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HIGH-TEMPERATURE BROAD-BAND SEMICONDUCTORS

Quarterly Technical Summary Report
for the Period
January 1, 1961 through March 31, 1961

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Project 65.00

April 10, 1961

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I. INTRODUCTION AND SUMMARY

This informal technical report summarizes work done in the research and development program under Bureau of Ships Contract NObs-77144 during the period January 1, 1961 through March 31, 1961. The object of the program is the study and development of new semiconductor materials for the direct conversion of heat to electricity in the temperature range above 800°K.

Fundamental work on Ce-S* is continuing in the attempt to achieve better understanding of the electrical and thermal transport mechanisms in this semiconductor as well as others having the Th_eP_4 structure. In addition, work has begun on the synthesis and evaluation of related compounds which also now show promise as high-temperature thermoelectric materials. These are the Th_3P_4-structure rare-earth sulfides of lanthanum, praseodymium and gadolinium.

The notable achievements during this reporting period for the Ce-S work have been in attaining improved $\alpha^2\sigma$ values for Ba-doped material. Values of zT slightly greater than unity at temperatures about 1500°K and about 0.4 at 800°K have been recorded, with an assumed value of $K = 0.01$ watt $cm^{-1}\,{}^{o}C^{-1}$. Concommitant with this high doping of samples has been a very large lattice stretching, and Hall mobilities as high as 4.0 $cm^2 v^{-1} sec^{-1}$ have been noted, higher than any yet recorded for undoped Ce-S. In addition, doping with monovalent cations gave indication of the presence of a Ce^{++++} state and the first indications of p-type cerium sulfide. Theoretical and experimental work will be directed towards a better understanding of both these effects.

Theoretical interpretation in the program during this period has included analysis of the Seebeck coefficient in polar semiconductors; an informal report on this work is included as the appendix to this report.

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* The designation Ce-S is used to indicate the single phase of $CeS_{1.33-1.50}$ which has the Th_3P_4 structure.

In particular, the emphasis of this work is placed on polaron theory, a transport mechanism which has first been applied to new semiconductors during the last ten years and which shows promise in application for the selection of better thermoelectric materials.

II. WORK ON Ce-S COMPOUNDS

CHEMISTRY OF DOPED Ce-S

Previous reports have dwelt on the electrical effects of adding varying amounts of BaS to Ce-S semiconductors. Usually, the extent of doping was about 4 atom-% and the only noticeable effect was that the localized Ba^{++} placed itself randomly on the Ce^{+++} sites and did not contribute any electrons or alter the mobility. During this reporting period greater barium concentrations were involved (up to 11 atom-%), with rather striking changes in the physical properties: lattice stretching, greater thermal expansion, and improved thermal, electrical and magnetic properties. These changes are discussed elsewhere in this report.

The chemistry of synthesizing these alloys as well as those with other alkaline earths has been described in the literature.(1) The synthesizing procedures have involved two basic recipes to produce bivalent alkaline earth-doped semiconductors:

1. Reagent grade $BaCO_3$ is converted to the sulfide by treating at elevated temperatures with H_2S to remove carbon, oxygen and excess sulfur. Fine-grained Ce_2S_3 and the H_2S-treated BaS are compressed in dies and annealed at 1500°C for an hour to minimize loss of BaS at the melting temperature of the alloy. The sintered specimen is then melted down and zone-leveled. Room-temperature conductivities are determined by the extent of BaS doping and by time and temperature at the melting point.
2. Treating with H_2S the mixture of $BaCO_3$ and CeO_2 at gradually increasing higher temperatures eliminates both carbon and oxygen, leaving behind an alloy of the composition Ce_2BaS_4. All vacancies of the Ce_2S_3 deficiency lattice are now occupied by Ba^{++} ions. The corresponding compound with Ca^{++} ions on the lattice sites was also prepared in this manner. In both cases the alloy was of the high-resistance form. Lower-resistivity samples were obtained by mixing with the proper amount of Ce_2S_3, melting down, and pumping off the additional sulfur.

An additional problem was concerned with doping with monovalent Li or Na to bring out p-type characteristics in the Ce-S semiconductors. Since Ce^{+++} and Ce^{++++} exist in a stable ion form, it was felt that the insertion of a Na^{+} ion substitutionally would force an additional electron from the Ce^{+++} state to the Ce^{++++} state. A small concentration of Ce^{++++} in the presence of a majority of Ce^{+++} states would behave as a p-type semiconductor. Initially an effort was made to introduce Li^{+} onto the Ce^{+++} sites by adding Li_2S to the melt. X-ray crystal pictures showed two phases. Since the calcite structure Li_2S had a Li-S interionic distance of 2.47 Å (the Ce-S distance is 2.98 Å), the Li_2S was not sufficiently soluble. Repeating the experiment with Na_2S (Na-S distance is 2.83 Å) was more successful; the Na_2S did go into solution substitutionally in the Ce-S semiconductor structure. To further reduce the creation of electron carriers by the loss of sulfur, CaS was also introduced. The resultant solid solution corresponded to the formula $Ce_8Ca_3NaS_{16}$. This alloy was red in color - - an indication of few electron carriers. Although the resistivity was high this alloy was a p-type thermoelectric material and had the deficiency crystal structure of Ce-S. Again, like Th-S reported previously,(2) the material converted reversibly at elevated temperatures (> 900°K) from p- to n-type.

THERMAL EXPANSION MEASUREMENTS

The greatly improved high-temperature thermoelectric performance values of the barium-doped samples which were inferred from the $\alpha^2\sigma$ vs T plots (Fig. 1) could be invalid if the thermal conductivity of the doped material were substantially less favorable than that of the undoped. In comparing materials the thermal conductivities were taken to be equal for both the value $K = 0.010$ watt $cm^{-1} {}^{\circ}C^{-1}$ being used. Direct reliable measurement of K is difficult, and it was not attempted during the present report period. Instead, the thermal expansion coefficient was measured, since the high-temperature thermal expansion and the high-temperature thermal

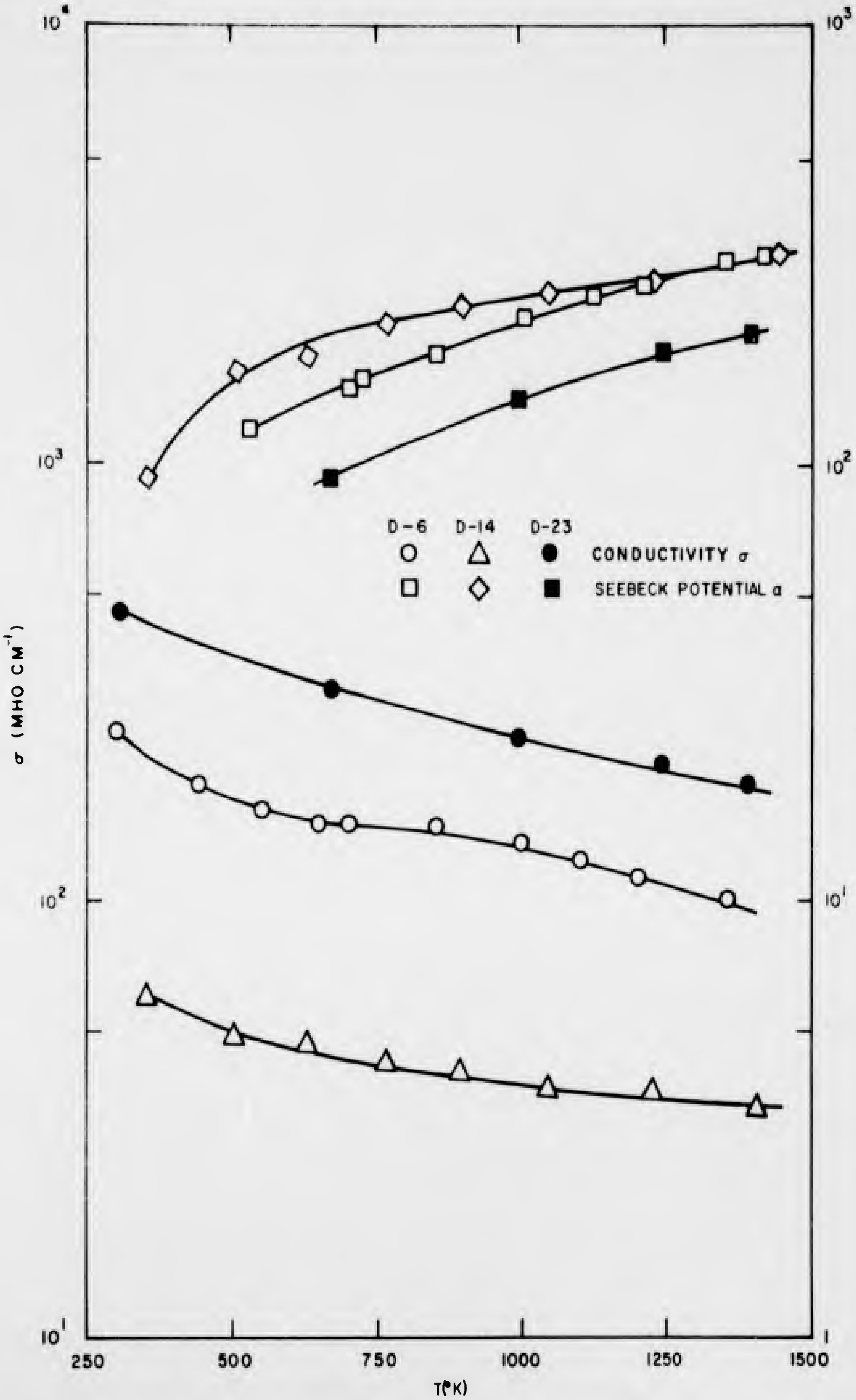

Fig. 1--Seebeck potential and conductivity of BaS-doped Ce-S.

conductivity both depend on the same property of the interatomic potential in the solid, namely its anharmonicity.

It is reasonably certain that if sample A has a higher thermal expansion coefficient than sample B, then the thermal conductivity of B will be greater than that of A, if all measurements are made at high temperatures, and if the electronic contributions to the thermal conductivities are equal.

Two specimens, each about 2 x 2 x 20 mm, one containing about 5 atom-% barium and the other containing no barium, were prepared. The thermal expansion of each was measured dilatometrically between room temperature and 1000°C, points being taken at 100°C intervals. The expansion in both cases was linear over the entire temperature range. The linear thermal expansion coefficient of the barium-doped sample was 4.5 percent greater than that of the undoped sample. From this we conclude that the addition of barium depresses the high-temperature thermal conductivity of cerium sulfide, thus making the relative conversion efficiency of the doped vs the undoped material even better than was inferred from the $\alpha^2\sigma$ plots. It seems unlikely that electronic contributions to K can upset this conclusion.

HALL COEFFICIENT MEASUREMENTS

In the study of transport phenomena in ordinary semiconductors the measurement of mobilities and carrier concentrations by the Hall effect has been of immeasureable value. For the Ce-S semiconductors, however, this effect is almost undetectable, and special Hall measuring equipment is required. Such equipment has been developed and used; a description of the technique has been described elsewhere.(3) In brief, Hall voltages as low as 10^{-10} volts can be detected by the utilization of impedance-matching transformers and narrow-band amplifiers (to reduce the noise level). The important features of these measurements may be summarized as follows:

1. Since both Hall coefficients and mobilities are low, accuracies to 25% are acceptable. The room-temperature conductivities spread over a range from 3×10^{8} Ωcm to 5×10^{-4} Ωcm. Thus, useful interpretations may be made without much instrumentation and with limited accuracies.
2. A comparison of $Ce_{2+x}S_{3+x}$ "undoped" with samples of the form $Ce_{2+x}Ba_{y}S_{3+x+y}$ "doped with barium" is made to investigate the presence of distorting Ba^{++} ions on the "hopping process" between neighboring Ce^{+++} ions.
3. Inasmuch as the Hall voltages are quite low and the change in conductivity with temperature is slight from 78°K to 1600°K as compared with the large conductivity variation of $\sim 10^{12}$ due to the S-Ce ratio alone, it was decided to restrict the measurement to room temperature. At other temperatures stray gradients would mask the galvanomagnetic effects.
4. The most effective low-resistance contacts were made by copper plating and then soldering with indium. This limited applications up to about 150°C.

The results of these measurements are shown in Figure 2, in which room-temperature carrier concentrations and mobilities are plotted against conductivity of undoped Ce-S. In the interpretation of Hall mobilities and concentrations the simplest interpretations have been used, the Hall constant being $R_H = (n_o e)^{-1}$, where n_o is the carrier concentration and the Hall mobility $\mu = R_H \sigma$, where σ is the conductivity. Complications arising from hopping processes or scattering mechanisms have been neglected. The obvious difficulties of the mean free path being the same as the interatomic distance and the inapplicability of the group velocity and effective mass concept commonly associated with high mobility semiconductors are no longer valid.(4)

Briefly, over the range of conductivities measured, the mobilities increase markedly with conductivity. The only interpretation offered here is in the synthesis of the sample at the extreme right of the conductivity scale ($\sigma = 2,200\ (\Omega cm)^{-1}$). This material was prepared by melting in the ratio of one mole of CeS to one of Ce_2S_3 to give the Ce_3S_4 portion of the stoichiometric range. Using the model that, for each mole of CeS melted

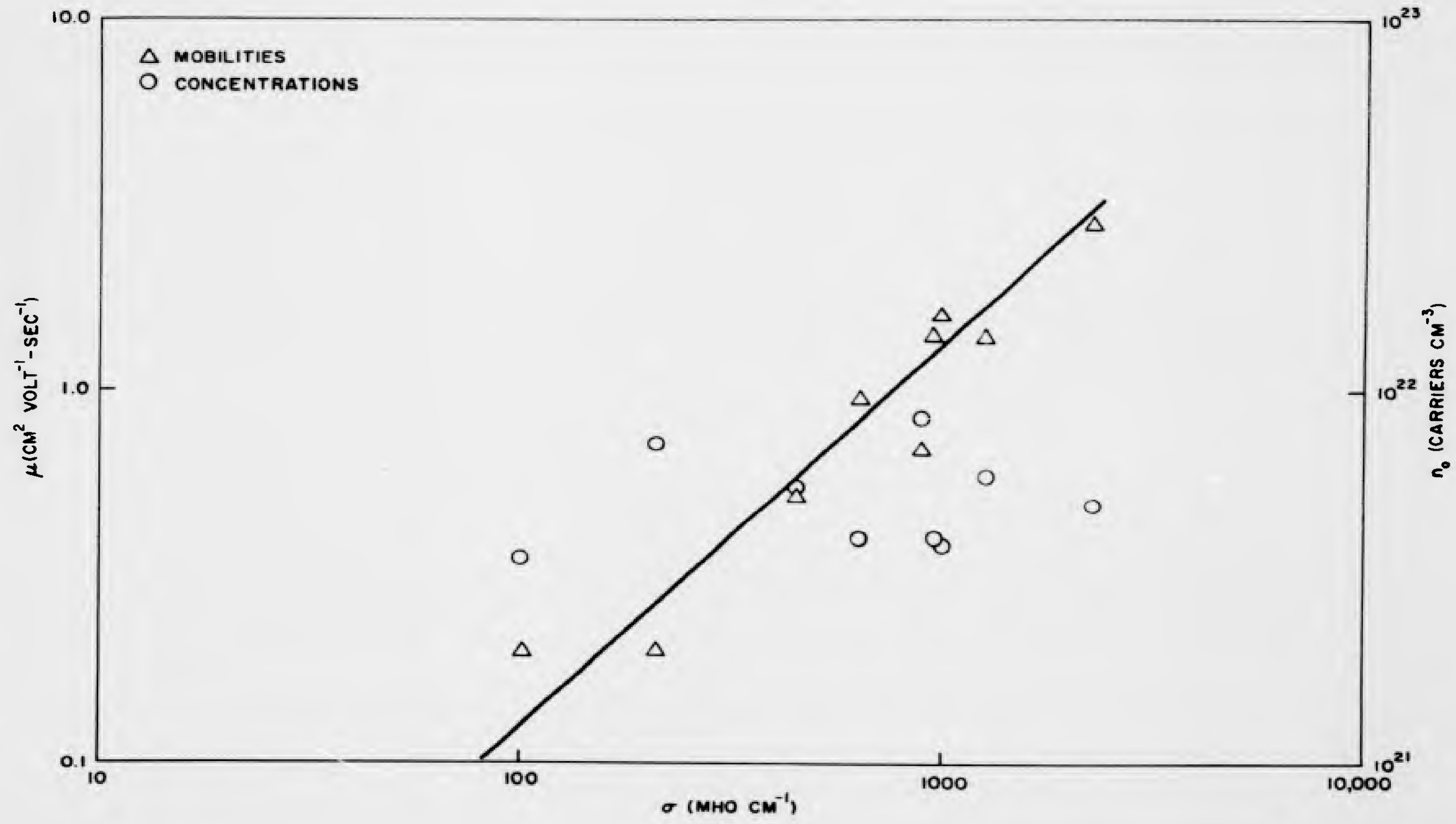

Fig. 2--Carrier concentrations and mobilities of undoped Ce-S at room temperature. The straight-line drawn is associated with mobilities (△).

into the alloy, 6×10^{23} (Avogadro's number) electrons are added, this results in a computed conductivity concentration of 2.1×10^{21} carriers per cm^3 and using the experimentally observed conductivity and one estimates a mobility of $6.7\ cm^2\ volt^{-1} sec^{-1}$. The measured concentration is higher, 5×10^{21} carriers cm^{-3}, and the mobility is $2.8\ cm^2\ volt^{-1} sec^{-1}$. The reason for the higher concentration is not known. However, the possibility is overruled that an additional electron may be provided by the Ce^{+++} going to a Ce^{++++} state because no indication of the latter ion is present in the magnetic susceptibility measurements of either Ce_2S_3 or Ce_3S_4(1).

LATTICE PARAMETER STUDIES

In a semiconductor such as Ce-S, where conduction electrons are few or absent, electrical properties may be expected to be sensitive to small changes in the lattice parameter, because of the exponential character of overlap integrals. The discovery that the lattice parameter of Ce-S is increased when barium is added was important in motivating further studies on the system. As seen in Figure 3, a plot of room-temperature lattice parameter vs y as measured in several compositions $Ce_{2+x}Ba_yS_4$, the lattice parameter increases roughly linearly with y, and the lattice parameter of the most heavily doped sample analyzed is more than 2 percent greater than that of undoped Ce-S. The data of Banks et al.,(5) at Westinghouse on strontium-doped Ce-S is included for comparison. The Sr^{++} ion is seen to be much less effective in expanding the lattice than is the Ba^{++} ion, as might be expected on the basis of ionic radii. This fact helps to explain the Westinghouse results with strontium-doped Ce-S; they found little improvement in the electrical properties on doping, in contrast to our experience with barium-doped material. Since Ca^{++} is a smaller ion even than Sr^{++}, doping of Ce-S with CaS should change neither the electrical properties nor the lattice parameter of Ce-S in the Th_3P_4 phase. We have prepared Ce-S with substantial additions of CaS, in order to verify this

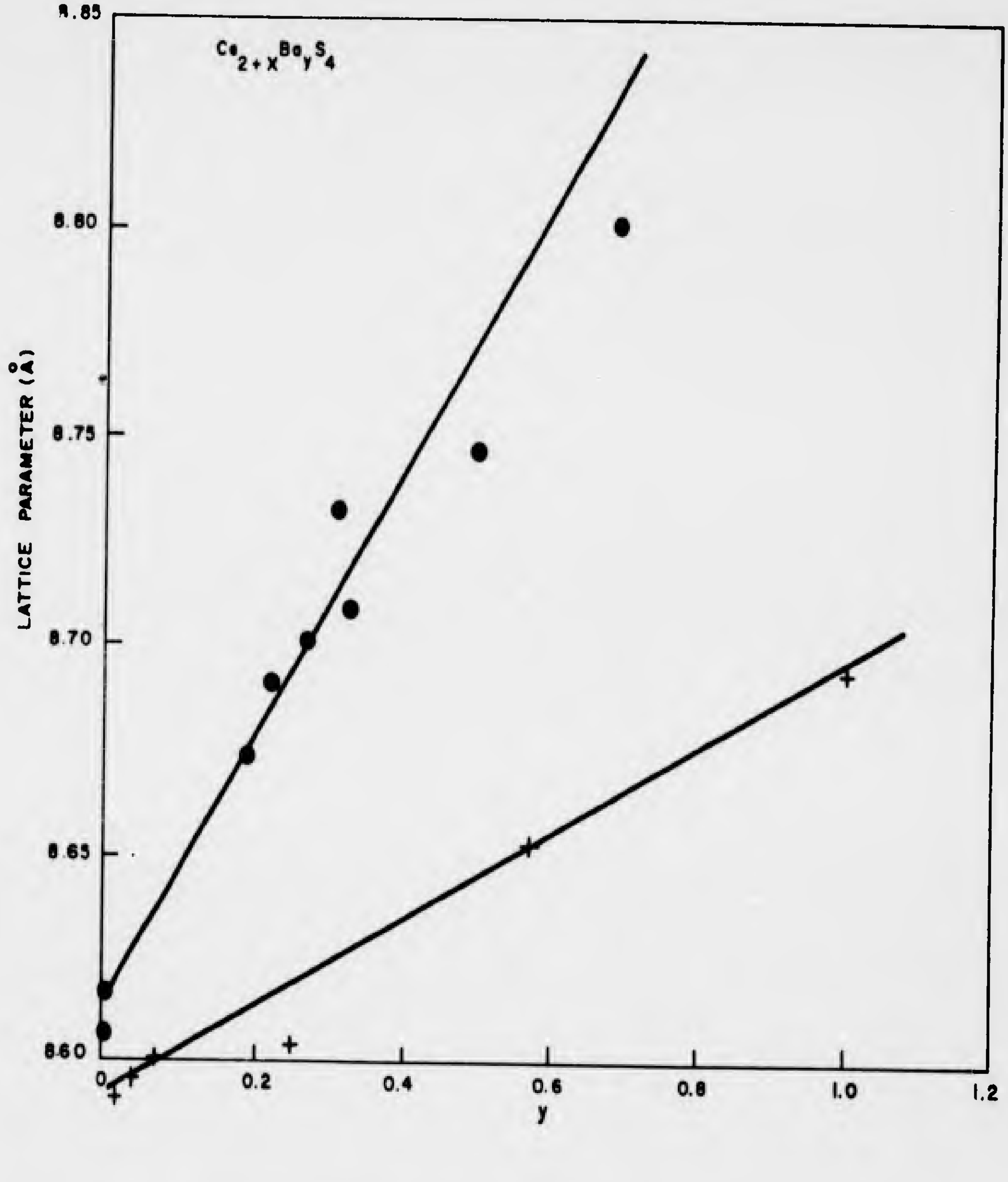

Fig. 3--Lattice parameter of $Ce_{2+x}B_yS_4$ at room temperature.

prediction. Powder patterns showed the Th_3P_4 structure without change of lattice parameter, and electrical measurements indicated little change in α or σ.

An interesting effect was noted in the x-ray powder patterns obtained from the barium-doped samples, especially those with higher barium concentrations. The powder patterns showed a broadening of the high-angle reflections, the broadening increasing with increasing Bragg angle, and, for a particular angle, with increasing barium concentration. We interpret this broadening, which is absent at low barium concentrations, as arising from a partial destruction of short-range order in the lattice because of the presence of the barium ions. The barium is present as Ba^{++} distributed randomly in a cation sublattice consisting mostly of Ce^{+++}. Since Ba^{++} is a substantially larger ion than is Ce^{+++}, localized lattice distortion is expected. Long-range order in the lattice, as characterized by the low-angle reflections, is unaffected.

HIGH-PERFORMANCE N-TYPE Ce-S

As previously mentioned, more effort has been made to establish the suitability of BaS as a doping material for altering the thermoelectric properties of Ce-S. It has already been found(6) that zT's of a barium-doped sample (A-23d2) ranged from 0.23 at 800°K to 0.37 at 1500°K. At these temperatures a typical undoped sample (B1-C) gives 0.1 (800°K) and 0.6 (1500°K). The zT's were evaluated by assuming a reasonable value for K, 0.01 watt $cm^{-1}\ {}^{o}C^{-1}$. During this quarter continued effort on barium-doped material has led to the discovery that 50 mole-percent BaS could be alloyed with Ce_2S_3 to alter the lattice parameter from 8.60 Å to over 8.80 Å without destroying the common γ phase structure. This remarkably strong effect of the Ba ions give credence to the notable results of the thermoelectric measurements to be described next. However, this must be verified by future experiments.

Runs of α and σ vs temperature on a melt-down of Ce_2S_3 + 0.10 atom-% BaS have given some remarkably enhanced electrical properties.

They show high conductivity and much higher thermoelectric powers. If the thermal conductivity were assumed to be 0.01 watt cm^{-1} ^{o}C^{-1}, these would lead to thermoelectric efficiencies at high temperatures which would place BaS-Ce_2S_3 alloys as a highly efficient thermoelectric material with zT's slightly above 1.0 at 1300^{o}K, dropping to zT = 0.4 at 800^{o}K. Other samples prepared with BaS doping have confirmed these runs. Whereas optimum doping has not been attained, other samples show a consistency in that if the thermoelectric powers run higher than those of sample D-6 (See tabulation below), the best effort to date, their conductivity runs lower. Again, if the thermoelectric powers run lower than that of D-6 there is compensation in conductivities running higher. Such data is shown in Figure 1, for three such samples: D-6, D-23, and D-14. Composition data for these samples are:

Sample	Composition
D-6	$Ce_{2.07}Ba_{0.7}S_4$
D-23	$Ce_{2.12}Ba_{0.54}S_4$
D-14	$Ce_{1.96}Ba_{0.73}S_4$

Great reliance should not be placed on these parameters because they do not weigh the influence of other impurities. Only Ba, Ce, and S were analyzed chemically. The difference in behavior between Ba- and Ca-doped material may be compared in Figure 4. The reference basis is for the formulae Ce_2BaS_4 and Ce_2CaS_4, both relatively nonconducting when compared to maximized material. If the thermoelectric powers are so close, then the conductivity provides an indication for the relatively higher efficiency of BaS-doped material.

SINGLE-CRYSTAL PREPARATION

Although no systematic attempt has been made to prepare single crystals of Ce-S, it has been noted that the appearance of the surface of

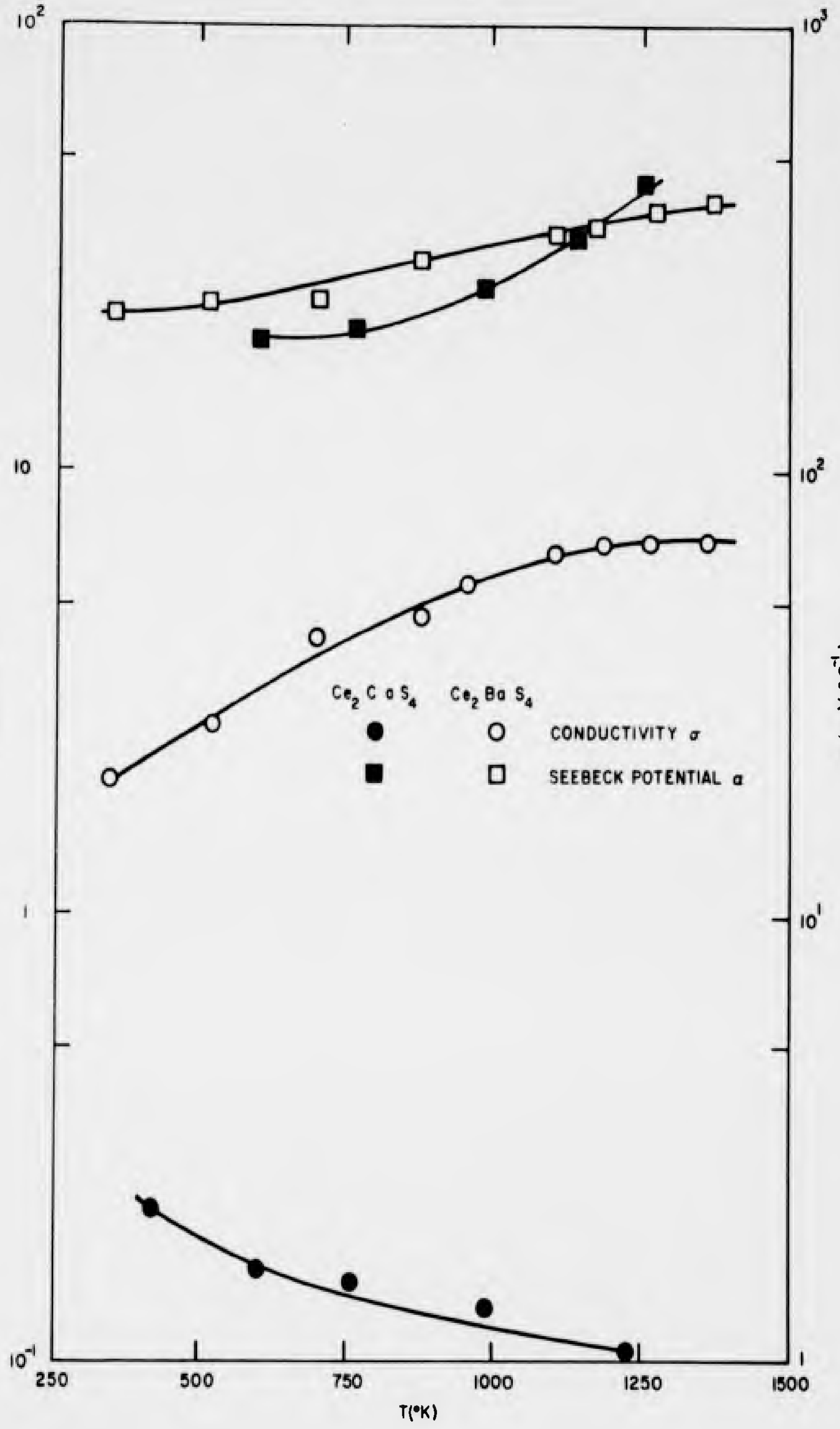

Fig. 4--Comparison of thermoelectric responses of Ce-S doped with BaS and with CaS.

the zone-melted material often suggests individual grains, of the order of a millimeter or two in size. In one case a "grain" about 5 x 10 mm, rather larger than usual, was observed. This area, delineated by surface markings on the ingot, was cut out and examined with x-rays to see whether or not it might be a single crystal.

To date, we have established that the sample is not polycrystalline on a fine scale; we hope, with different apparatus, to confirm the suspicion that the "grain" is in fact a single crystal. If single crystals can be prepared, measurement of elastic constants becomes possible. Knowledge of the elastic constants and Debye temperature would be very useful in interpreting data already obtained and in guiding future experiment.

INDEX OF REFRACTION

The optical dielectric constant (index of refraction) of Ce_2S_3 is of interest because a comparison with the static dielectric constant yields the degree of polar bonding in the crystal. Previous theoretical work at this laboratory had indicated that the index of refraction at visible wavelengths might be approximately $n = 2.3$. Because of the uncertain accuracy of this value it was thought worthwhile to try to obtain a better value. The Christiansen filter technique was used(7), with TlCl as a matrix material. The index of refraction of TlCl varies between 2.2 and 2.4 in the visible range, and a transmission peak should be observed if the value of n for the particles of Ce_2S_3 dispersed in the matrix is in this range. No peaks were observed, indicating that n for Ce_2S_3 is not between 2.2 and 2.4. Further runs with other matrix materials are planned (TlBr, TlI). Since Na_2S subtracts from the electron concentration, another effort is in process for measuring the index of refraction from reflection and transmission measurements. This work will help fix the index of refraction so that the Christiansen filter matrix may be determined.

III. WORK ON SULFIDES OF La, Pr AND Gd

Samples of sulfides of La, Pr and Gd have been prepared in much the same manner as those of Ce-S. The metal oxides have been flushed with H_2S at 1200°C to 1450°C in a graphite container and the resulting high-sulfur-content powders melted in vacuuo in a tungsten boat at temperatures from 1800°C to 2500°C.

CONCENTRATION GRADIENTS

When the melt is brought to a uniform high temperature and then decoupled from the source of power, cooling takes place first on the top and bottom surfaces of the flat boats used to contain the melt. This is followed by a rapid but continuous motion of the freezing zone toward the middle of the melt. Since the sulfur-rich compositions have lower melting points than the sulfur-poor ones, the sweep of the freezing region results in a higher concentration of sulfur in a plane region halfway between the front and back surfaces of the frozen sample. Furthermore, the shrinkage of the material on cooling coupled with the freeze having started on the outer surfaces, causes voids in the central region.

Preferentially zoning the sulfur into a region halfway between the top and bottom surfaces of the casting has on occasion been noted by a slight change in color at the centerline of a sliced section of a quick-frozen cast sample. When thermal emf measurements are taken with a temperature gradient from the top to the bottom of the casting, and resistivity measurements are taken with the current flow in a horizontal direction of the original casting, a high but false value of $\alpha^2\sigma$ is obtained; a high conductivity value is produced by the more metallic outer surface of the casting, while the sulfur-rich central section introduces a high value for the thermoelectric power. Such errors as these have always been carefully avoided in the program by measuring α and σ in the same direction. The occurrence of the phenomenon may be avoided by slowly pulling a zone in the horizontal direction, to result in a solid casting without voids and with a small gradient in the sulfur concentration in the horizontal direction and along the length of the boat, but with almost no gradient in the vertical direction.

CONTACT EXPERIMENTS

Some experiments have been performed to investigate the possibility of electrically spot-welding small wires of refractory metals to rare-earth sulfides using condenser discharges at high temperatures. The samples used were mostly those of La-S, but some wires were also spot-welded to Ce-S samples. The motivation was twofold. First, we anticipate an eventual need, in Hall effect measurements, for reliable electrical contacts on preformed samples, where the samples will subsequently be subjected to excursions over a range of temperatures from helium temperatures to 1000°C or more. Second, the contacts are easy to make, and the electrical characteristics of the contacts give information on the possibility of doping the rare-earth sulfides with refractory metals.

The wires tested - - of tantalum, molybdenum, tungsten, and niobium - - ranged in diameter from 0.0225 in. to 0.010 in. The wires were pressed against the samples, the wires and samples heated to 1400°C to assure sample plasticity, and the pairs sparked together using a condenser discharge. Tantalum was found to almost invariably give a strong, junction, with a resistance of three to ten ohms for a wire of 0.010 in. diameter. Molybdenum was nearly as satisfactory, giving bonds of almost the same resistance range and nearly as strong. Tungsten and niobium were unreliable.

No directional character was noticed in any of the junctions, with the exception of one of the tantalum bonds. As shown by Figure 5, this bond was definitely a rectifying junction.

A simple metal semiconductor contact is rectifying in the case where there is no alloying. However, since the tantalum junctions were

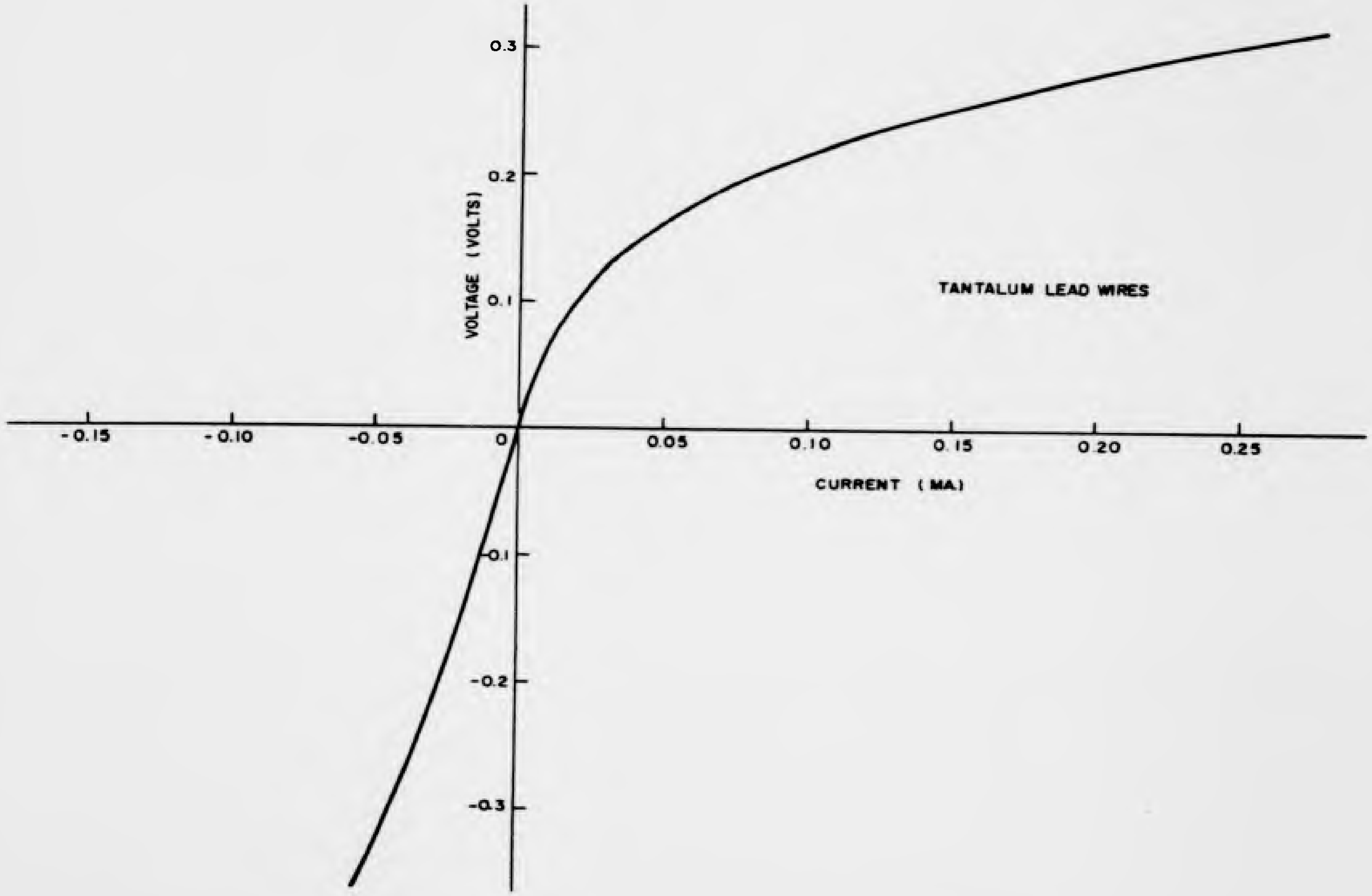

Fig. 5--Voltage-current characteristic of a sparked Ta wire on $LaS_{1.41}$ compound. The measurements were made at room temperature.

the strongest mechanically of those tested, and since the junction in question was spark-formed, we conclude that the tantalum alloyed into the sample, and that the rectification was caused by the existence of a p-type region. From all this we suspect that either tantalum sulfide is p-type, or that some tantalum-rare-earth-sulfide phase is p-type. The experience with wire contacts has led us to conclude that there is less affinity between tungsten and rare-earth sulfides than there is between tantalum and rare-earth sulfides, or between molybdenum and rare-earth sulfides, and we tentatively recommend the use of tungsten boats in preparing cast samples.*

RESULTS OF ELECTRICAL MEASUREMENTS

The results of some recent electrical measurements on La-S, Gd-S, and Pr-S samples are shown in Figures 6, 7, and 8. The results of x-ray studies of these samples reveal that they are all of the Th_3P_4 structure. However, there is a slight trace of an extraneous phase in the $GdS_{1.34}$ material. The $GdS_{1.34}$ has the highest value of $\alpha^2\sigma$ for the samples reported and has a corresponding value of $zT = 0.6$ at about 1000°C if we assume $K = 0.01$ watt $cm^{-1}{}^oC^{-1}$. An attempt was made to improve the figure of merit of Pr-S by mixing the fully sulfided powder with 10 atom-% BaS, pressing it, and sintering it prior to melting. This procedure resulted in a predominately Th_3P_4 structure with a slight amount of an extraneous phase. The lattice of the Th_3P_4 phase was expanded by about 2%, but the zT value was dissappointing, being only 0.15 at 1000°C.

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*Two LaS samples, which had been melted in tungsten boats, were analyzed for the presence of tungsten. The analysis showed that the upper limits to the tungsten concentrations were 1.8 per million and 0.9 parts per million. This is about two orders of magnitude less than the molybdenum concentration in a sample of cerium sulfide melted in a molybdenum boat.

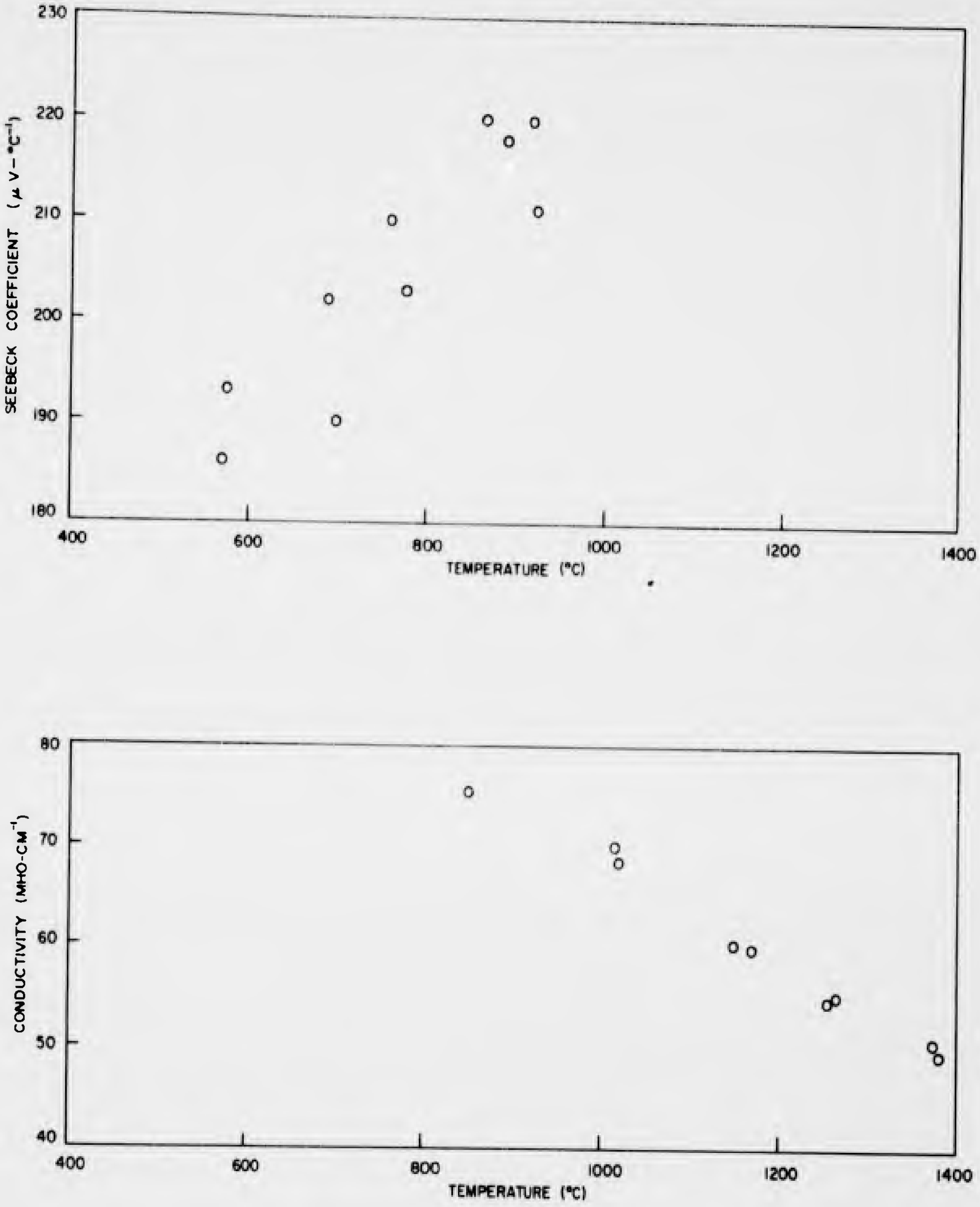

Fig. 6--Seebeck potential and conductivity of $LaS_{1.41}$ at high temperatures.

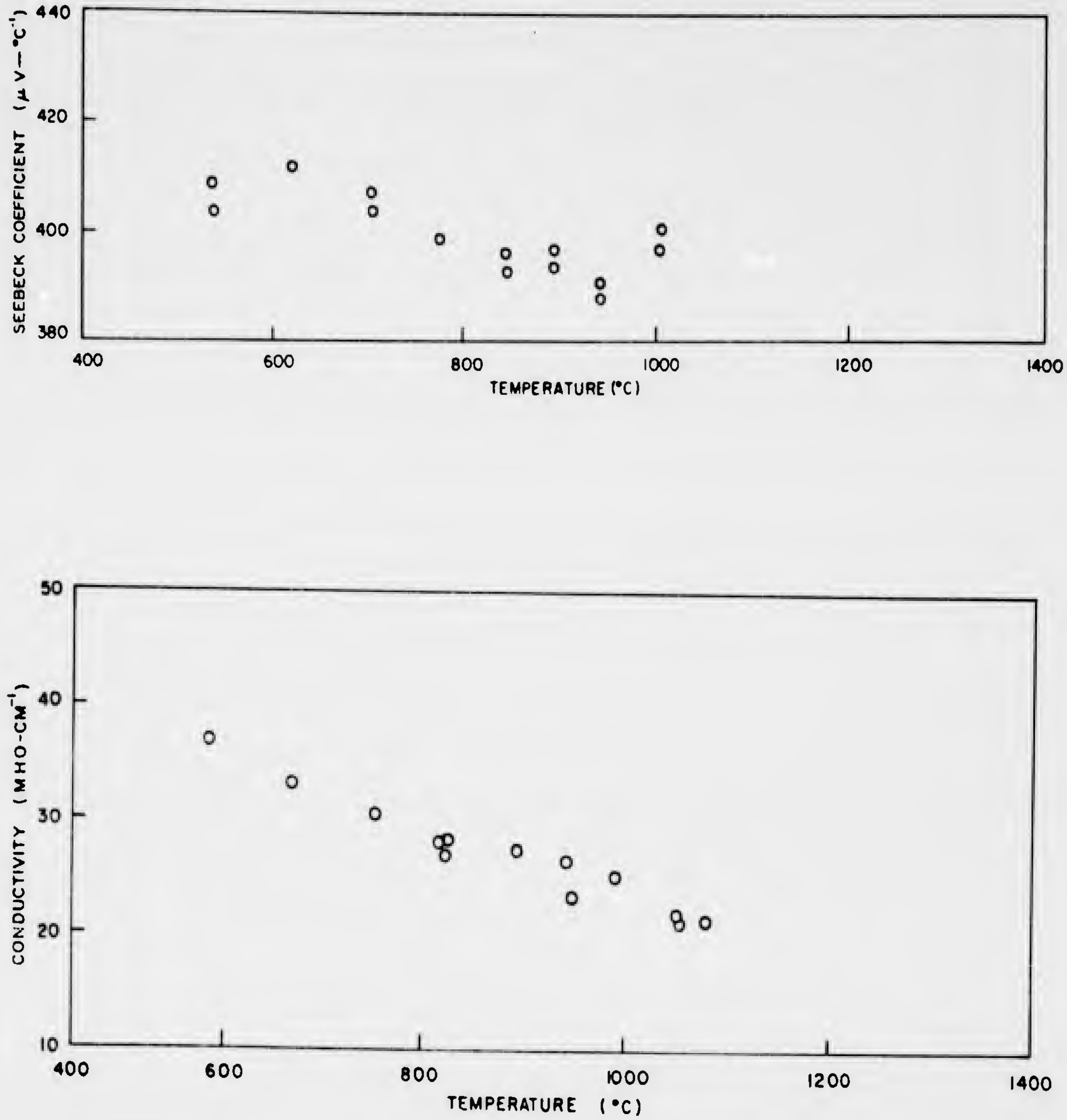

Fig. 7--Seebeck potential and conductivity of $GdS_{1.34}$ at high temperatures.

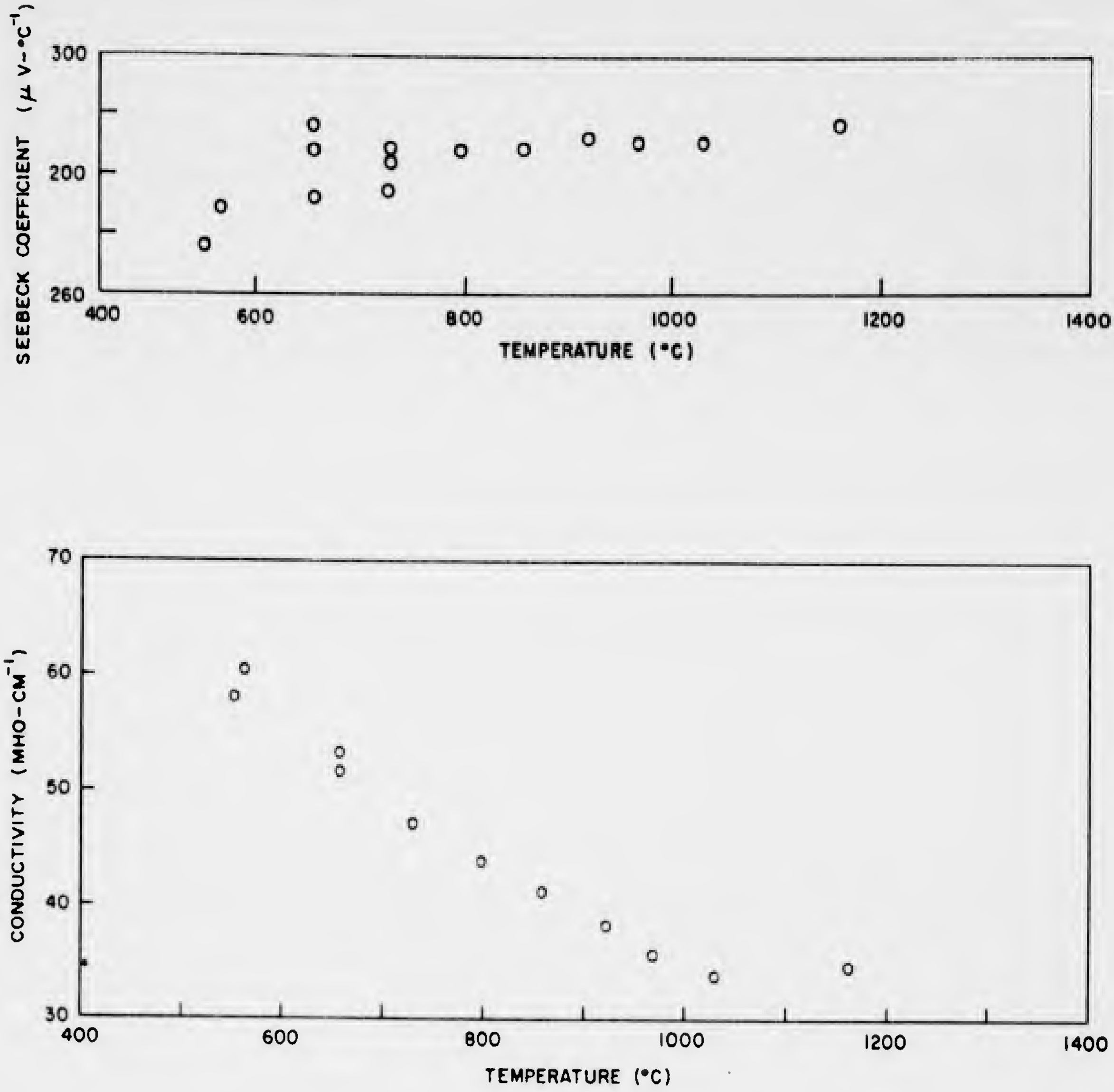

Fig. 8--Seebeck potential and conductivity of $PrS_{1.45}$ at high temperatures.

IV. PERSONNEL

The over-all program has been conducted under the general supervision of Dr. P. H. Miller, Jr. Dr. S. W. Kurnick has been responsible for the progress of the work on Ce-S compounds, and the work on La-S, Pr-S, and Gd-S, in a separate aspect of the program, has been conducted by Dr. G. L. Guthrie. The theoretical work has been performed by Dr. J. Appel. L. LaGrange has contributed strongly to the chemistry associated with the program.

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Appendix

MATERIALS SHIPPED, TALKS, AND PUBLICATIONS

Material was shipped during this quarter to Forrest Carter of Westinghouse for low-temperature (helium range) runs. In turn, Westinghouse has been very cooperative in exchanging sintered samples.

Two talks on the thermoelectric properties of Ce-S were given at the Symposium on Thermoelectric Energy Conversion in Dallas, January 8 - 12, 1961. To be published in the proceedings of the conference, these papers have in addition been disseminated as General Atomic reports and are included in this appendix. Also included is an informal report on theoretical work on the Seebeck effect in semiconductors.

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RARE EARTH SULFIDES AS HIGH-TEMPERATURE THERMOELECTRIC MATERIALS

S. W. Kurnick, M. F. Merriam, and R. L. Fitzpatrick

This report was given by the senior author at the Symposium on Thermoelectric Conversion, Dallas, Texas, January 8 - 12, 1961.

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Work reported done under Navy Contract NObs-77144.

January 20, 1961

RARE EARTH SULFIDES AS HIGH-TEMPERATURE THERMOELECTRIC MATERIALS[*]

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ABSTRACT

The rare earth sulfides appear promising for use as high-temperature power conversion thermoelectric materials because of low lattice thermal conductivity and good chemical stability above 1000°C. We are making an intensive study of cerium sulfide, and to a lesser extent lanthanum sulfide and thorium sulfide, in the stoichiometric range in which these compounds are semiconducting. Some measurements have been made on barium sulfide - cerium sulfide solid solutions.

Electrical, optical, thermoelectric, and magnetic measurements have been made on crack-free cast samples of centimeter dimensions prepared by vacuum melting in molybdenum crucibles. Doping of the semiconductor by molybdenum is not belived to be serious, in view of the low Mo concentrations (~100 ppm or less) indicated by chemical analysis, and of the high carrier concentrations measured. Measurements of the thermoelectric parameters have been made at elevated temperatures, using small area contact techniques as well as more conventional methods. Values of $zT = 0.3$ have been measured in cerium sulfide, without doping. Carrier concentration and Hall mobility have been measured by a simple and sensitive ac method. Mobilities measured to date in cerium sulfide are low ($\sim 1 \text{cm}^2/\text{volt-sec}$) and carrier concentrations are high (up to $10^{22}/\text{cm}^3$), depending on the stoichiometry. Conduction mechanisms consistent with the data at hand are discussed.

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[*] Research conducted under Navy contract NObs-77144.

INTRODUCTION

The selection of high-temperature semiconductor materials which can provide optimum thermal conversion efficiencies is a problem which must rely a great deal for its solution on experimental methods modified by some empirical rules. The selection of the semiconducting compound Ce-S* as such a thermoelectric candidate may best be understood from the work of previous investigators.(1 - 7) The two most important features of the compound as far as thermoelectric conversion is concerned are its high-temperature stability and low lattice thermal conductivity, which may be inferred from empirical relations.(8) The semiconductor is an electrical insulator at the Ce_2S_3 end of the composition range ($\sigma = 3 \times 10^{-9}$ mho/cm), but its conductivity increases with increasing cerium content, the Ce_3S_4 composition being semi-metallic ($\sigma = 3 \times 10^{3}$ mho/cm). This is a remarkably large range in conductivity for a single phase.

For a better understanding of the electrical and thermal transport mechanisms involved in this semiconductor, we have stressed three aspects in the intensive study of Ce-S:

1. The utilization of new techniques in thermoelectric measurements at high temperatures (800 - 1800°K):
    a. Measurements of the semiconductor efficiency parameter zT and the Seebeck potential α by a small area technique(9) to avoid radiation corrections.
    b. Measurements of the Hall effect to achieve better insight into the mechanism of conductivity and into the relative importance of mobilities and carrier concentration at different stoichiometries.
2. Metallurgical preparation of material by melting. This avoids certain disadvantages inherent in sintered materials, such as atmospheric deterioration at room temperature. In addition, low-temperature heat treatments are characterized by mixed phases which are avoided by quenching from the melt.(7)

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*The designation Ce-S is used to indicate the single phase of $CeS_{1.33 - 1.50}$ which has the Th_3P_4 structure.

3. Accumulation of data leading to an ultimate performance study of related semiconductors so as to apply the progress achieved on Ce-S to the problem of selecting materials from other rare earth sulfides (pure and doped) to obtain ultimate performance in temperature regions for which Ce-S alone is unsuitable.

Results to date indicate that qualitatively different transport mechanisms are dominant in different composition ranges. This work is not complete, but measurements to date already show promise, with directly measured zT's as high as 0.33. Values of zT synthesized from $\alpha^2\sigma$ measurements and assumed values of κ have been as large as 0.7. This places Ce-S in the role of a leading high-temperature thermoelectric candidate.

PREPARATION OF SAMPLES

All measurements have been made on cast material having 100% of theoretical density. Porous Ce_2S_3, obtained by H_2S reduction of CeO_2 in the presence of carbon, is melted in vacuum in a molybdenum container at a temperature in the neighborhood of 2000°C. Some loss of sulfur occurs during this processing, and the cast material has a composition intermediate between Ce_2S_3 and Ce_3S_4. Melting in graphite containers was found to be unsatisfactory; the cerium sulfide reacted with the graphite used. Tantalum is also attacked. With molybdenum, on the other hand, the casting usually separates cleanly from the container after both have been cooled to room temperature. The visual appearance of the container wall indicates at most only slight attack, and chemical analysis indicates fairly low Mo concentrations (usually 100 ppm or less) in the semiconductor. Melting is carried out in either an induction furnace (in which case a graphite susceptor is used to transfer power from the induction coil to the Mo boat) or in a resistance furnace (in which case the Mo crucible is suspended in the center of the helical graphite resistance element). After melting, the charge is cooled to room temperature over periods of 1 - 12 hours.

From the resulting cast material, slabs several centimeters in dimension are obtained free of cracks, as determined both visually and by electrical probing. It has proved possible to polish these slabs into blanks for optical measurements and to cut out samples for other physical measurements, using standard semiconductor techniques. The cast slabs and the samples cut from them are stable in air at room temperature. No changes in properties of either the surface or the bulk have been observed over periods of months. (An insulating layer, presumably oxide, does, however, form on the surfaces of samples heated in air at 300°C for a few minutes.)

The complex x-ray patterns characteristic of oxysulfides(4, 6) are not observed in our melted material. The lower temperature phases of cerium sulfide(2, 5) are likewise absent, the pattern showing only the characteristic lines of the Th_3P_4 structure.

MEASUREMENTS

Electrical conductivity and Hall effect measurements at room temperature are performed by ac methods at 570 cps. Conductivity is measured with the standard four-wire technique, the output from the potential probes being fed directly to a Hewlett-Packard wave analyzer (as a narrow band amplifier). The equipment for the Hall measurement, which is described more completely elsewhere,(10) includes an impedance matching transformer and a preamplifier between the sample and the wave analyzer. Signals can be detected down to noise levels of a few times 10^{-10} volts. Low impedance leads and contacts are necessary. "Noiseless" magnetic fields of up to 5000 gauss are provided by permanent magnets.

Simultaneous measurements of electrical conductivity and Seebeck coefficient at temperatures from room temperature to 1600°C are obtained with the apparatus shown in Figure 1. The temperature gradient existing in the furnace is used to generate the Seebeck potential. Temperature-position profiles in an empty furnace indicate the actual temperature distribution in the sample is probably not far from the constant gradient assumed. The electrical conductivity is measured by a four-wire ac method similar to that used at room temperature.

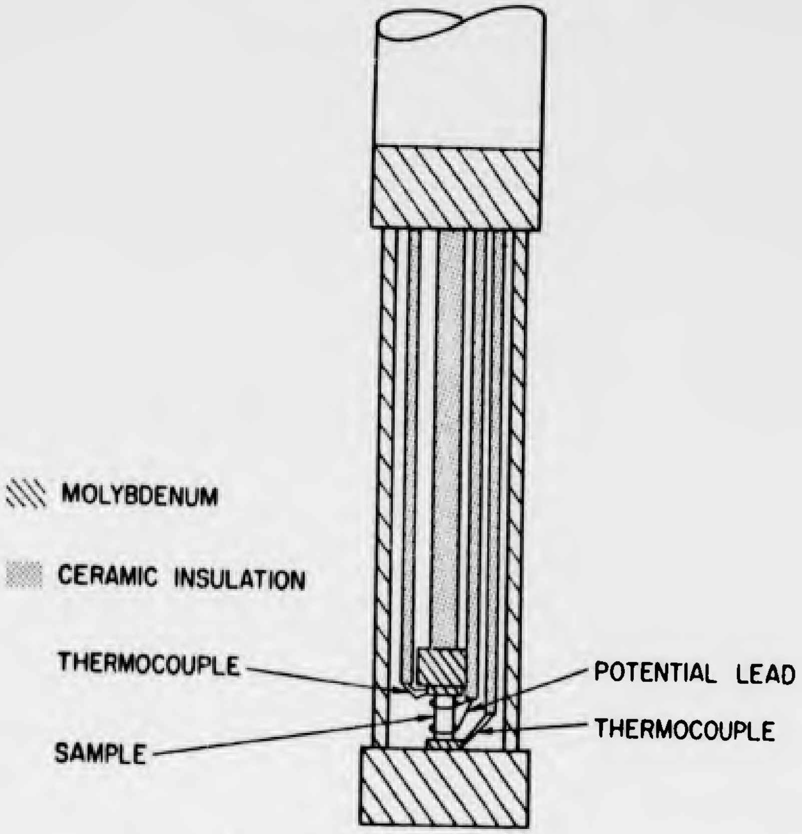

Fig. 1--Seebeck potential and conductivity rig for small samples.

The direct measurement of zT at various temperatures is accomplished with the small area device developed at General Atomic by Cutler.(9) This device has the advantage that the thermoelectric performance parameter, $zT = (\alpha^2 \sigma \kappa^{-1})\ T$, is measured directly. Combination of measurements obtained on different samples, of uncertain comparability, is thereby avoided. It is possible to make measurements on small samples, or on samples with flaws, without any adverse effect on reliability. Another advantage of the method comes from the fact that, if the small area contact is small enough, the measurements are insensitive to radiative heat transfer. The device is thus well suited to high-temperature measurements.

A dc current applied between the center wire and the outer can(9) causes the temperature of the center of the sample to rise above that of the more distant part, because both the Peltier heating and the Joule heating are more intense near the center. After a steady state has been established,

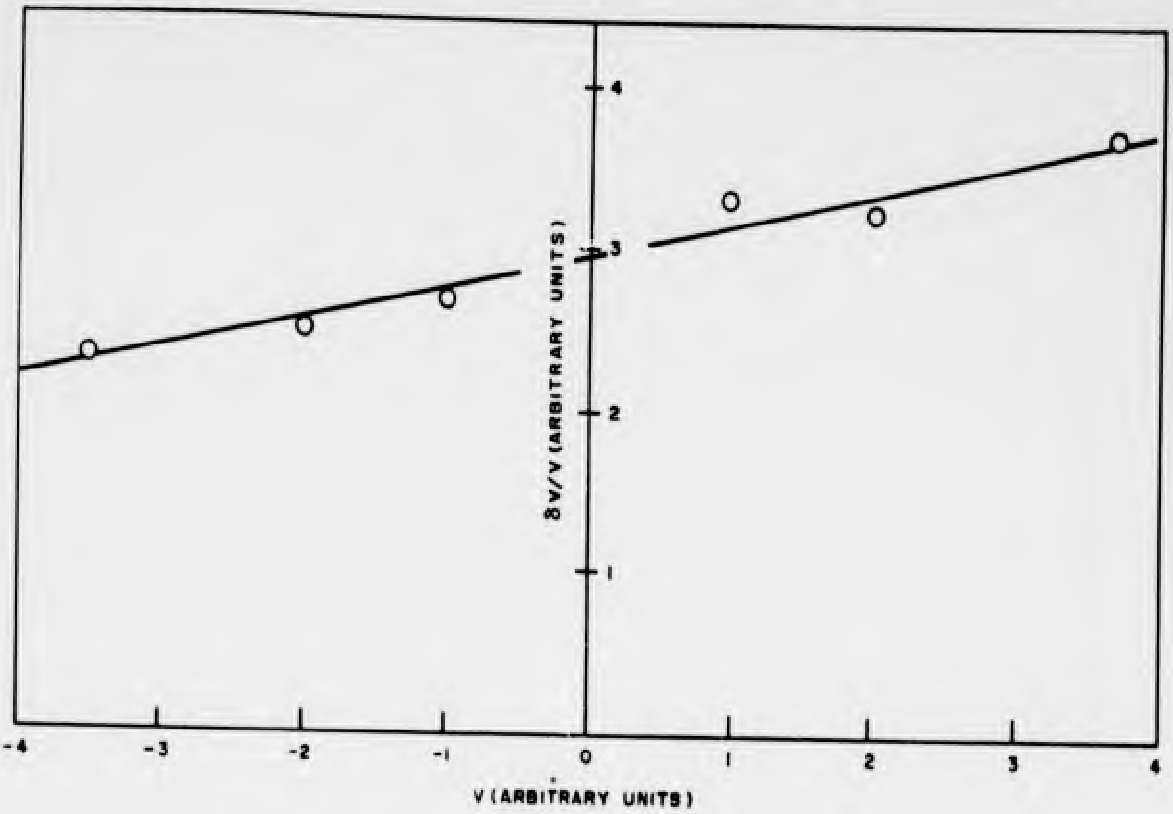

Fig. 2--Data from the small area contact technique; zT is obtained from the intercept and α from the slope of the straight line plot.

the current is suddenly switched off. Since a temperature gradient exists between the center wire and the outer can, a transient thermoelectric voltage will appear between these two conductors, decaying to zero as the semiconductor comes to thermal equilibrium. By measuring δV, the initial magnitude of the thermoelectric transient, and comparing with V, the voltage initially applied, the value of zT can be deduced, according to the equation

$$\frac{\delta V}{V} = \gamma + \frac{\gamma}{2\alpha T} V \qquad \text{where } \gamma = \frac{zT}{1 + zT} .$$

In fact, by plotting $\delta V/V$ vs V one can, in favorable cases, obtain both zT (from the intercept) and α (from the slope). This is illustrated in Figure 2. Since the small area device, as applied in this laboratory, also includes potentiometric leads, the electrical conductivity is obtained concurrently with the zT and α measurement. The thermal conductivity can thus be obtained at high temperatures (up to 1600°C).

RESULTS AND DISCUSSION

The measurements to date are generally consistent with existing descriptions of the nature of cerium sulfide. There are, however, differences in detail. Physical understanding is still possible only in broad terms, though some progress has been made toward narrowing the range of possible models.

The Hall effect in compound semiconductors similar to cerium sulfide is usually small, and few measurements to date have been reported on this type of material. Consequently, theoretical interpretation has also lagged. It seems fairly certain, however, that a measured Hall voltage can be interpreted in terms of carrier mobility and carrier concentration. We have converted Hall voltages and conductivities to mobilities and carrier concentrations in the usual manner, ignoring any complications arising from large carrier concentrations and the possible presence of hopping processes. Room temperature Hall effect measurements are summarized in Table 1. They show high carrier concentrations, of the order of 10^{21} - 10^{22} cm^{-3}, and low mobilities, or the order of 0.1 - 1 cm^2/volt-sec. Although there is some scatter in the data, it appears that higher conductivity is achieved both through higher carrier concentrations and through increased mobilities. All the material manufactured to date has been n-type.

The room-temperature electrical conductivity of samples prepared by melting has varied from a few mho/cm to a few thousand mho/cm. Because sulfur is lost in the high-temperature processing our samples receive, we would not expect to obtain very highly insulating material. (The only insulating samples with which we have worked so far were prepared by heat treating blanks in either a sulfur or a hydrogen sulfide atmosphere.)

Our room temperature data are thus consistent with the usual interpretation of the conductivity transition from insulating Ce_2S_3 to high conducting Ce_3S_4. In Ce_2S_3 the cerium ions are trivalent (Ce^{+++}).

Table 1

HALL MEASUREMENTS

σ (mho-cm^{-1})	Hall Coefficient (cm^3 coulomb^{-1})	n (carriers/cm^3)	μ (cm^2/volt-sec)
100	1.7×10^{-3}	3.5×10^{21}	0.2
210	0.85×10^{-3}	7.4×10^{21}	0.2
900	0.73×10^{-3}	8.5×10^{21}	0.7
960	1.5×10^{-3}	4.0×10^{21}	1.4
1270	1.1×10^{-3}	6.0×10^{21}	1.4
2200	1.65×10^{-4}	3.8×10^{22}	0.4
2700	4.2×10^{-4}	1.5×10^{22}	1.1

If to m "molecules" of Ce_2S_3 are added n "molecules" of CeS, in which cerium is divalent (Ce^{++}), resulting in $Ce_{2+x}S_{3+x}$ where $x = (n/m)$, there are x electrons per "molecule" which are less strongly bound than the valence electrons. These extra electrons provide electrical conductivity, and, as x approaches unity, result in the metallic bonding characteristic of Ce_3S_4. The question of whether these "extra" electrons are essentially free, or whether they form part of a more complex mobile entity, e.g., a polaron,(11) is best left open at this time. It seems in any case likely that the applicability of any particular model will depend upon the value of x.

One might suppose that the high carrier concentrations and low mobilities found in the "metallic" Ce_3S_4 would render the transport properties in that material insensitive to doping. Such apparently is not the case. For example, when a sample of material having a conductivity of 1000 mho/cm was remelted in a general-purpose (and thus contaminated) vacuum system and held above the melting point for several hours in an attempt to drive off any remaining sulfur, the room-temperature conductivity, instead of increasing, decreased to a value between 1 and 50 mho/cm, depending upon location in the ingot. Experience to date (perhaps half a dozen experiments) indicates that high-conductivity material is more sensitive to doping than is low-conductivity material. This is not, however, conclusively established. We note also that the data of Table 1 show less than perfect correlation between conductivity and the Hall effect. Correlation between mass density (an index of stoichiometry(4)) and electrical conductivity is likewise not exact.

The behavior of α and σ as functions of temperature in a highly conducting sample is shown in Figure 3. It is at once apparent that Ce_3S_4 is no ordinary metal. Both the magnitude and the temperature dependence of the Seebeck coefficient are more characteristic of a refractory ceramic insulator than of a metal.

The temperature dependence of α is particularly interesting. If the usual formula for the entropy of mixing contribution to the Seebeck coefficient of a semiconductor is considered, neglecting all complications,

$$\alpha = \frac{k}{e} \ln \frac{2(2\pi m^* kT)^{3/2}}{nh^3} ,$$

where m^* is the effective mass and n the number of carriers, we see that a temperature-dependent effective mass is necessary in order to fit the results of Figure 3. It is believed that this is the major contribution in these materials.

The data of Figure 3 yield $zT \approx 0.7$ at 1500°K if a rather conservative value of 0.01 w/cm-°C is assumed for the thermal conductivity. This is a higher zT than has been reported to date for a material operating at this temperature. A rough measurement of zT with the small area technique on a less conducting material indicated, however, a maximum value of $zT = 0.3$. We believe that this illustrates the danger of drawing conclusions from $\alpha^2\sigma$ data alone, particularly in the case of high temperatures.

The effect of doping Ce-S with BaS has also been investigated. This study is not completed, but it appears that one effect of the BaS is to increase the rise in the Seebeck potential with the increase in temperature.

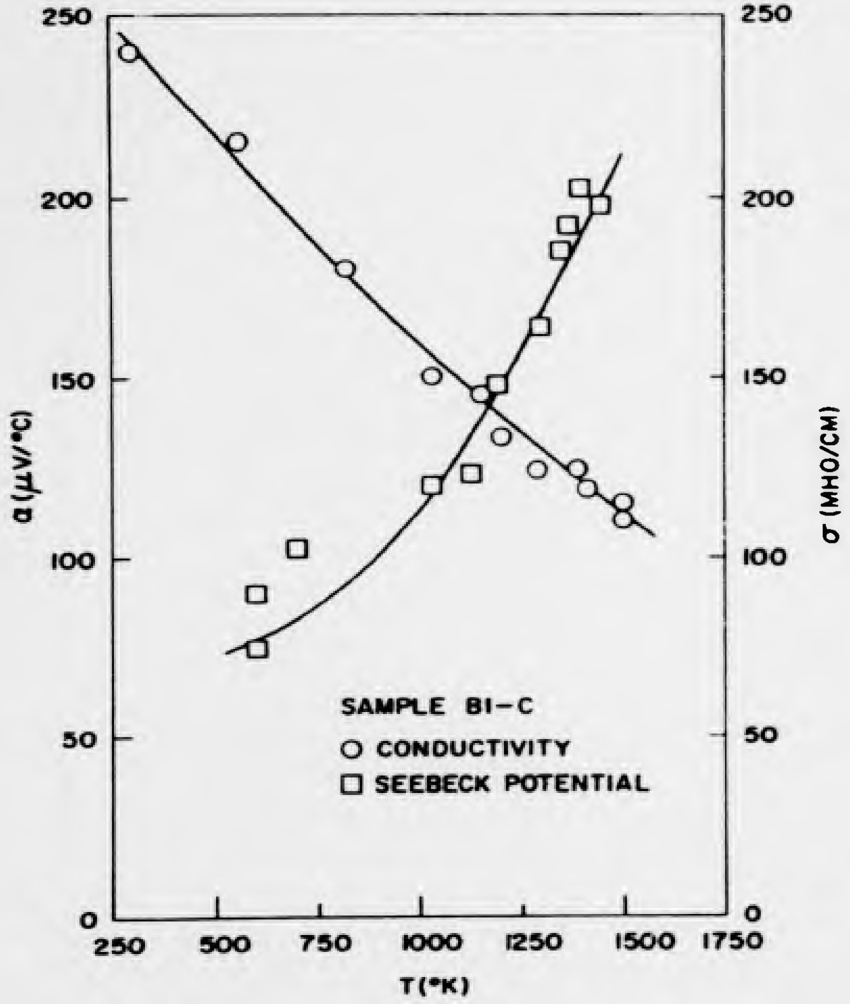

Fig. 3--Seebeck potential and conductivity vs temperature for undoped Ce-S sample.

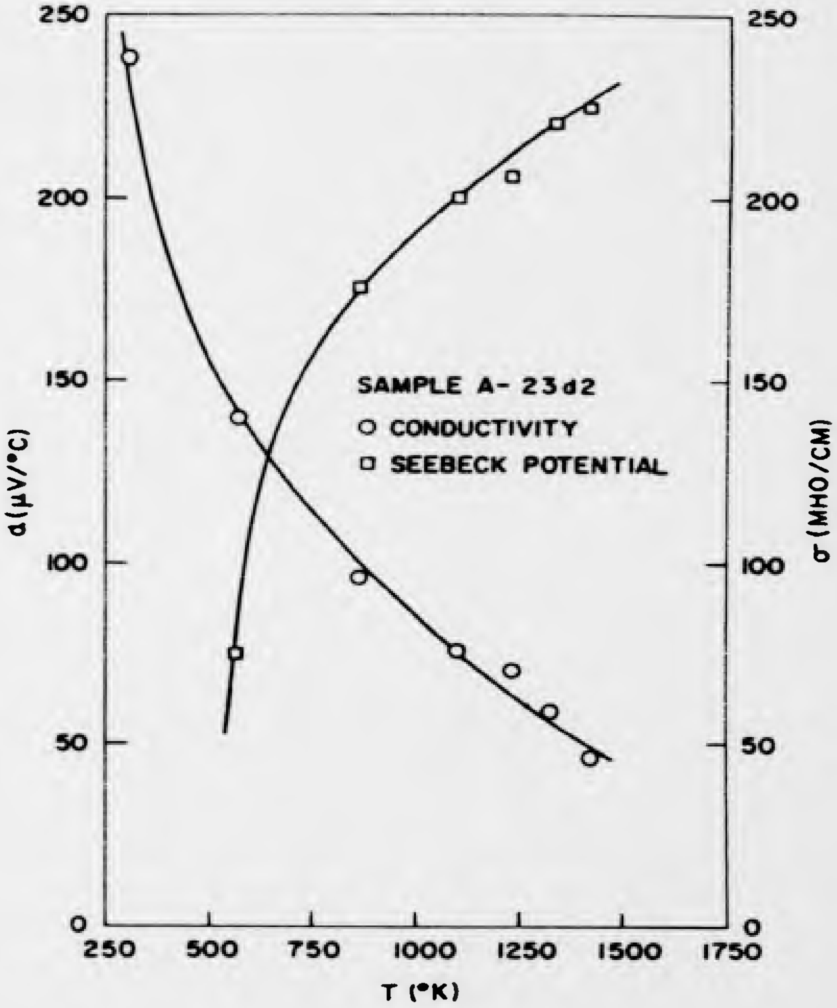

Fig. 4--Seebeck potential and conductivity vs temperature for highly doped sample ($Ce_8BaS_{12.8}$).

Such an effect may lower the temperature at which maximum efficiency is attained. Data on a representative sample appears in Figure 4.

We are attempting to extend our Hall coefficients to higher temperatures in the hope that this may lead to a clarification of transport mechanisms and in turn to the optimization of the material for thermoelectric applications.

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SOME REMARKS ON THE ULTIMATE PERFORMANCE OF RARE EARTH SULFIDES*

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SOME REMARKS ON THE ULTIMATE PERFORMANCE OF RARE EARTH SULFIDES*

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The rare earth sulfides have been under investigation at General Atomic for the past two years. Specimens of cerium sulfide of various compositions have been prepared and studied. Measurements have also been made on lanthanum and samarium sulfide, and other systems are presently being investigated. Some theoretical studies have been made of the electronic eigenstates and transport properties of these materials. Sufficient progress has been made that one can begin to speculate about the ultimate efficiency for thermoelectric conversion in these materials.

These semiconductors, which possess the Th_3P_4 structure, exhibit large departures from stoichiometry. A typical composition can be written in the form $Ce_{2+x}S_{3+x}$, where $0 < x < 1$. When $x = 1$ the material is a semi-metal; in this case two thirds of the cerium ions are trivalent and one third are divalent. When $x = 0$ the material is an insulator; all the cations are trivalent, and eleven percent of the cation sites are vacant.

The conduction mechanism is not fully understood, but it is not believed to be the activated d-band type of conduction discussed by Morin(1)--of which undoped nickel oxide is a typical example--nor does

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the simple Verwey model(2) of the mixed valancy semiconductors appear to apply(3). Rather, the extra electrons appear to form a narrow band of their own and the polaron model independently suggested by Sewell(4) and Holstein(5) probably enters the picture. For a solid characterized by polar bonding there must be a difference between the static and optical dielectric constants. The static dielectric constant of Ce_2S_3 has been measured at 1000 cycles and found to be 18. The optical dielectric constant, estimated from a measurement of Brewster's angle on an imperfectly polished sample, is of the order of 9.

Before discussing the conduction mechanism further, let us look at the general expression for the efficiency of thermoelectric converters. The dimensionless figure of merit is given by

$$zT = \frac{S^2 \sigma T}{K}.$$

It is convenient to express the ratio of the thermal conductivity K, to the electrical conductivity σ, by the Wiedemann-Franz ratio(6). This can be written

$$\frac{K}{\sigma} = A \left(\frac{k}{e}\right)^2 T,$$

where k is the Boltzmann constant, e is the electron charge, and A is a dimensionless parameter dependent on the scattering mechanism.

We also write for convenience the Seebeck coefficient, S, as some numerical factor B times k/e,

$$S = B \left(\frac{k}{e}\right).$$

Thus, the dimensionless figure of merit becomes $zT = B^2/A$.

To make A as small as possible one wants to deal with a material in which the thermal conductivity of the electrons is comparable to but not much larger than the lattice heat conductivity. The value of A depends primarily on the electron scattering processes and on the reduced Fermi energy $\mu^* = \zeta/kT$ and ranges from 2 to 4 for typical cases in which the lattice conductivity is small. A is very large in comparison with unity when σ is less than 10 $\text{ohm}^{-1}\ \text{cm}^{-1}$.

The Seebeck coefficient is approximately equal to the specific heat per electron(7). A general expression for B applicable to semiconductors and metals with spherical energy surfaces and a power law for the energy dependence of the mean free path are given by Joffe(6):

$$S = \pm \frac{k}{e} \left[\frac{r+2}{r+1} \times \frac{F_{r+1}(\mu^*)}{F_r(\mu^*)} - \mu^* \right] .$$

The symbols are defined in detail in his book. The index r represents the power of the energy dependence of the mean free path, and $F_r(\mu^*)$ are Fermi integrals defined in the usual way.

We have

$$\mu^* = \ln \frac{N_c}{n}$$

where $N_c = \dfrac{2(2\pi m^* kT)^{3/2}}{h^3}$.

The first term in S represents the contribution to the Seebeck coefficient from the kinetic energy of the particles averaged over the free path, while the second term represents an entropy term arising from the total number of quantum states available for n electrons. In the case of nondegenerate semiconductors the main contribution to S comes from the second term.

In mixed valancy materials like $Li_xNi_{1-x}O$, one has $\mu^* = \log \frac{1}{x}$ when x is small.

For highly doped materials in which the electron gas is degenerate, the first two terms tend to cancel each other and B approaches $\frac{kT}{\zeta}$. For metals this is a small number since $\zeta >> kT$.

The standard equations which are used by Joffe and all the other workers assume both spherical energy surfaces and a power law for the energy dependence of the mean free path. In narrow-band semiconductors these assumptions may no longer be valid, and it would be of interest to work out the exact expressions for such cases.

In order to have a concentration of electrons large enough that they will determine the thermal conductivity, it is necessary to keep the material from becoming so degenerate that the thermoelectric power approaches the small value typical of metals. This can be achieved if one has a high density of states:

$$N_c = \frac{2(2\pi m^* kT)^{3/2}}{h^3}$$

Thus, one is led to a search for semiconductors in which the electron mass has unusually large values. There must be reasonable values for the mobility in such systems so that an electrical conductivity of 100 $\text{ohm}^{-1}\ \text{cm}^{-1}$ or greater is achieved without the density of electrons being made too large.

Appel(8) at General Atomic has studied Sewell's theory to understand the nature of the electron eigenstates in cerium sulfide. His method is essentially that of the Bloch tight-binding approximation but takes the electron-lattice interaction into account when calculating polaron eigenstates. Therefore, the overlap integrals, which play a central role in the tight-binding approximation, depend on electron <u>and</u> phonon quantum numbers. By taking an appropriate thermal average over the eigenvalues, finally the low-lying energy eigenvalues of the small polarons can be defined in terms of a temperature-dependent effective mass m^*. It may be expected that, in a certain temperature interval around the Debye temperature which corresponds to the frequency of the polarization phonons, the 'small polaron' effective mass is given by the simple formula

$$m^* = m_o \exp(+T/T_o).$$

Here m_o is the rigid lattice mass and T_o is a parameter represented by a rather complicated expression given in Sewell's paper(9).

Experimentally, as shown in the paper read at this meeting by Kurnick et al.,(10) the electrical conductivity decreases slowly with temperature while the thermoelectric power continues to increase with increasing temperature and reaches a value of several times $\frac{k}{e}$. Sewell's formula for the effective polaron mass not only tends to keep the material from becoming degenerate but also contributes a linear term in temperature to the Seebeck coefficient. This is in reasonable agreement with the experimental results.

According to standard theory in which one writes the mobility μ as $\mu = e\tau/m^*$, where τ is the mean relaxation time, one might expect the electrical conductivity to decrease very rapidly. However, when one examines Sewell's model in more detail(11) he finds that when the band is narrow in comparison with kT then at high temperatures the mobility may be independent of the effective mass and has a value of approximately 1 cm^2 $volt^{-1}$ sec^{-1}. The theory is not sufficiently detailed to allow estimates for the numerical value of the effective mass. The density of carriers and their mobility have been measured at room temperature at General Atomic and found to be 10^{22} cm^{-3} and about 1 cm^2 $volt^{-1}$ sec^{-1}.

We can now estimate what figures of merit are likely to be obtained in such semiconductors. It has been found that if the cerium sulfide approaches the Ce_3S_4 semi-metallic state then the conductivity decreases with increasing temperature and the thermoelectric power goes up. It is believed that at a temperature of 1500^oK we can achieve an electrical conductivity of 500 ohm^{-1} cm^{-1} along with a Seebeck coefficient of 250 $\mu v/^oC^{-1}$. The lattice thermal conductivity at this temperature is approximately 0.01 watts $\mathrm{cm}^{-1}{}^{\circ}\mathrm{C}^{-1}$. With a Wiedemann-Franz contribution from the electrons added, the total thermal conductivity would be 0.02 watts $\mathrm{cm}^{-1}{}^{\circ}\mathrm{C}^{-1}$. This gives for the dimensionless figure of merit a value of 1.2.

We are investigating a number of rare earth sulfides in addition to cerium sulfide. Results obtained by Guthrie on zirconium sulfide and lanthanum sulfide show encouraging Seebeck coefficient along with reasonable electrical conductivity. Thermal conductivity measurements have not yet been made on these materials.

Another interesting effect might result in a further improvement in the performance of these materials. As electrons are added to the system there is phonon-electron scattering, which reduces the mean free path for the phonons. In metals this effect is carried to an extreme and the phonon heat conductivity is negligibly small. The following formula is a theoretical estimate of the magnitude of this effect(12) on the basis of conventional theory for nonpolar crystals:

$$K_{ph} = K_{ph}^{(o)} \left[1 + \frac{2\pi}{9} \; \frac{ne}{T\mu} \; \frac{(\bar{\ell}_{ph}\, u)^2}{K_{ph}^{(o)}} \right]^{-1}$$

where μ is the mobility, $K_{ph}^{(o)}$ is the insulator heat conductivity, u is the velocity of sound, and $\bar{\ell}_{ph}$ the mean free path of those phonons which interact with the charge carriers.

It is very hard to estimate $\bar{\ell}_{ph}$. If $\bar{\ell}_{ph}$ is the order of 10^{-7} cm (the mean free path for the phonon heat conductivity), the correction is the order of 1%. If, however, the mean free path for the phonons interacting with the electrons is 10 times larger, then the effect may be quite important. It has been shown that this effect is negligible in bismuth telluride(13), but is important in Group III doped germanium at low temperatures(14).

There is also the possibility of further modifying the material by filling the vacant sites with other cations. This doping may help decrease the lattice thermal conductivity in the usual manner. We have been investigating the effects of barium and other materials. Some of the results for barium are reported in the paper by Kurnick. We believe that the effect of doping may also affect the electronic eigenstates, and theoretical and experimental investigations on this subject are being carried out.

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GENERAL ATOMIC

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GAMD - 2091

ON THE APPLICATION OF THE SEEBECK EFFECT IN SOLIDS

Work done by:	Report written by:
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This document, which was prepared primarily for internal use at General Atomic, may contain preliminary or incomplete data. It is informal and is subject to revision or correction; it does not, therefore, represent a final report.

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March 10, 1961

GENERAL

From the conservation laws of the electrical current density, the heat current density, and the energy density(1) it follows that the usefulness of a semiconductor or a semi-metal(2) as thermoelectric material is determined by a single parameter, the "figure of merit" ZT, defined by Joffe(3), as

$$ZT = \frac{\alpha^2 T}{\kappa \rho} \qquad (1)$$

where α is the Seebeck coefficient, ρ is electrical resistivity and T is the absolute temperature. The thermal conductivity κ is composed of the electronic contribution κ_{el}, of the insulator lattice contribution κ_{latt}, and of a superposition term which depends on the properties of both systems, electrons and phonons:

$$\kappa = \kappa_e + \kappa_{latt} + \Delta\kappa \qquad (2)$$

Only in case of small charge carrier concentrations ($n < 10^{13} cm^{-3}$) $\Delta\kappa$ is negligible at all temperatures. The usefulness of a solid as thermoelectric power generator, i.e., the technical utilization of the Seebeck effect, and for thermoelectric cooling devices, i.e., the technical application of the Peltier effect, depends on ZT as the pertinent quantity.* In principle (with respect to ZT) a material which is useful for thermoelectric cooling is also useful for thermoelectric power generation. However, the fact that both technical applications cover different temperature regions, makes it necessary to use different materials. Nevertheless, some important conclusions about the technical application of the Seebeck effect can be drawn from the two-decade experience in the applied physics of the Peltier effect. Thus, we think that the optimum ZT values which one has obtained for thermoelectric cooling devices may also be achieved at high temperatures for thermoelectric power generators. The ZT value of a thermoelectric cooling substance which has been found by Birkholz(4) is about 1 at T = 300°K.

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*See also P. H. Miller, Jr., GA-2018, for a discussion of the figure of merit of rare earth sulfides.

From the physical point of view the pertinent question with respect to heat conversion reads: What kind of material which is stable at high temperatures gives the optimum ZT value? We shall try to suggest an answer to this question. The different aspects of the problem will be considered in successive order of their importance and their physical sensibility.

THERMOELECTRIC POWER AND ELECTRONIC EIGENSTATES

A good thermoelectric material will be characterized by a significant amount of polar bonding between the lattice particles. In such a case one is usually concerned with an extrinsic semiconductor not only at low but also at high temperatures (because of a wide forbidden zone). Thus, the number of charge carriers depends on the chemical composition and the doping; in other words, the charge carrier concentration can be controlled. Furthermore, the chemical bond has some influence on the electronic structure. Eigenstates of electrons in polar crystals are not only determined by the crystal potential of the static lattice, but also by the polarization potential which an extra electron induces by displacing neighboring lattice particles and by deforming the electron cores. Thereby the rigid lattice potential is changed in such a way that the electron feels an additional polarization potential. This effect, due to a reacting-potential-field occurs in any solid when an extra electron is introduced, its investigation represents a special test-particle problem. However, in nonpolar semiconductors the polarizability of the lattice is small and the static dielectric constant is approximately equal to the high frequency dielectric constant. Therefore, it is reasonable to approximate the polaron (= electron + polarization) by an electron with the rigid lattice effective mass m^*. However, in semiconductors with mixed covalent and polar bonding the polaron is the appropriate charge carrier. This can be true also when the charge carrier concentration is large, as is usually the case in thermoelectric materials like Ce-S. The reason is the following: the rigid lattice eigenstates of those electrons, which in a deformable lattice together with an associated cloud of optical phonons form the polaron, consist of a proper superposition of atomic orbitals, i.e., of <u>localized</u> wave functions.

Consequently, the charge carriers are not very effective in shielding the charges of the lattice particles, whereas, in a metal the free electrons succeeded in almost perfect screening of the metal-ions, this means the electrostatic potential of a metal-ion drops rapidly with distance. The low-lying energy eigenvalues of the polaron eigenstates can be defined in terms of a polaron effective mass m^{**}. Usually m^{**} is large, the polaron band is narrow, provided the corresponding overlap integrals have small values. A large effective mass favors the value of the thermoelectric power(5)

$$Q = -\frac{k_B}{e}\left[b + \log(N_c/n)\right] \tag{3}$$

where n is the negative charge carrier concentration and N_c the density of states in the conduction band. The number b depends somewhat on the polaron-lattice interaction. With respect to good cerium sulfide semiconductors we think the following data are reasonable for $T = 1200^\circ K$:

$$Q = -250\ \mu V/^\circ K, \quad \left.\begin{matrix} n = 10^{21} cm^{-3} \\ N_c = 6.5 \times 10^{21} cm^{-3} \end{matrix}\right\} \log(N_c/n) = 2.$$

We have assumed that $m^{**}/m = 10$. The negative sign of the thermoelectric power indicates that the electrical current is carried by negative charge carriers. This is to be expected because those Ce-S compounds which contain doubly charged cerium ions are electrical conductors, whereas Ce_2S_3 with triply charged cerium ions is an insulator. Thus, there is a band gap for Ce_2S_3 and, roughly speaking, its width corresponds to the energy necessary for the reaction $Ce^{++} \rightarrow Ce^{+++} + e^-$.

It can be easily shown that $\log(N_c/n) = 2$ results in an optimum ZT value if one assumes

$$\rho \propto 1/n, \text{ b and } \kappa \text{ independent of n.}$$

We then have with Eq. 1 the relation

$$Z(n) = \text{const}\left[b + \log(N_c/n)\right]^2 n. \tag{4}$$

A simple extremal calculus shows that the maximum value of Z for given N_c is obtained by a carrier concentration n such that $\log(N_c/n) = 2$. In the considered case it is fairly reasonable to suggest a temperature dependence of the Fermi energy $\zeta = k_B T \log(n/N_c)$ as shown in Fig. 1.

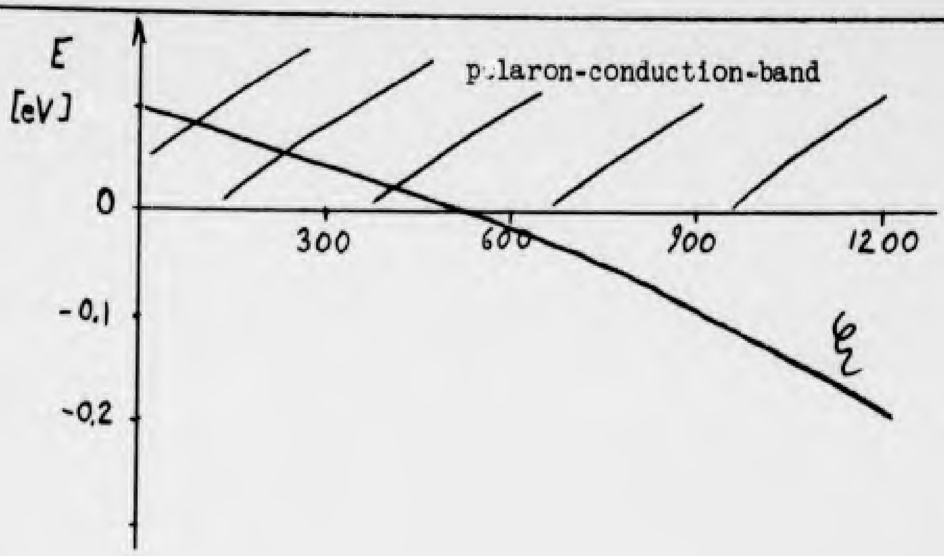

Fig. 1 Schematic diagram of the suggested temperature dependence of the Fermi energy in a thermoelectric material characterized by optimum ZT value at T = 1200°K.

To improve the thermoelectric power one should find out if it is possible to affect m^{**}. The effective mass is inversely proportional to the rigid lattice overlap integral. If one can stretch the lattice and thereby increase the distance between two neighboring cerium ions, one might expect a larger value for m^{**}. Correspondingly, one has to increase the charge concentration n so that one gets the optimum value for $\log(N_c/n)$, but now connected with a higher electrical conductivity.

INSULATOR HEAT CONDUCTIVITY AND CRYSTAL LATTICE

The crystal lattice, i.e., the lattice structure, the lattice constituents, and the nature of the chemical bond determine the magnitude of lattice heat conductivity $\kappa_{latt.}$ So far there is no structure sensitive theory of the thermal conductivity in dielectrica. On the basis of a simple model - monatomic face centered cubic lattice, central forces between the next and next-nearest neighbors characterized by two constants, a spring constant f and an anharmonicity constant g - Leibfried and Schlömann(6) have calculated the lattice thermal conductivity at high temperatures. Their results is given by

$$\kappa_{latt} = \text{const} \times \frac{N}{V} \times \frac{M^3 \omega_D^5 u^2}{T \gamma^2} \qquad (5)$$

where N is the number of particles with mass M in volume V. The Grüeisen constant γ can be written as

$$\gamma = - \frac{r}{6} \times \frac{g \text{ (= anharmonicity constant)}}{f \text{ (= spring constant)}} \qquad (6)$$

where r is the nearest neighbor distance in a fcc lattice. The Debye frequency $\omega_D \propto (f/M)^{1/2}$, the average sound velocity $u = (MN\chi/N)^{-1/2}$ where χ is the compressibility. From Eq. 5 one can draw some general conclusions about the lattice thermal conductivity which may also apply for compound lattices. A small value of κ_{latt} is favored by a large value of the Grüneisen constant γ. Thus, one would like to find a crystal with a large g value, i.e., with large cubic dilation, and with a small f value. Furthermore, according to Eq. 5, the thermal conductivity should be a decreasing function of the average atomic weight. However, it has been shown by Keyes(7) on the basis of the present empirical knowledge that not only the average atomic weight but also the ratio of the atomic weights of the constituents are significant for the value of κ_{latt} in a binary compound. A large ratio favors a small thermal conductivity. As an example let us compare bismuth telluride with cerium sulfide:

semiconductors	Bi_2Te_3	Ce_2S_3
average atomic weight	1.78	7.5
average weight ratio	1.65	4.5
κ_{latt} at $T = 300^\circ K$ ($W\ cm^{-1}\ {}^\circ K^{-1}$)	0.02	0.01

Although the atomic weight of Bi_2Te_3 is larger than that of Ce_2S_3, the latter compound has a smaller conductivity than the former. This may be due to the different atomic weight ratios. However, in case of cerium sulfide one must take into account that the compound Ce_2S_3 crystallizes in a defect lattice. The vacancies represent additional scattering centers for the high frequency phonons. The corresponding influence on the thermal conductivity can perhaps be determined experimentally by measuring the thermal conductivity of Ce_3S_4 where all the lattice sites are occupied. Now, the electronic contribution to the thermal conductivity of Ce_3S_4 is certainly important, however, in a strong magnetic field the electronic part κ_e approximates the value 0.

Finally it may be mentioned that in thermoelectric materials the concentration of charge carriers is fairly large and thus the reduction of the insulator heat conductivity due to the scattering of phonons by charge carriers may be important. Then, the superposition term $\Delta\kappa$ cannot be neglected. For $\Delta\kappa$ we have the relation

$$\Delta\kappa = \text{function}\ (n\ x\ \frac{\ell_{ph}}{\ell_e}, \qquad (6)$$

where ℓ_{ph} is the mean free path of those phonons which interact with the charge carriers (mean free path ℓ_e). The larger the ratio ℓ_{ph}/ℓ_e and the larger the carrier concentration n, the stronger is the reduction of the insulator heat conductivity.

We have noticed some aspects of the heat conduction problem for thermoelectric materials because we think that at this stage of our knowledge about the electrical properties of cerium sulfide semiconductors it is important to investigate carefully the thermal conductivity as a function of temperature, composition, and doping. Then in the Ce-S system including ternary compounds based on Ce-S, we may find the semiconductor with optimum ZT value. This semiconductor has the lowest insulator heat conductivity which is compatible with the requirement for the optimum values of the electrical conductivity and the thermoelectric power i.e., $\log(N_c/n) = 2$. The value of n, according to our experience with thermoelectric cooling substances should be such that the lattice and the electrical part of the thermal conductivity are comparable. In other words: if N would be a free parameter, one would choose n so that

$\kappa_e \approx \kappa_{latt}$ and $\log(N_c/n) \approx 2$.

Since a low insulator heat conductivity may be considered as a basic condition for a thermoelectric material, accurate measurements of the thermal conductivity of other suitable materials are important. A number of such materials have been discussed with respect to their physical properties, known so far, by Guthrie(9). Thorium phosphide Th_3P_4, e.g., has an average atomic weight of 117, and the atomic weight ratio of both constituents is nearly 8.

THE ELECTRICAL CONDUCTIVITY

The electronic conductivity in semiconductors with low mobility is not yet fully understood. There is no quantitative theory of the carrier mobility, and some qualitative considerations of Fröhlich and Sewell(9) and of Sewell(10) have, naturally, a limited value only. From the theoretical point of view there are two possibilities which can lead to a low carrier mobility. If the band model applies the usual perturbation theory of electron-lattice interaction and particularly the relation $\mu = e \tau_e/m^{**}$ may break down, because the band may be so narrow (band width less than $k_B \theta_D$) that the absorption and emission of a <u>single</u> phonon becomes impossible in view of energy and wave vector conservation. However, assuming the polaron picture and thus avoiding perturbation theory from the very beginning, Fröhlich and Sewell show that the matrix elements for the interaction of polarons with acoustical phonons correspond already in zero order to two-phonon scattering processes (single phonon scattering processes are forbidden because of the conservation laws) and that the resulting polaron mobility may be independent of the effective mass m^{**}. On the other hand there are substances where the band model becomes invalid, at least for high temperatures. In such a case the carrier-lattice interaction is so strong that the charge carriers move from one ion to the next more easily by many phonon-activated processes than by tunneling. In such a case - NiO is an example - the electronic mobility is much less than 1 cm^2/v sec. Although the mobility increases with temperature it is still small at high temperatures. Since in compounds with phonon-activated jump conduction the electrical conductivity is certainly smaller than in the other substances, the thermoelectric power should be larger to compensate for the lower conductivity. It may be possible that at very high temperatures the phonon-activated jump conduction gives the largest ZT value, but at this time there is no final answer to this question.

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