

## Electronic Transport in High-Resistivity Cerium Sulfide\*

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Electronic transport has been studied in  $Ce_{3-x}S_4$  samples with compositions in the range  $x > 0.30$ . The results show systematic trends as a function of temperature and composition which suggest a transition between behavior typical of metals and behavior typical of insulators. The resistivity curves as a function of temperature generally go through a minimum and have an activation energy in the low-temperature range. The Seebeck coefficient and Hall coefficient also show systematic changes suggesting a division into two characteristic transport ranges. The low Hall mobility at low temperatures and the behavior of the Seebeck coefficient support the idea that the electrons are in localized states in the semi-insulator region and move by a hopping process.

### I. INTRODUCTION

ALTHOUGH cerium sulfide  $Ce_{3-x}S_4$  has semi-metallic behavior over most of its stoichiometry range ( $0 < x < 0.30$ ), it has an essentially ionic crystal structure. The metallic transport is due to the large concentration of electrons which occurs except when  $x$  approaches  $1/3$ ; the transport behavior in the semi-metallic domain has been described in an earlier paper.<sup>1</sup> The remaining range of composition,  $0.30 < x < 1/3$ , though small in an absolute sense, corresponds to electron concentrations which decrease over many decades. It is known that cerium sulfide is an insulator at the limit of  $x = 1/3$ . It is a matter of some interest to investigate the electronic transport over this composition range and to examine the transition from a metallic to an insulator type of transport.

There has been considerable interest in the transition between metal and insulator behavior. A number of theoretical studies have been made by Mott and others relating to systems that one might call "dilute metals."<sup>2</sup> Mott has suggested that such systems may have a sharp metal-insulator transition when the concentration of the metal atoms is sufficiently low. The main type of experimental system to which these ideas have been applied is impurity bands in semiconductors such as germanium and silicon,<sup>3</sup> and recent work has provided connections between experimental and theoretical results in these systems. Other examples of "dilute metals" are alkali metal solutions in liquid ammonia,<sup>4</sup>

solutions of metals in molten salts such as Bi-BiI<sub>3</sub>,<sup>5</sup> and electropositive metals in their molten salts.<sup>6</sup>

It is not yet clear where essential differences may exist between cerium sulfide in the low electron range of concentrations and these "dilute metal" types of systems; but there is no doubt that they have much in common. Experimentally, one observes a negative temperature coefficient of resistivity at low-electron concentrations (usually with an activation energy) and a positive coefficient at high-electron concentrations. (In the case of liquids, the electronic conductivity generally falls low enough so that the motion of ions may be expected to play a dominant role in the conductivity.) The low-mobility, low-electron-concentration type of transport is believed to occur by "hopping" processes, with the electrons in localized states. In the domain of high-electron concentrations, one expects to find electrons in nonlocalized states where the electronic motion can be described more appropriately in terms of motion of wave packets.

Previous studies of transport in cerium sulfide  $Ce_{3-x}S_4$  has been confined to the metallic range of compositions.<sup>1,7,8</sup> Although the insulator composition with  $x = 1/3$  is readily prepared in a powdered form, fused samples invariably lose sulfur to the extent that one obtains compositions in the metallic range. The present work is based on samples prepared by equilibrating fused cerium sulfide with sulfur at elevated temperatures where diffusion occurs readily. These samples had electron concentrations from about

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<sup>1</sup> M. Cutler, J. F. Leavy, and R. L. Fitzpatrick, *Phys. Rev.* **133**, A1143 (1964), preceding paper.

<sup>2</sup> (a) N. F. Mott and W. D. Twose, *Advan. Phys.* **10**, 107 (1961); (b) N. F. Mott, *Phil. Mag.* **6**, 287 (1961); (c) A. Miller and E. Abrahams, *Phys. Rev.* **120**, 745 (1960).

<sup>3</sup> C. S. Hung and J. R. Gliessman, *Phys. Rev.* **96**, 1226 (1954); H. Fritzsche, *ibid.* **99**, 406 (1955); also *Phys. Chem. Solids* **6**, 69 (1960); H. Fritzsche and M. Cuevas, *Phys. Rev.* **119**, 1238 (1960); F. J. Morin and J. P. Maita, *ibid.* **96**, 28 (1954).

<sup>4</sup> E. C. Evers and R. L. Kay, *Ann. Rev. Phys. Chem.* **11**, 32 (1960).

<sup>5</sup> L. F. Grantham and S. J. Yosim, *J. Chem. Phys.* **38**, 1671 (1963); D. O. Raleigh, *ibid.* **38**, 1677 (1963).

<sup>6</sup> A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, *Discussions Faraday Soc.* **32**, 188 (1961); M. A. Bredig, *J. Chem. Phys.* **37**, 914 (1962).

<sup>7</sup> (a) S. W. Kurnick, M. Cutler, R. L. Fitzpatrick, and J. F. Leavy, in *Conference on Rare Earth Research*, edited by E. V. Kleber (Macmillan Company, New York, 1961), p. 241; (b) F. M. Ryan, I. N. Greenberg, and R. C. Miller, *J. Appl. Phys.* **33**, 864 (1962); (c) F. L. Carter, R. C. Miller, and F. M. Ryan, *Advanced Energy Conversion* **1**, 165 (1961); (d) J. Appel and S. W. Kurnick, *J. Appl. Phys.* **32**, 2206 (1961); (e) S. W. Kurnick, M. F. Merriam, and R. L. Fitzpatrick, *Advanced Energy Conversion* **1**, 157 (1961).

<sup>8</sup> M. Cutler, R. L. Fitzpatrick, and J. F. Leavy, *Phys. Chem. Solids* **24**, 319 (1963).

$10^{20}/\text{cm}^3$  to  $5 \times 10^{17}/\text{cm}^3$  at room temperature. In this range of composition, a study of the transport properties (resistivity  $\rho$ , Hall coefficient  $R_H$ , and Seebeck coefficient  $S$ ) shows evidence of a gradual change from those characteristics typical of metals to those typical of insulators.

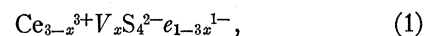
The division between the compositions considered in this paper and those considered in Ref. 1 is somewhat arbitrary and is based largely on the method used in preparation. The behavior is discussed in terms of a transition between metallic and insulator types of transport. One cannot make a qualitative distinction between semiconductor behavior and insulator behavior in the experimental domain. In the present case, there are ranges at high temperatures where the electrons are nondegenerate and where transport appears to involve nonlocalized electrons, as is typical for semiconductors. We prefer to use the word "insulator" since the situation developing at low-electron concentrations seems, on the whole, typical of the qualitative behavior of insulators, in the everyday use of the word. Although it is not yet clear what are the basic physical factors underlying the general behavior of insulators as compared with semiconductors, one factor suggested by our results is the dominant influence of large potential fluctuations. This already plays an important role in the metallic range, as discussed in Ref. 1, and it would seem that the removal of electrons leads to a direct transition to a situation typical for insulators.

In comparison with other materials whose electronic properties have received extensive study, the unusual character of cerium sulfide seems to arise from its having an ionic lattice with a defect structure. That is, the stoichiometric composition  $\text{Ce}_2\text{S}_3$  occurs in a lattice composition  $\text{Ce}_{3-x}\text{S}_4$ , with  $x=1/3$  representing vacancies at random cerium sites of the perfect lattice. This gives rise to an unusual situation; starting with an insulator ( $x=1/3$ ), as one adds cerium atoms one introduces  $\text{Ce}^{3+}$  ions at vacancy sites, which are identical to the other cerium ions, together with three electrons per ion. Thus, one introduces electrons without adding impurities and one can increase the electron concentration to a large value ( $\sim 10^{20}/\text{cm}^3$ ) before the vacancy concentration is changed appreciably. This leads to an unusual possibility of adding electrons to a polar crystal without materially changing the lattice. On the other hand, the random position of the vacancies also gives this lattice an unusual character.

## II. PHYSICAL STRUCTURE AND PREPARATION OF CERIUM SULFIDE

The crystal structure of the gamma phase of cerium sulfide was described by Zachariasen,<sup>9</sup> and the chemistry of this phase has been studied in several investiga-

tions.<sup>10-12</sup> The gamma phase is in a cubic  $\text{Th}_3\text{P}_4$  type lattice, which has a complicated unit cell containing 28 lattice sites. The Bravais lattice is face-centered cubic. There are twelve cerium atom sites, each having eight sulfur neighbors, and the sixteen sulfur atoms each have six cerium neighbors. Magnetic susceptibility measurements<sup>10,12</sup> and studies of the electronic behavior indicate that there is an ionic structure which can appropriately be described by the formula:



where the vacancies  $V$  are at the cerium sites. The extra electrons  $e^-$  are in a conduction band which, there are reasons to believe, arises largely from the  $5d$  atomic orbitals of the cerium ions.<sup>8</sup>

The concentration of the  $\text{Ce}_{3-x}\text{S}_4$  units is  $6.25 \times 10^{21}/\text{cm}^3$ , so that the formulas for the volume concentration of electrons  $n$  and vacancies  $N_v$  are:

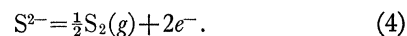
$$n = 1.88 \times 10^{22} (1/3 - x) / \text{cm}^3, \quad (2)$$

and

$$N_v = (6.25x) \times 10^{21} / \text{cm}^3. \quad (3)$$

$x$  varies between the limits 0 and  $1/3$ , so that  $N_v$  varies between 0 and  $2.08 \times 10^{21}/\text{cm}^3$ , and  $n$  varies between  $6.25 \times 10^{21}/\text{cm}^3$  and zero. Previous studies have been concerned with compositions with  $x < 0.30$ , where  $n \gtrsim 6 \times 10^{20}/\text{cm}^3$ , and the vacancy concentration changes over a large factor. In this range, there is statistical degeneracy ( $N_v \sim 1 \times 10^{20}/\text{cm}^3$  at  $T = 300^\circ\text{K}$ ), and the electronic transport is described well by theoretical equations developed for metals, particularly with regard to the effect of temperature. One can conveniently determine  $x$ , and hence  $n$ , in the metallic range by accurate measurements of the density.

The techniques used in our laboratory for preparing cerium sulfide have been described previously.<sup>7a,8</sup> The first step is to sulfurize  $\text{CeO}_2$  at  $1400^\circ\text{C}$ , which yields the insulating powder ( $x=1/3$ ), and then to melt the sulfide. The melting temperature is between  $1900$  and  $2100^\circ\text{C}$ , depending on the value of  $x$ , and the melting process occurs with the loss of an appreciable amount of sulfur. The vapor pressure of sulfur above the melt increases rapidly as  $x$  approaches  $1/3$ , no doubt because the reaction involves the loss of electrons by sulfur ions; i.e.,



Thus, if  $n$  is small [ $x \cong 1/3$  in Eq. (2)], the equilibrium in Eq. (4) is shifted strongly to the right. The lowest electron concentrations that could be obtained directly in fused samples was about  $6 \times 10^{20}/\text{cm}^3$ , corresponding to  $x \cong 0.30$ .

The technique used for preparing fused samples,

<sup>10</sup> E. D. Eastman, L. Brewer, L. A. Bromley, R. W. Giles, and N. F. Longren, *J. Am. Chem. Soc.* **72**, 2250 (1950).

<sup>11</sup> E. Banks, K. F. Stripps, H. W. Newkirk, and R. Ward, *J. Am. Chem. Soc.* **74**, 2450 (1952).

<sup>12</sup> M. Picon, L. Domange, J. Flahaut, M. Guittard, and M. Patrie, *Bull. Soc. Chim. France* **2**, 221 (1960).

<sup>9</sup> W. H. Zachariasen, *Acta Cryst.* **2**, 57 (1949).

with  $x$  approaching  $1/3$  but less than the extreme value, was to diffuse sulfur back into the lattice at temperatures below the melting point. Diffusion occurs quite readily at  $1400^\circ\text{C}$ , and our diffusions were generally carried out at this temperature. Diffusion equilibration has been carried out previously by Kurnick, with a resulting sample that had a very high resistivity at room temperature ( $>10^6 \Omega \text{ cm}$ ).<sup>13</sup> This was done by equilibrating with hydrogen sulfide at a pressure of approximately 1 atm (at room temperature). Our equilibrations with lower sulfur pressures were carried out in two ways:

(1) In a dynamic system where a mixture of hydrogen sulfide and hydrogen flowed through a carbon vessel containing the crystals. A large  $H_2/H_2S$  ratio was used to reduce the partial pressure of sulfur.

(2) In a sealed molybdenum vessel where the excess sulfur was provided by  $Ce_2S_3$  ( $x=1/3$ ) in the powdered form.

Our success in obtaining suitable samples was very spotty, as the result of a problem which is discussed below. The samples that we used were obtained more or less accidentally, and we cannot state sufficient conditions for their preparation.

The problem in the preparation arises from the fact that the gamma phase is very metastable over most values of  $x$ , below some unknown maximum temperature which probably increases with decreasing  $x$ , and which is well above  $1000^\circ\text{C}$ . The stable phase below this temperature seems to be the one described as the beta phase by Flahaut and his associates.<sup>12</sup> In the normal preparation of cerium sulfide by fusion, the sample is cooled rapidly enough through the transition region to subsequently impede the transition kinetically. Irreversible increases in resistivity are often noted in samples with normal metallic compositions when measurements are carried out in the vicinity of  $1000^\circ\text{C}$ . After observing this under circumstances where the effect could not reasonably be ascribed to contamination, we established that a beta-phase transition is occurring. This was done by an experiment involving heating the samples in sealed tubes at  $1000^\circ\text{C}$  over a period of days to force the transition toward completion. The presence of the beta phase is verified by characteristic x-ray diffraction lines<sup>14</sup>; it seems to be the same as that referred to by Banks *et al.* as the "complex phase."<sup>11</sup> The incipient appearance of these lines has been correlated with samples suspected of having excessive resistivity in two types of situations:

(1) Samples which suffered irreversible increases in resistivity after exposure to high temperature, as mentioned above.

(2) Samples of newly prepared material whose mobility turned out to be lower than the one normally

<sup>13</sup> S. W. Kurnick (private communication).

<sup>14</sup> We are indebted to Dr. Flahaut for providing data on his beta-phase x-ray lines for making the comparison.

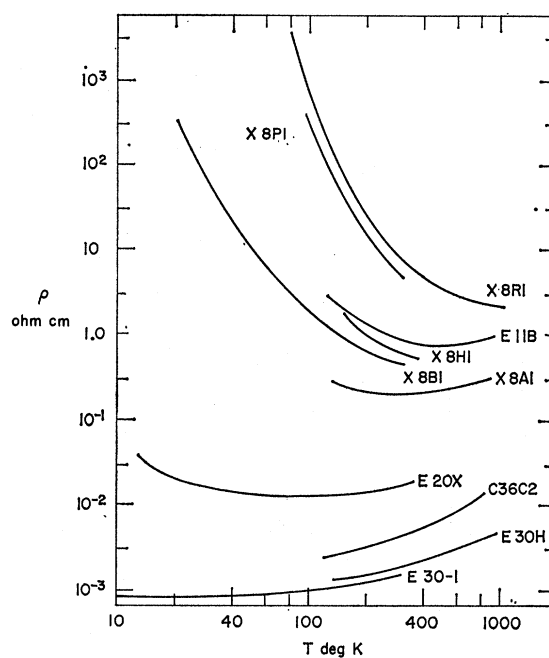


FIG. 1. Resistivity as a function of temperature. Samples C36C2, E30H, E30-1 have, respectively,  $n=0.60$ ,  $1.26$ , and  $1.42 \times 10^{21}/\text{cm}^3$ . The other samples are described in the table.

expected for that composition; that is, they fall out of line from curves based on all samples.

The incipient beta-phase x-ray lines appear as a hump on either side of the strong gamma-phase line at  $12 \text{ deg (Mo } K \text{ lines)}$ ,<sup>15</sup> and as small rises in the vicinity of  $16\text{--}16.5 \text{ deg}$  where no gamma-phase lines occur and a number of beta-phase lines exist. After establishing these facts, we found that we could obtain very consistent variations in the measured transport parameters by rigorously excluding samples which showed x-ray patterns with any evidence of beta-phase contamination. The beta phase, which is apparently an insulator, drastically affects the transport measurements by depositing on the grain boundaries on the surfaces of the microcrystallites. It probably also forms new surfaces within larger crystals by aggregating on dislocations and regions of lineage.<sup>16</sup>

This tendency to form the beta phase presents a formidable obstacle when one wishes to change the composition by diffusing sulfur into a crystal at a temperature near  $1400^\circ\text{C}$ ; this is probably below the transition temperature for  $x \lesssim 0.30$ . We attempted to establish criteria for carrying on the diffusion without causing the transformation. As already noted, we could not find any consistent conditions for doing this but ended up, by chance, with a number of samples which

<sup>15</sup> They are identical with the pattern reproduced in the paper by Banks *et al.* (Ref. 11).

<sup>16</sup> We are indebted to Dr. P. K. Gantzel, of our laboratories, for making a metallographic examination which suggested these conclusions.

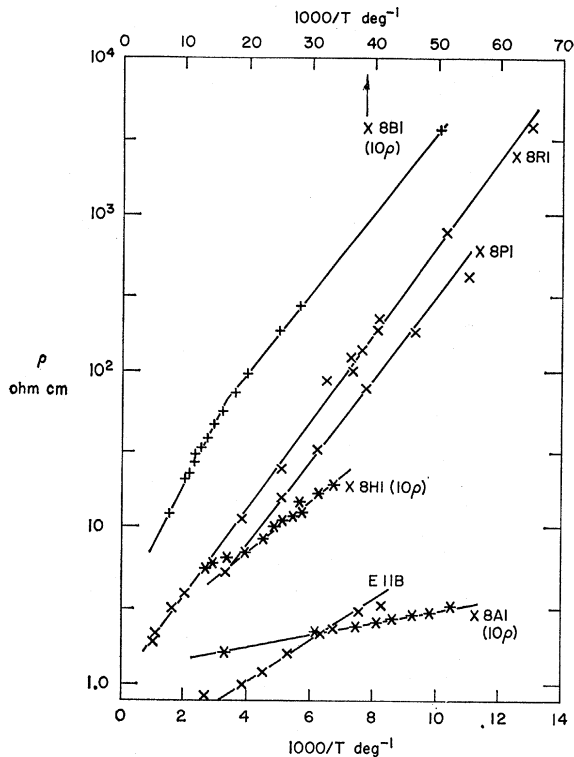


Fig. 2. Low-temperature region of resistivity curves. We plot  $10\rho$  for samples X8H1, X8A1, and X8B1. The abscissa for X8B1 is on the top of the graph.

did not contain any beta phase; these samples were used in the measurements. There are indications that the presence of carbon helps to inhibit the formation of the beta phase. Since the samples were fragile, and our supply for a given composition haphazard, we were not able to make a complete set of measurements at each composition, nor to cover the range in a uniform fashion. However, it will be seen that there is sufficient overlap and consistency in the results to provide a clear pattern and to derive some definite conclusions.

## II. EXPERIMENTAL RESULTS

### A. Resistivity

The resistivity  $\rho$  was measured in temperature ranges lying between 10 and 1000°K. The curves are shown in Fig. 1, which includes, for reference, some samples in the higher conductivity "metallic" range. Information relevant to the samples is listed in Table I. We will often characterize samples by their electron concentration  $n_H$  as deduced from room-temperature Hall measurements; i.e.,  $n_H = 1/R_H e$ .

Starting with E20X, which has the highest electron concentration of the group considered in this paper ( $\sim 8 \times 10^{19} \text{ cm}^{-3}$  at room temperature), the samples show a distinct minimum in  $\rho(T)$ , which occurs at an increasing temperature as one goes to lower electron concentra-

TABLE I. Data on samples.

Sample	Room-temperature electrical conductivity (mho/cm)	$n_H$ ( $10^{18} \text{ cm}^{-3}$ )	Activation energy for resistivity ( $10^{-3} \text{ eV}$ )
E20X	52.0	83	3.2
E20A	54.6	83	
X8A1	5.4	14	8.6
X8B1	1.96	5.2	15.3
			10.1 (low $T$ )
X8H1	1.54	4.3	31.6
E11B	1.3	4.9	21.6
X8P1	0.191	0.87	50
X8R1	0.119	0.5	55

tions. This statement does not apply to the two samples with the highest resistivity, for which  $d\rho/dT$  is still negative at the highest temperature of measurement, although there is a trend toward a minimum evident at 1000°K.

The behavior of  $\rho(T)$  at temperatures above the minimum is qualitatively similar to that occurring in the metallic samples. Indeed, the sample E20X obeys the equation  $\rho = \text{const} + \text{const}T^{3/2}$ , as expected for lattice scattering of nondegenerate electrons. The higher resistivity samples do not have a wide enough range where  $d\rho/dT > 0$  to make further analysis of the temperature behavior meaningful.

In the temperature ranges where  $d\rho/dT < 0$ , the data, fall well on straight lines in activation energy plots, as seen in Fig. 2. The activation energies, listed in the table, increase as one goes to samples with increasing values of room-temperature resistivity. Sample X8R1

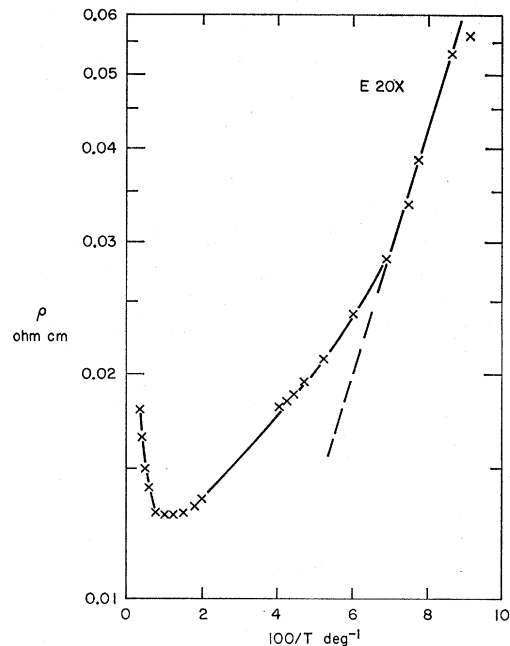


Fig. 3. Low temperature resistivity curve for E20X.

has the same slope between 100 and 1000°K. Sample X8B1, which was measured between room temperature and liquid-helium temperatures, showed a second smaller activation energy below 100°K. We do not have enough other data in this temperature range to state whether that is a general phenomenon.

The activation energies in  $\rho(T)$  and their dependence on the electron concentration would not in themselves be inconsistent with trapping of electrons at a single impurity site, since the increased shielding at high-electron concentrations is known to decrease the distance of trapping levels below the band edge. Although the screening may play an important role in  $\rho(T)$ , measurements of the Hall coefficient and the Seebeck coefficient, described below, indicate that simple trapping does not occur.

Figure 3 has a more detailed plot of  $\rho(T)$  of sample E20X for the region where  $d\rho/dT < 0$ , below 100°K. Although the slope in the activation energy plot is not constant over a very wide range, the magnitude (0.0032 eV for the dashed line) is very interesting. According to a calculation based on the assumption that a normal band model is applicable, the sample is degenerate in this temperature range, and the Fermi energy is 0.020 eV above the band edge. This is much larger than the activation energy, and would be hard to explain in terms of normal electronic mechanisms. An explanation in terms of potential fluctuations between microscopic regions is given below.

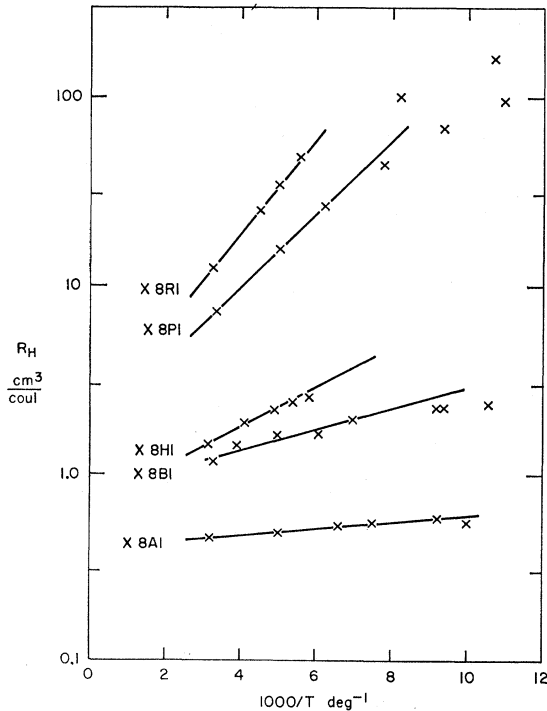


FIG. 4. Hall coefficient versus temperature. Samples are described in the table.

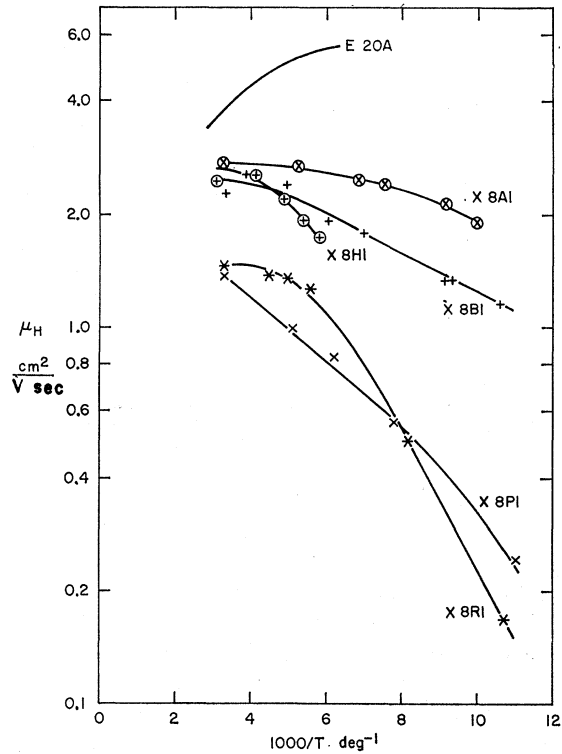


FIG. 5. Hall mobility versus temperature. Samples are described in the table.

### B. Hall Coefficient and Hall Mobility

We were able to measure the Hall coefficient of a number of samples between 100 and 350°K. An ac technique, described previously, was used for the most part.<sup>8</sup> With the higher resistivity samples, particularly at lower temperatures, it was found that the Hall coefficient decreased with increasing frequency, and dc measurements were used in these cases. (This was also true for the resistivity measurements.)

The experimental values of the Hall coefficient are plotted in Fig. 4 with coordinates appropriate for determining an activation energy. (The samples are *n* type, and we always refer to the absolute value of the Hall coefficient or the Seebeck coefficient.) The slopes are all significantly lower than those for  $\rho(T)$ . The decreasing slope with decreasing temperature and the magnitude of the slope ( $E \lesssim kT$ ) both indicate that it would be arbitrary to assume an activated process. Indeed,  $R_H(T)$  gives good straight lines on a log-log plot, with  $d \ln R_H / d \ln T$  ranging from about  $-1$  to  $-3$  between the samples with highest and lowest conductivity (excluding E20). The Hall coefficient of E20 was essentially constant between room temperature and 150°K. We were unable to make measurements down to liquid-helium temperatures, where  $d\rho/dT < 0$ . The electron concentration  $n_H$ , corresponding to the room temperature values of  $R_H (\equiv 1/n_H e)$ , is listed in the table.

The corresponding values of the Hall mobility

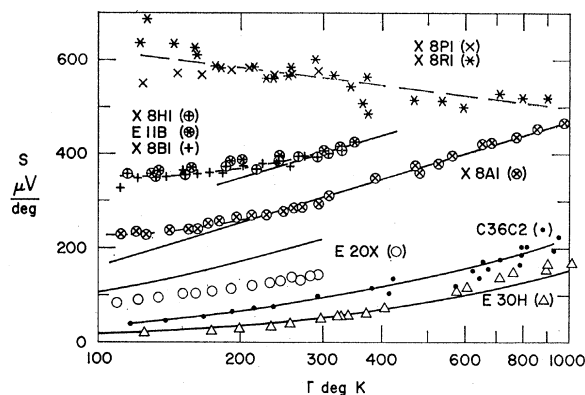


FIG. 6. Seebeck coefficient versus temperature. C36C2 and E30H are high-conductivity samples with  $n=0.60$  and  $1.26 \times 10^{21}/\text{cm}^3$ , respectively. Theoretical curves are drawn for these and E20X using  $m^*/m=3$ ,  $R=0$ , and the value of  $n_H$ , instead of  $n$ , in the case of E20X. The solid lines for the remaining samples have a theoretical slope of  $3k/2$ .

$\mu_H (=R_H/\rho)$  are plotted in Fig. 5. In contrast to the metallic behavior of E20, where  $d\mu_H/dT < 0$ , the higher resistivity samples have a Hall mobility which decreases with decreasing temperature. This occurs more rapidly as one goes to lower  $T$  and higher values of the resistivity. None of the curves for  $\mu_H(T)$  fit well with a power law equation  $\mu_H \propto T^c$ , where  $c$  is a constant, as would be expected for a single scattering process in a band model.

It is of some interest to consider these data in the light of the scattering distance  $\lambda_s$ . Using the value  $m^*/m=3.1$ , which fits the transport equations in the metallic range, the scattering distance is derived from the relationship:

$$\lambda_s = 0.735 \mu_H (T/100)^{1/2} \quad (5)$$

when  $\lambda_s$  is in angstrom units, and  $\mu_H$  is in  $\text{cm}^2/\text{V sec}$ .  $\lambda_s$  ranges from about  $4 \text{ \AA}$ , at largest  $n$  and  $T$ , to values approaching  $0.1 \text{ \AA}$  for lower values of  $n$  and  $T$ . For comparison, the de Broglie wavelength for electrons with thermal energy is  $4.6 \text{ \AA}$  at  $300^\circ\text{K}$ , and  $8.3 \text{ \AA}$  at  $100^\circ\text{K}$ . The distance between neighboring cerium ion sites in the lattice is  $4.0 \text{ \AA}$ .

The fact that  $\lambda_s$  is below  $1 \text{ \AA}$ , for samples with lower values of  $n$  and  $T$  (samples X8P1 and X8R1, at  $T < 150^\circ\text{K}$ ) suggests that one is getting into a range where the transport mechanism is a hopping process for localized electrons. An equivalent way of stating this is that the energy of interaction  $E_s = \hbar/\tau_s$  becomes larger than the estimated width of the conduction band ( $\sim 1-2 \text{ eV}$ ). This is supported by the fact that this range of  $\lambda_s$  coincides with a larger magnitude of the slope in  $\mu_H(T)$ . Further support for this conclusion is provided by measurements of the Seebeck coefficient, discussed below.

### C. Seebeck Coefficient

Experimental results for the Seebeck coefficient  $S$  are plotted versus  $\ln T$  in Fig. 6, which again includes

some curves in the metallic range for reference. All data for  $S$  contain corrections for the reference metal to put  $S$  on an absolute scale. Normal band theory predicts that one should obtain straight lines with slope  $3k/2e$  in the Maxwell-Boltzmann range. Straight lines with the required slope are fitted to some of the data in Fig. 6, but the experimental slopes are less than the theoretical values at temperatures below room temperature. In the case of E20, one is near degeneracy, and the theoretical curve is computed with the use of appropriate Fermi-Dirac integrals<sup>17</sup> on the basis that  $n = n_H$ , and  $R (=d \ln \lambda_s / d \ln E)$  is equal to zero. Different values for  $n$  and  $R$  would mainly shift the theoretical curve horizontally, so that it appears here, too, that the experimental slope is too small. The two samples with the highest resistivity, X8R1 and X8P1, have negative slopes; i.e.,  $dS/dT < 0$ .

Measurements were extended below  $100^\circ\text{K}$  for two samples with higher conductivities, X8B1 and E20X, with results shown in Fig. 7. The difference in behavior is very suggestive of the distinction between metallic and insulating transport. E20X acts like a metal in that  $S$  seems to approach zero as  $T$  approaches zero. In X8B1, on the other hand,  $S$  goes through a minimum and starts to increase with decreasing  $T$ , suggesting that transport is becoming dominated by electrons in localized states characteristic of insulators. In this temperature range, the behavior is similar to that of higher resistivity samples X8P1 and X8R1 at higher tem-

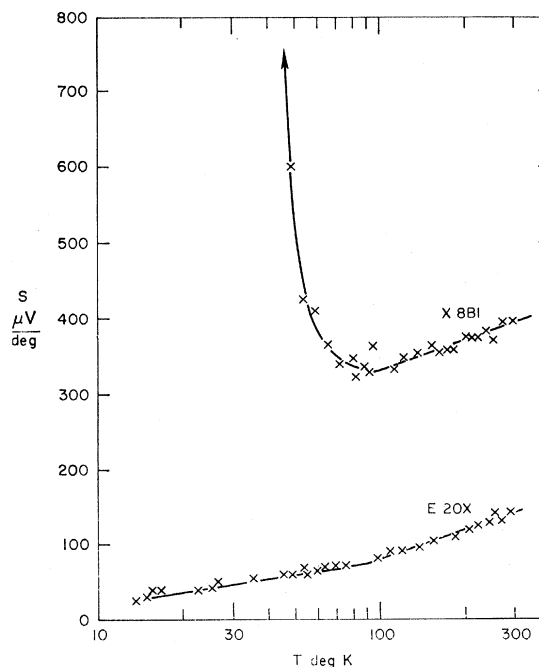


FIG. 7. Low-temperature curves for Seebeck coefficient of X8B1 and E20X.

<sup>17</sup> A. F. Ioffe, *Semiconductor Thermoelements and Thermoelectric Cooling* (Translation from the Russian by A. Gelbtuch) (Infosearch Ltd., London, 1957), p. 90.

peratures. In the latter compounds, as already noted, the behavior of the Hall mobility also suggests transport by localized electrons. We were not in a position to carry out Hall measurements with X8B1 in the temperature range where  $dS/dT < 0$ .

#### IV. DISCUSSION

It has already been noted that the mobility of our samples is, for the most part, in a range where the scattering distance  $\lambda_s$  is smaller than the de Broglie wavelength  $\lambda_d$ . This calls into question the applicability of the results of usual transport theory in analyzing the present data for those ranges of  $n$  and  $T$  where the electrons are apparently in nonlocalized states. The theory for transport in which  $\lambda_s < \lambda_d$  is not very well developed. Since it is not necessarily true that any particular conclusion derived in normal transport theory ceases to be correct when  $\lambda_s < \lambda_d$ , a useful approach which we will follow is to examine the data in the light of normal transport theory and to ascertain where significant deviations occur.

A key question is the interpretation of the Hall measurements, since an evaluation of the electron concentration plays a major role in interpreting the data. In contrast to the semimetallic range ( $x < 0.30$ ), the measurement of density does not provide a sensitive means for determining  $n$  or  $x$ . The precision of density measurements ( $\pm 0.2\%$ ) leads to an uncertainty in electron concentration  $\Delta n \sim 1 \times 10^{20}/\text{cm}^3$ . As a result, a direct evaluation of  $R_H n e$  (or its equivalent  $\mu_H/\mu$  or  $n/n_H$ ) is possible only for  $n \gtrsim 5 \times 10^{20}/\text{cm}^3$ . However, some interesting information can be obtained from an examination of  $\mu_H$  and  $\mu$  over the entire range where data are available.

Figure 8 is a plot of room-temperature value of  $\mu_H$  and  $\mu$  as a function of electrical conductivity; it includes data from the metallic range. The extreme right-hand side of the figure, where  $\mu_H < \mu$ , has been discussed previously and is believed to arise from convolutions in the Fermi surface which appear as the conduction band is filled.<sup>8</sup> However, at the lowest values of  $n$  ( $\sim 5 \times 10^{20}/\text{cm}^3$ ) where density determinations gave significant results,  $\mu_H/\mu$  has risen to values significantly larger than

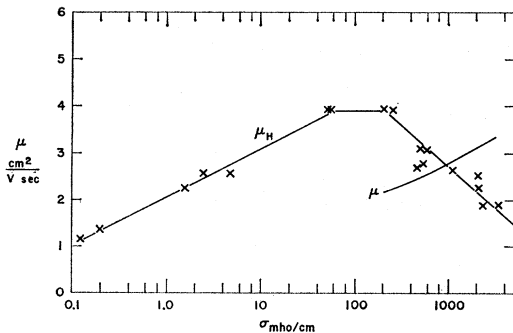


FIG. 8. Temperature of the Hall mobility ( $R_H \sigma$ ) and drift mobility ( $\sigma/ne$ ) as a function of electrical conductivity.

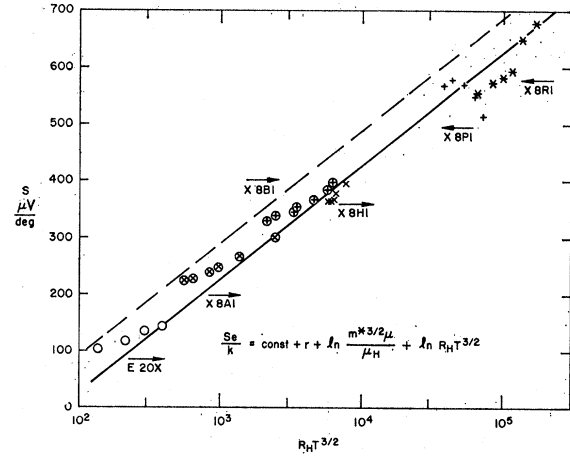


FIG. 9. Dependence of  $S$  on  $R_H T^{3/2}$ . Arrows indicate direction of increasing temperature for the sequence of points for each sample.

unity, approaching two. At lower values of  $\sigma$ , where  $\mu$  cannot be determined,  $\mu_H$  remains approximately constant until one gets to samples where  $n_H \lesssim 10^{19}/\text{cm}^3$ , at which point  $\mu_H$  begins to drop.

A large value of  $\mu_H/\mu \cong 2$  in the range of  $n \sim 6 \times 10^{20}/\text{cm}^3$  is not explicable in terms of conventional transport theory; there is considerable degeneracy, which leads to  $\mu_H/\mu \cong 1$  in conventional theory. However, as noted in Ref. 1, the large fluctuations in potential experienced by the electrons in the metallic range open to question the use of conventional theory. Therefore, the large value of  $\mu_H/\mu$  can be regarded as an empirical fact which may be related to the potential fluctuations.  $\mu_H$  remains at a high level as  $n$  decreases by a decade below the point where it can be measured directly. This suggests the possibility that  $\mu_H/\mu$  also has the same high value also in this range.

A comparison of the Seebeck coefficient  $S$  and the Hall coefficient  $R_H$  for various samples suggests that, at least in some sense, the normal interpretations of the Hall coefficient and the Seebeck coefficient are not far from the mark. In the Maxwell-Boltzmann range, normal transport theory requires that

$$S = (k/e) \{ 2 + R + \ln [ 2(2\pi m^* kT)^{3/2} / h^3 n ] \}, \quad (6)$$

where  $R = d \ln \lambda_s / d \ln E$  and  $E$  is the energy of an electron.<sup>17</sup> If one substitutes for  $n$  the relationship

$$n = (1/R_H e) (\mu_H / \mu), \quad (7)$$

and gathers in one term all the parameters which can be measured and the parameters reflecting the electronic structure or transport mechanism in a second term, one obtains

$$S(e/k) = C_1 + [ R + \ln (\mu / \mu_H) m^* ]^{3/2} + \ln R_H T^{3/2}, \quad (8)$$

where  $C_1$  involves only universal constants.

In Fig. 9,  $S$  is plotted against  $\ln R_H T^{3/2}$ , using all available data. The lines are drawn with the theoretical slope. For the points from each sample, an arrow

indicates the direction of increasing temperature. The theoretical curve, based on the values parameters obtained in the metallic range ( $m^*/m=2.13$ , and  $R=0$ ) and assuming  $\mu_H/\mu=1$ , is given by the dashed line; the solid line assumes  $\mu_H/\mu=2$ . The fact that the points all lie so close to a single curve over the very wide range of  $n$ , where the experimental behavior of  $\rho(T)$ ,  $S(T)$ , and  $R_H(T)$  show qualitative changes, suggests that an important aspect of the relationship between  $S$  and  $R_H$ , given in conventional theory, is preserved over the entire range. It seems likely that the essential relation has to do with an effective concentration of mobile carriers  $n^*$  with  $R_H \sim 1/n^*e$ , and  $S \sim (k/e) \ln(N_c/n^*)$ . Therefore, the data for  $R_H$  and  $S$  can be regarded as providing a proper indication of an effective electron concentration of mobile carriers, whatever the appropriate model for transport may be.

It is worth noting in Fig. 9 that the higher conductivity samples (E20X, X8A1, and X8B1) show the same trend with temperature, indicating either an increasing value of  $S$  or a decreasing value of  $\mu_H/\mu$  with decreasing temperature as compared with the over-all relationship. The magnitude of the shift agrees roughly with the deviations of the  $S(T)$  from the theoretical slopes in Fig. 6. This suggests that the unorthodox behavior occurs in  $S$  rather than in  $R_H$ . The higher resistivity samples do not show a clear trend with temperature, but they lie closer to the line given by the points at the high-temperature end of the lower resistivity samples.

So far, we have considered the following systematic effects:

(1) There is an increase in  $\mu_H/\mu$  which appears to occur below  $n \sim 1 \times 10^{21}/\text{cm}^3$ .

(2) There is a tendency for  $S(T)$  to have a positive shift from the theoretical slope as the temperature falls below room temperature.

Other pertinent observations are:

(1) Although  $R_H$  is independent of  $T$  at  $n_H \sim 8 \times 10^{19}/\text{cm}^3$ , it starts to increase with decreasing  $T$  for  $n_H \lesssim 10^{19}/\text{cm}^3$ .

(2) The slope of  $S(T)$  changes to a negative value at low  $n$  and  $T$ . The occurrence of a negative slope seems to correlate best with the magnitude of the resistivity ( $\gtrsim 3 \Omega \text{ cm}$ ), although one is tempted to associate it physically with a small scattering distance and a hopping mechanism for transport.

The behavior of  $S(T)$  can be put into three ranges: (1)  $S$  is a linear function of  $\ln T^{3/2}$ ; (2)  $dS/dT > 0$ , but with a smaller slope than for range (1); and (3)  $dS/dT < 0$ . These ranges occur at decreasing temperatures for a given sample, and range (3) occurs at higher temperatures with decreasing  $n_H$ . A hypothesis which is suggested by this is that region (1) represents the behavior of carriers whose wave functions are not localized, while regions (2) and (3) reflect increasing fractions of carriers in localized states.

Putting this in the analytic form of a two-band model, one can divide the transport into two parts: One due to localized carriers with conductivity  $\sigma_L$  and thermoelectric power  $S_L$ , and a second due to nonlocalized carriers with parameters  $\sigma_n$  and  $S_n$ . The over-all value of  $S$  is  $(\sigma_n/\sigma)S_n + (\sigma_L/\sigma)S_L$ , where  $\sigma = \sigma_n + \sigma_L$ . In range (1), most of the carriers are nonlocalized; since they are more mobile,  $\sigma_n \gg \sigma_L$ ,  $S \cong S_n$ , and the theoretical temperature dependence of  $S(T)$  predicted Eq. (6) with constant  $n$  is observed. At a lower temperature, in range (2), an appreciable fraction of the carriers are beginning to fall into localized states, although the same inequalities apply. As a result,  $S(T)$  decreases less rapidly with decreasing  $T$  because  $n$  in Eq. (6) is decreasing. At some range of decreasing  $T$  the relative number of electrons in localized states will become so large that  $\sigma_L \gtrsim \sigma_n$ , so that  $S \cong S_L$ . One would expect that  $S_L$  would be much larger than  $S_n$  because of a large entropy of transport associated with the polarization of the lattice near a localized electron.<sup>18</sup> Range (3) would correspond, then, to the transition region where  $\sigma_n S_n / \sigma \sim \sigma_L S_L / \sigma$ , with  $dS/dT < 0$  because  $\sigma_L/\sigma$  is a decreasing function of  $T$ . Basic considerations require that  $S_L$  should approach zero at sufficiently low temperatures. This would cause another change in slope of  $S(T)$  at sufficiently low temperatures, presumably below the experimental range, where  $\sigma_L/\sigma$  has become constant.

In the absence of an explicit model for transport, it seems premature to try to interpret the observations beyond the loose suggestions already made. The next question to be considered will be the extent to which present theoretical understanding may provide such a model.

It is worthwhile to consider first the physical structure of the cerium sulfide. As noted previously, the vacancy concentration is approximately constant with a value of  $2.1 \times 10^{21}/\text{cm}^3$ . This corresponds to one missing cerium ion for every nine sites. Each cerium site is surrounded by eight  $S^{2-}$  ions and each  $S^{2-}$  ion is surrounded by six cerium ion sites.<sup>9</sup> The background charge due to all of the ions in the perfect lattice corresponds to a formal charge of  $+1/3$  for each cerium ion site. Removal of a cerium ion gives rise to an effective charge of  $-3$  at the site, compared to the perfect lattice, and formal charge of the vacancies is  $-8/3$ . The concentration of electrons is given by Eq. (2), and this relationship corresponds to the excess density of cerium ions over vacancies, weighted by their formal charges ( $+1/3$  and  $-8/3$ , respectively). In the experimental range,  $(\frac{1}{3} - x) < 0.005$ .

From the sign of the effective charge, one can see that the vacancies repel electrons, in contrast to the

<sup>18</sup> R. R. Heikes, in *Conference on Rare Earth Research*, edited by E. V. Kleber (The Macmillan Company, New York, 1961), p. 247. We obviously do not subscribe to this author's hypothesis that  $4f$  electrons are participating in transport in cerium sulfide, but his model shows correctly the general influence of local polarization on the Seebeck coefficient.



usual situation where crystal imperfections often act as traps. One would tend to consider individual cerium ions as possible traps, but their formal charge of  $+1/3$  suggests that the orbital of a trapped electron would include many cerium sites. In a later paragraph, we will discuss further the possible size of electron orbitals.

The positions of the vacancies in the lattice are believed to be random.<sup>9</sup> When one considers the possible fluctuations in positive charge in the lattice, it seems clear that the large average concentration of vacancies will lead to a wide range of local concentrations and depth of traps arising from negative deviations in the concentration of vacancies from the average value. As an illustration, the probability that any given cerium ion will have no vacancy at the next nearest neighbor sites is  $(8/9)^8 = 0.39$ . Such a complex would have an effective charge of  $3+$  and a radius of  $4.4 \text{ \AA}$ . Using the static dielectric constant  $19$ ,<sup>7b</sup> one calculates a potential of  $0.52 \text{ eV}$ , if the charge distribution is assumed to be uniform beyond this complex. If one considers that one must multiply the probability  $0.39$  by a very large concentration of such possible sites ( $\sim 10^{21}/\text{cm}^3$ ) and the fact that much larger complexes free of vacancies have appreciable probabilities, one is apt to wonder that any electrons are free to move at all. Part of the answer, of course, is that the pertinent question is the connectivity of the various potential valleys; it is very likely that a potential well of the type calculated above would have some similar ones adjoining it, and the statistical problem of the potential topography is a good deal more complicated.

The case for fluctuations is probably overstated in the above argument. The positions of the vacancies will not be entirely random, since correlation effects will be introduced by the high potentials engendered by extreme fluctuations. Therefore, the fluctuations in the samples will reflect the fluctuations of the potential energy of vacancies at the temperature of equilibration, which is about  $1600^\circ\text{K}$ . This corresponds to a thermal energy of about  $0.14 \text{ eV}$ . This number refers to the vacancies and does not directly indicate the potential energy fluctuations seen by electrons at lower temperatures.

These considerations provide a qualitative picture of the physical situation. In the absence of excess electrons, the fluctuations in the vacancy positions would cause a widely varying potential in the crystal, which might be compared with a two-dimensional analog of a physical surface containing a wild jungle of peaks and dips with a roughness scale of the order of  $5 \text{ \AA}$ . As electrons are added to the lattice, the deepest depressions are filled and the passes between these depressions are high. This would presumably correspond to samples, with electron concentrations below  $\sim 10^{17}/\text{cm}^3$ , which would be insulators. As more electrons are added, the relatively deep depressions are filled, and the height of the passes between the "flood plains" will become smaller. This corresponds to most of our samples, where

activation energies of  $0.050$  to  $0.005 \text{ eV}$  are observed. As more electrons are added, one will reach the point where barriers exist only between relatively few larger regions, and these barriers would be relatively small. This may be the situation in E20X, where  $\rho(T)$  starts to increase only at very low temperatures, with an activation energy of about  $0.003 \text{ eV}$ , even though the Fermi energy is  $+0.020 \text{ eV}$ . Of course, as the electron concentration is increased, screening will tend to further decrease the height of the barriers.

The situation described here merges with one considered in Ref. 1. At  $x \cong 0.30$ , one has a high-electron concentration with a metallic transport and with only a suggestion of  $d\rho/dT < 0$  at  $T \sim 10^\circ\text{K}$ . But the vacancies are so close together that most of the electrons are in regions of strongly fluctuating potentials. As  $x$  is decreased further, the average distance of the vacancies becomes larger than the range of unscreened potential. One starts to have a large fraction of the volume of the crystal containing regions of uniform potential, and the maximum local concentration of electrons ( $6.25 \times 10^{21}/\text{cm}^3$ ) in these uniform regions.

Most of the efforts for quantitative interpretations of transport in the general "dilute metal" problem have been applied to the study of impurity bands in substances like germanium and silicon.<sup>2</sup> On considering the possible applicability of these results to cerium sulfide, it appears that an important difference arises from two factors; first, cerium sulfide has a polar lattice; and, second, a relatively large density of possible donor sites occurs in cerium sulfide. The second problem is probably the most formidable and also poses difficulties at one end of the range, the "transition range," in the impurity band problem.

In the typical impurity band semiconductor, the density of donor sites is small enough so that one can regard a localized electron as having an orbital centered on a particular donor ion, with the distance of neighboring ions larger than the orbital radius. (To be specific, we discuss the case most analogous to cerium sulfide, which is a highly compensated  $n$ -type semiconductor.) There are problems in adapting the theoretical models to cerium sulfide, and indeed it would be difficult to define exactly what would correspond to donor and acceptor ions. Taking into account the periodicity of the sulfur sublattice, and the fact that the wave functions of the electrons would have low densities at sulfur ion positions, one possibility that suggests itself is to regard each cerium ion as a donor site with a charge  $+1/3$  and each vacancy as equivalent to an acceptor site with a charge  $-8/3$ . However, as noted before, the orbital of a localized electron would probably include a large number of cerium ions. The usual criterion for overlapping donor sites is  $a_0(4\pi N_d/3)^{1/3} \gtrsim 1/3$ , where  $a_0$  is the hydrogenic Bohr orbital radius and  $N_d$  is the density of donor sites.<sup>2a</sup> In the present case, using the static dielectric constant  $19$ ,  $a_0$  is  $3.4 \text{ \AA}$  for  $m^*/m = 3$  and  $10 \text{ \AA}$  for  $m^*/m = 1$ . (According to

Ref. 1, this is the possible range for  $m^*/m$ .) The second factor in the inequality is approximately the reciprocal of the Ce-Ce distance (4.0 Å) so that the criterion for overlapping donor is readily met; *a fortiori*, in the present case, since the cerium sites have a formal charge of  $+1/3$ .

Various aspects of a possible metal-insulator transition has been considered in a number of papers, notably by Mott.<sup>2</sup> The situation in cerium sulfide seems to correspond to one not commonly encountered experimentally. That is one where the number of electrons is much smaller than the number of possible donor sites. Mott has discussed the possible relation of such a situation to one hypothesized by Wigner, in which an electron gas can "crystallize."<sup>2b</sup> He has derived a transition radius  $r_0 \cong 20a_0$ , where  $r_0 = (3/4\pi n)^{1/3}$ . It is hard to determine, from our experimental results, a unique value for  $n$  in cerium sulfide at which a transition might occur between transport by electrons in localized and nonlocalized states. The clearest indication of this kind of transition occurs in the minimum of  $S(T)$  for sample X8B1 in Fig. 7. At the temperature of the minimum, the Hall coefficient indicates an electron concentration of  $3 \times 10^{18}/\text{cm}^3$ , which corresponds to  $r_0 = 44$  Å, as compared with  $a_0 \sim 4-10$  Å. However, we are doubtful about the relationship between this transition and the kind that Mott was discussing.

In the present case, there are large potential fluctuations caused by the random positions of the vacancies which have the effect of putting many of the electrons into deep traps.<sup>19</sup> As the temperature is increased, it seems likely that many of these electrons are thermally excited into regions of higher potential energy, where they have a higher mobility because of a better connectivity with other regions of similar potential energy. It would appear that the transition we are speaking of occurs when the concentration of electrons not in deep traps reaches a characteristic value. The fact that the  $S(T)$  curves tend to converge at high temperatures suggests the presence of electrons in deep traps in the higher resistivity samples. Mott treats a situation where the concentration of electrons is independent of temperature, and the effects of large permanent potential fluctuations due to the random positions of the compensating charge does not occur in his model. The connection which we make in terms of "concentration of untrapped electrons" at a particular temperature may be open to question.

The small value of the mean free path, as well as the exponential behavior of the resistivity curve, suggests that transport is by a hopping process in the high-resistivity samples at low temperatures. It is generally expected that electronic conduction in such a domain

<sup>19</sup> A recent paper by E. O. Kane, Phys. Rev. **131**, 79 (1963), deals with the distribution of electronic states in a highly doped semiconductor. It takes into account the fluctuations in potential caused by random positions of impurities. Although the treatment is for a nonpolar lattice, many of his considerations seem pertinent to the case of cerium sulfide.

would show a frequency dependence in the resistivity and the Hall coefficient.<sup>20</sup> We observed frequency effects in measuring  $\rho$  and  $R_H$  for these samples and changed to dc measurements for that reason. However, this may have been caused by stray capacitance; this question would have to be investigated more carefully before one can be assured that the frequency effect truly occurs.

## V. CONCLUSIONS

The experimental data suggests strongly that the transport behavior can be divided into two extreme categories: (1) a hopping process with electrons in localized states, and (2) motion of nonlocalized electrons, whose scattering distance may be shorter than the de Broglie wavelength. There is a wide range of continuous variation between the two extremes which depends on composition and temperature. The insulator extreme is characterized by a mean free path smaller than interatomic distances, by negative slopes in  $\rho(T)$  and in  $S(T)$ , and by a Hall mobility that decreases rapidly with decreasing temperature. The metallic extreme has a constant Hall coefficient, and  $\rho(T)$  and  $S(T)$  tend to follow equations of conventional theory. It is important to note that behavior at low  $n$  is not equivalent to that at low  $T$ ; samples with larger values of  $n$  show no sign of a minimum in  $S(T)$ , even though one finds a range where  $\rho$  increases with decreasing  $T$ . The latter reflects potential barriers between microscopic regions which have nonlocalized electronic states, rather than transport by electrons in localized states.

Although many theoretical and experimental studies have been made of other systems which have similarities to the present one, there are many differences. The random position of the vacancies, which occur in a high concentration in cerium sulfide and which have a high effective charge, must give rise to large fluctuations in the potential. This fact, together with the large number of possible donor sites compared with the number of electrons, make the present problem quite different from most situations which have received theoretical study. As a result, it has not been possible to make specific comparisons between our results and theoretical predictions. The extent to which our experimental results can be fitted empirically to equations of conventional transport, particularly the observed relation between  $S$  and  $R_H$  in Fig. 9, is of considerable interest and may provide a guide in future development of appropriate theoretical models.

## ACKNOWLEDGMENTS

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<sup>20</sup> M. Pollak and T. H. Geballe, Phys. Rev. **122**, 1742 (1961); T. Holstein, *ibid.* **124**, 1329 (1961).