experiments which showed that the Hall coefficient must be a tensor and hence could not be independent of the field and current directions as earlier theories predicted even for anisotropic crystals. The speaker pointed out the importance of the newer model in properly employing Hall experiments to determine the number and mobility of carriers.

G. C. Danielson (Iowa State University) opened the second day's sessions with a description of his thermal diffusion measurements at high temperatures. The striking advantages of Danielson's methods are that (1) no elaborate guard rings are needed, in fact losses are desirable, and (2) no precise calibration of thermocouples is required. An accuracy of 2% is obtained over the range 300°K to 1300°K. The experiments as described are quite straightforward and since $k=K/cd$ (where k is the thermal diffusivity, K is the thermal conductivity, c is the specific heat, and d is the density), the figure of merit $Z=S^2/K\rho$ becomes $S^2/kcd\rho$. He gave a rather detailed account of the experimental techniques (which are in the literature) and the mathematical analysis of his data on metals since no work has been done on semiconducting materials thus far. Curves of the thermal diffusivity of Armco iron showed very clearly the Curie temperature and α-γ transformation temperature—information which could not be obtained as well from thermal conductivity or electrical resistivity curves. All the data showed that k is very sensitive to imperfections and impurities in crystals. B. Abeles (RCA) described steady state measurements of thermal conductivity of germanium at high temperatures. T. C. Haramon (Battelle) discussed the use of Peltier heat to produce a temperature gradient in a specimen in a paper on special techniques for the measurement of thermoelectric properties. D. Kahn employed irreversible thermodynamics in a theoretical justification for the preceding paper. Several short contributions (15 minutes) were made concerning various high-temperature measurement apparatus and techniques: S. J. Schneider (NBS), in discussing mechanical properties of ceramics at elevated temperatures, described recording dilatometer and x-ray lattice parameter measurements of thermal expansion coefficients in vacuo and gas atmospheres and both dynamic and static measurements of the modulus of elasticity. Measurements were made at temperatures in excess of 1500°C. G. H. Fetterly (Norton Co., Canada) in his short paper on electrical and thermal conductivity of insulators confined his remarks primarily to MgO. An "*S* Meter" was delineated by P. H. Klein (GE, Syracuse) in describing a rapid screening technique for determination of electrical resistivity and Seebeck coefficient at high temperatures. D. C. Ginnings (NBS) talked about standards of heat capacity and thermal conductivity. K. G. Skinner (NRL) showed how differential thermal analysis at high temperatures can be used to detect phase changes.

The final session, titled quite generally "Physics and Chemistry of Materials", was opened by P. Aigrain, (Ecole Normale Supérieure) with a paper on semiconductivity in disordered mixtures. He pointed out the advantages of using alloys instead of pure compounds: (1) lower heat conductivity associated with mass fluctuations and consequent enhanced scattering of phonons, (2) alloys can be engineered or tailored to desirable temperature range, (3) since the figure of merit cannot be a minimum for the whole range of temperature for one composition, a graded alloys system will achieve most of the advantages of a multistage unit and a better specific power output, (4) alloys make use of accidental degeneracies in the band structure. He then presented the salient features of the theory of mass point fluctuation scattering using the "virtual crystal" model. Apparently the efficiency of a thermoelectric generator decreases as the temperature spread between the hot and cold junctions increases. According to Aigrain, the optimum operating temperature spread is about 600°C. A. W. Searcy (University of California) discussed some chemical considerations in the production of thermoelectric power. The temperature limitations to the use of materials are (1) thermal stability, (2) reactivity toward a second element or "hot" conductor, (3) diffusion instability. At high temperatures, diffusion across barriers and in the thermal gradient of a single material itself will be extremely important and must be reckoned with in considering graded alloys. Searcy then showed how such problems could be formulated and attacked using binary and ternary phase diagrams. In his paper on thermionic emission, Virgil Stout (General Electric) showed how the temperature dependence of the work functions can be used as the driving force for a thermionic energy converter—a rather new application of thermionic emission. He discussed the relative advantages of several materials such as the alkali earths, hexaborides, and carbides as cathodes and also delineated the development of expressions for the efficiency of a thermionic converter in terms of the material parameters. "The Thermionic Properties of Porous Semiconductors", the paper delivered by E. B. Hensley (University of Missouri), also pointed toward a novel device. A layer of barium and strontium oxides on a substrate of nickel can be made about three quarters empty and, when used as an electrode, the system is in effect a *gaseous type of semiconductor* because of the space charge in the pores. Because there is no lattice, there are no phonons and hence the thermal conductivity is low since it is only due to the electrons and the radiation from the pore walls. He pointed out that the phenomenon could be used as a very accurate method for measuring electron affinity. Hensley indicated several promising directions for research, one of which is the possibility of replacing the pores with a second phase. R. J. Marcus in discussing the estimation of liquid properties showed he could get very good agreement with measured values of the heat of vaporization by a relatively simple five-minute calculation. It is hoped that the application of this type of calculation will lead to reasonable estimates of thermal conductivities.

The success of the conference was aided considerably by the absence of simultaneous sessions and the fact that, except where noted, the papers were of the order of one hour each with adequate time allotted to discussion. The proceedings (papers and discussions) will be published in due course. Judging by the spirited discussions and the enthusiasm of the participants (many of whom were numb at both ends, as it were, from a summer replete with conferences and meetings) this conference eminently succeeded in fulfilling its purpose ". . . to provide an opportunity for all of the people interested or active in this area of technology to become acquainted, and to become familiar with the nature of the work performed by persons representing the various disciplines in science". A word of appreciation is due Dr. Paul Egli of NRL and his committee for this well-planned and timely meeting.

It is important (and, to this observer, encouraging) that scientists from so many disciplines were present and that such a wide spectrum of interests from "pure" research to device development was represented. Whereas such overlap and mutual stimulation of ceramics, chemistry, metallurgy, and physics is fostered in industrial and government laboratories, it is unfortunate that most of our universities are unable or unwilling to encourage this "cross fertilization" to any appreciable degree. Such departmentalization is inimical to the rapid and continued growth of an integrated "science of materials", an approach whose importance to fundamental research was vividly demonstrated by this Conference on Thermoelectricity. In addition, as E. W. Herold stated at the Symposium on the Role of Solid-State Phenomena in Electric Circuits in April 1957: "We may look forward to the day when the chemical synthesis of an improved compound, the technology of its use, and/or the discovery of a new useful effect in these solid materials, can do more to revolutionize the performance of an electric circuit than can all the classic ingenuity of the circuit designer." That day has come.