

## Electronic Transport in Semimetallic Cerium Sulfide\*

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The electrical resistivity  $\rho$  and Seebeck coefficient  $S$  have been measured between 10 and 1000°K in  $Ce_{3-x}S_4$  with values of  $x$  ranging from 0 to 0.30. The electrical behavior is semimetallic and can be fitted, in large measure, to the equations of conventional transport theory for  $S(T)$  and  $\rho(T)$ . However, examination of the electrostatic effects of the vacancies shows that they introduce large effective charges which are poorly screened. Consequently, there are wide fluctuations in potential in the crystal which cast doubt on a literal interpretation of the theoretical equations; at present, they must be regarded as providing a largely empirical description of the experimental results. There is a relatively large residual resistivity which indicates a very large cross section per vacancy in samples with small values of  $x$ . This can be accounted for by the abnormally large screening distance. In the temperature range below 100°K, anomalies are observed in  $S(T)$  and  $\rho(T)$  in samples with small vacancy concentrations. Anomalies in  $S(T)$  seem to be caused by phonon drag. The cause of the resistivity anomalies is not yet clear; we consider the possibilities that they are caused by local lattice vibrations or by spin scattering by electrons in the  $4f$  shell of the cerium ions.

### I. INTRODUCTION

THE gamma phase of cerium sulfide, which has a cubic  $Th_3P_4$  structure, has been of some interest because of its thermoelectric properties at high temperatures.<sup>1-3</sup> Its physical makeup, however, differs considerably from that of most compounds with well-studied electronic behavior. The compound has a wide range of stoichiometry, with an ionic defect lattice.<sup>4</sup> It can be described by the formula  $Ce_{3-x}S_4$ , and in more detail



where the vacancies  $V$  are at cerium ion sites and  $0 < x < \frac{1}{3}$ . The electrons  $e^{1-}$  required to compensate the charge have a range of concentration from zero to  $6.25 \times 10^{21}/\text{cm}^3$ . Measurements of magnetic susceptibility show that the electrons are not closely associated with the cerium ions and must be in a conduction band.<sup>5-7</sup> In contrast to the usual situation, the perfect lattice has many extra electrons in the conduction band. Because of this unusual crystal structure, a detailed study of its electronic transport behavior is of considerable interest.

In a previous paper,<sup>7</sup> we reported a study of cerium sulfide which dealt with the nature of the conduction band, as inferred mainly from measurements of Seebeck coefficient and Hall coefficient at room temperature. This work was based on compositions in a semimetallic range where  $n$  is relatively high; i.e.,  $6 \times 10^{20}/\text{cm}^3$  to  $6 \times 10^{21}/\text{cm}^3$ . Reasons were discussed which suggest that the conduction band arises from the (5d) atomic orbitals of the cerium ions. The present paper is concerned with a more detailed study of electron transport, using samples with electron concentrations in the same range as in Ref. 7. The experimental measurements are of the electrical resistivity and Seebeck coefficient in the range between 10 and 1000°K. (The Hall coefficient was found to be independent of temperature and will not be considered to any extent in this paper.) A study of electron transport in samples which have a lower range of electron concentrations is reported in Ref. 8; in that study a transition toward a type of behavior typical of insulators is found.

Previous workers have obtained general information about transport behavior of cerium sulfide, particularly at higher temperatures.<sup>1-3,9</sup> Detailed analyses of the results have been hampered, however, by difficulty in determining the correct electron concentration in the samples, so that the behavior of electrical conductivity and the Seebeck coefficient could not be translated readily into information about the mobility and the Fermi energy. Experimentally, the problem is manifested by a poor correlation between the electrical conductivity and other quantities relating to the electron concentration, such as the composition or Hall coefficient.

Above 100°K, the electrical resistivity  $\rho$  and the Seebeck coefficient  $S$  show a dependence on temperature which seems consistent with a simple model for trans-

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<sup>1</sup> S. W. Kurnick, M. Cutler, R. L. Fitzpatrick, and J. F. Leavy, *Conference on Rare Earth Research*, edited by E. V. Kleber (Macmillan Company, New York, 1961), p. 241; S. W. Kurnick, M. F. Merriam, *Advan. Energy Conversion* **1**, 157 (1961).

<sup>2</sup> F. M. Ryan, I. N. Greenberg, and R. C. Miller, *J. Appl. Phys.* **33**, 864 (1962).

<sup>3</sup> F. L. Carter, R. C. Miller, and F. M. Ryan, *Advan. Energy Conversion* **1**, 165 (1961).

<sup>4</sup> W. H. Zachariasen, *Acta Cryst.* **2**, 57 (1949).

<sup>5</sup> E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Giles, and N. F. Longren, *J. Am. Chem. Soc.* **72**, 2250 (1950).

<sup>6</sup> M. Picon, L. Domange, J. Flahaut, M. Guittard, and M. Patrie, *Bull. Soc. Chim. France* **2**, 221 (1960).

<sup>7</sup> M. Cutler, R. L. Fitzpatrick, and J. F. Leavy, *Phys. Chem. Solids* **24**, 319 (1963).

<sup>8</sup> M. Cutler and J. F. Leavy, *Phys. Rev.* **133**, A1153 (1964), following paper.

<sup>9</sup> J. Appel and S. W. Kurnick, *J. Appl. Phys.* **32**, 2206 (1961).

port. It suggests that there is a combination of thermal scattering and impurity scattering; the latter is presumably caused by the high concentration of vacancies. The dependence of  $S$  on the electron concentration  $n$  is also consistent with this simple theory. However, the dependence of the mobility  $\mu$  on  $n$  or on the vacancy concentration shows deviations from predictions of simple theory, and the scattering cross section of the vacancies seems abnormally large.

On examining the physical situation more carefully, we find that an unusual situation exists in that the vacancies must repel electrons over a large distance—about 5 Å. This arises from the fact that vacancies have the same sign of charge as the electrons, and the relative charge at a vacancy ( $3e$ ) is much larger than the normal electronic charge at equivalent sites ( $\frac{1}{3}e$ ). Electrons are repelled from a large region near each vacancy in order to neutralize its effective charge. As a result, one can account in large measure for the large scattering cross section of the vacancies. However, the simple interpretation suggested by the experimental results disappears, and the agreement with the simple model seems largely fortuitous. As a result of the relatively large vacancy concentration in the experimental range (1 to 10% of the cerium ion sites), the physical situation is much more complicated than any envisaged in a simple model. This is mainly because the regions in which the potential is drastically affected by the presence of vacancies constitute a large fraction of the total volume, so that electrons are generally in regions where potential energy fluctuations are comparable to the Fermi energy. Nonetheless, the equations for the transport parameters based on the simple model provide a surprisingly faithful description of the transport behavior, although their use must be regarded as largely empirical. Therefore, reference is made to the simple model in presenting experimental results in Sec. II, and comparisons are made which are appropriate for developing this empirical description. In Sec. III, we discuss the mobility as determined from vacancy scattering at low temperatures and present a description of the apparent physical situation. In Sec. IV, we discuss other aspects of the results.

Measurements made below 100°K show interesting deviations in  $\rho(T)$  and  $S(T)$  from the pattern established at higher temperatures. They consist of deviations from Matthiessen's rule and an increment in  $S$  which appears to be caused by phonon drag. These effects occur in the low vacancy limit of the range of compositions. There does not, at present, seem to be sufficient information to determine their origin. We discuss some possible interpretations in Sec. IV.

## II. EXPERIMENTAL RESULTS

### A. Resistivity

The samples of cerium sulfide were prepared and characterized as described in Ref. 7. Figure 2 of Ref. 7,

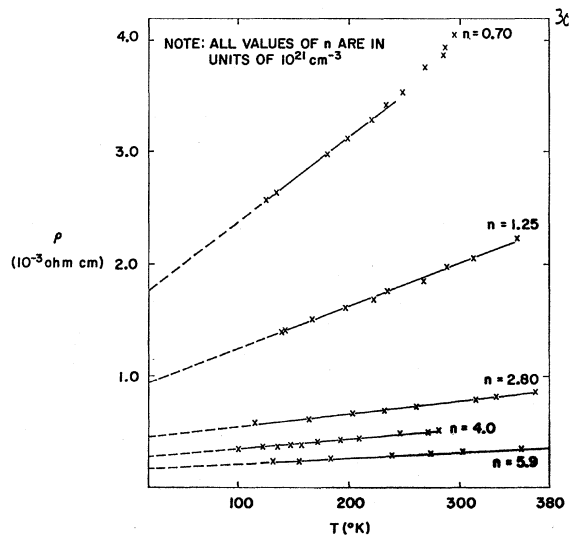


FIG. 1.  $\rho(T)$  between 100 and 400°K for samples with different values of  $n$  (indicated in units of  $10^{21}/\text{cm}^3$ ).

which relates the electrical conductivity  $\sigma$  to the electron concentration  $n$  deduced from density measurements, was used in later samples to deduce  $n$  from  $\sigma$ . In addition to the discussion in Ref. 7, Ref. 8 presents further considerations used in avoiding spurious results arising from the presence of extraneous phases in the samples.

The resistivity  $\rho$  is a linear function of temperature  $T$  between 100 and 400°K, as seen in Fig. 1. This type of behavior was observed previously in praseodymium sulfide, which is believed to be similar to cerium sulfide.<sup>10</sup> The implication is that Matthiessen's rule applies in these samples for a combination of scattering by imperfections (vacancies) in the lattice and by thermal vibrations. Our observation, in several samples, that the Hall coefficient is constant between 100 and 300°K shows that the electron concentration is constant, as expected in a semimetal. Since the electron concentrations are known, one can calculate the corresponding mobilities which combine according to the formula

$$1/\mu = 1/\mu_x + T/\mu_1, \quad (1)$$

where  $\mu_x$  is the mobility associated with scattering by vacancies, as determined from the extrapolated resistivity curves;  $\mu_1/T$  is the mobility associated with thermal scattering. (We will often denote  $\mu_1/T$  by  $\mu_T$ .) Results for  $\mu_x$  and  $\mu_1$ , determined in this way, are plotted as a function of  $n$  in Fig. 2.

According to Wilson,<sup>11</sup> the thermal mobility can be written as

$$\mu_1/T = Am^{*-2} M a^2 \theta^2 n C^{-2} T^{-1/4/3}, \quad (2)$$

where  $A$  involves only universal constants,  $M$  is the atomic weight,  $a$  is the interatomic distance,  $\theta$  is the

<sup>10</sup> G. Guthrie and R. Cesena, Bull. Am. Phys. Soc. 6, 502 (1961).

<sup>11</sup> A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York), 2nd ed., p. 264.

Debye temperature, and  $C$  is the coupling constant.<sup>12</sup>  $f$  is the ratio  $n_a/4n$ , where  $n_a$  is the density of atoms, provided that this ratio is greater than unity; otherwise,  $f=1$ . In the experimental range, the maximum value of  $n$  is approximately  $n_a/4$ , so that Eq. (2) predicts that  $\mu_1$  should vary as  $n^{-1/3}$ , whereas the experimental results shows that  $\mu_1$  increases with increasing  $n$ .

A theory for impurity scattering would have  $\mu_x$  varying inversely as the vacancy concentration, at least in the first approximation. The vacancy concentration  $N_v$  is related to  $n$  by the relation

$$N_v = (6.25 \times 10^{21} - n)/3. \quad (3)$$

The experimental values of  $\mu_x$  are constant in a range where the vacancy concentration  $N_v$  is increasing by a factor of ten. This inconsistency seems to be resolved when the resistivity measurements are extended to liquid-helium temperatures, with results shown in Fig. 3. There are deviations from Matthiessen's rule which are most pronounced at large  $n$  and small  $N_v$ . Using mostly measurements of resistivity of samples immersed directly in liquid helium, new values of mobility, denoted  $\mu_0$ , were obtained which are also plotted in Fig. 2.

Although  $\mu_0$  does not increase quite as rapidly as  $1/N_v$ , the dependence seems to be reasonable. However, when the magnitude of  $\mu_0$  is examined, one finds an extraordinarily large value of the scattering cross section ( $\sim 10^{-14} \text{cm}^2$ ), particularly at low  $N_v$  (large  $n$ ). This led to a re-examination of the physical situation, de-

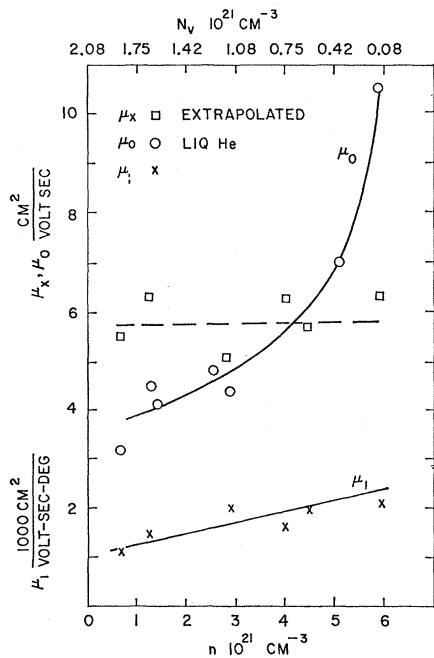


FIG. 2. Thermal mobility coefficient  $\mu_1$ , extrapolated residual mobility  $\mu_x$ , and liquid-helium value of residual mobility as a function of  $n$ . The upper scale is the vacancy concentration  $N_v$ .

<sup>12</sup> This is for an atomic lattice. It is sufficient for our purposes to regard  $M$  and  $a$  as suitably averaged quantities in the present case of a diatomic lattice.

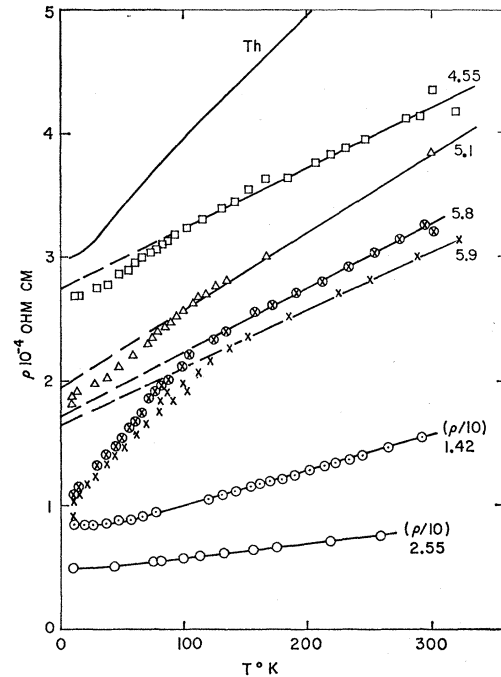


FIG. 3.  $\rho(T)$  to liquid-helium temperatures for different values of  $n$  (in units of  $10^{21}/\text{cm}^3$ ). The curve marked Th indicates the shape predicted by the Bloch-Grüneisen relation.

scribed in Sec. III, which suggests that the true situation is much more complicated than one would infer from the conventional behavior of the experimental curves.

Measurements of resistivity up to temperatures of the order of  $1000^\circ\text{K}$ , plotted in Fig. 4, exhibit an extension of the low-temperature behavior, except for samples with relatively low values of  $n$ . For the latter, an upward curvature is observed in  $\rho(T)$ . In addition, several curves show some evidence of a small downward curvature at very high temperatures.

The upward curvature can be explained very well in terms of conventional theory. Equation (2) is written in a form appropriate for a completely degenerate free electron band, in terms of  $n$ . A more appropriate parameter is the average energy  $\langle E \rangle$  of the electrons, and the equation indicates that the thermal mobility  $\mu_T (= \mu_1/T)$  varies as  $T^{-1}\langle E^{1/2} \rangle^{-1}$ . At low  $n$  and high  $T$ , degeneracy is incomplete, and the average energy of the electrons starts to rise above the Fermi energy  $E_f$  (more accurately,  $3E_f/5$ ). The average energy is  $kT$  in the extreme of a nondegenerate system, and the formula transform to the usual one for semiconductors with  $\mu_T \sim T^{-3/2}$ . In the experimental intermediate region, one would use Fermi-Dirac integrals to find the value of  $\langle E^{1/2} \rangle$ .<sup>13</sup> We calculated a corrected temperature scale

<sup>13</sup> These integrals are discussed in a number of places, including Ref. 11. Some very good tables appear in J. S. Blakemore, *Semiconductor Statistics* (Pergamon Press, Inc., New York, 1962); a description of their use in the application appears in A. F. Ioffe, *Semiconductor Thermoelements and Thermoelectric Cooling* (Infosearch Ltd., London, 1957), p. 90.

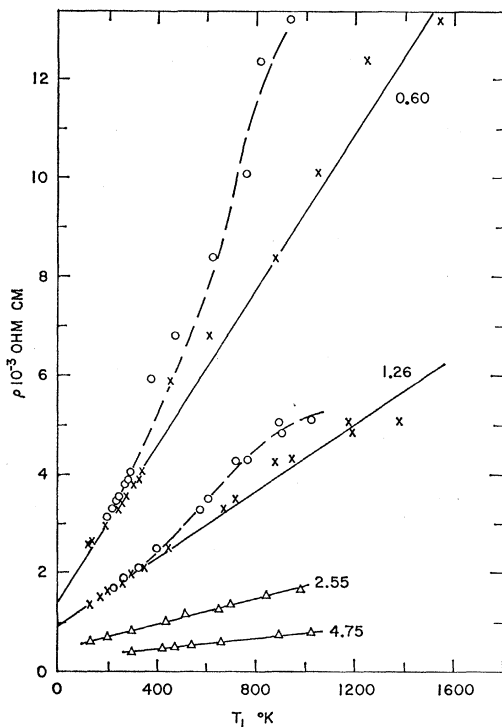


FIG. 4.  $\rho(T)$  to 1000°K. The experimental points O are on a normal temperature scale. The points X are the corresponding points on an adjusted temperature scale based on  $m^*/m=3$ ,  $R=0$ .

$T_1 (= \text{const.} T \langle E^{1/2} \rangle)$ , with the constant determined by the limiting value of  $E_f^{-1/2}$  at low temperatures, and found that the resistivity fell on a straight line when plotted on this adjusted scale, as shown in Fig. 4. The calculations were based on an assumed effective mass  $m^* = 3.1m$ , which is the number obtained from the data for the Seebeck coefficient.

### B. Seebeck Coefficient

According to simple theory for nearly free electrons, the Seebeck coefficient  $S$  is given by

$$S = (\pi^2 k^2 T / 3e) (8m^*/h^2) (\pi/3n)^{2/3} (1+R), \quad (4)$$

where

$$R = (d \ln \lambda_s / d \ln E)_{E_f},$$

and  $\lambda_s$  is the scattering distance.<sup>11</sup> In Ref. 7, it was shown that room temperature values of  $S$  varied as  $n^{-2/3}$ , as required by Eq. (4). The dependence of  $S$  on  $T$  is shown in Fig. 5, where  $S/T$  is plotted versus  $n$  in the range of 100–400°K. (Cerium sulfide is  $n$ -type and we will refer only to the absolute value of  $S$ . All experimental values are corrected for the reference metal to put them on an absolute scale.) Except for regions of small  $T$  and large  $n$ , the experimental points lie on horizontal lines, which again confirms Eq. (4). The deviations at low  $T$  and large  $n$ , which are probably caused by phonon drag, are discussed below. In Fig. 6, the values of  $S/T$ , taken from the horizontal lines in Fig. 5, are plotted versus  $n$

on a log-log scale. They fall very well on a line which has a theoretical slope of  $-2/3$ .

The effective mass can be calculated if one can determine the value of  $R$ . On the surface, the data for  $\rho(T)$  would set the value at zero since lattice scattering in the domain where  $n < n_a/4$  [see Eq. (2)] and impurity scattering in metals where the impurity ion is strongly screened, both give  $\lambda_s$  independent of  $E$ . This was the assumption that was used in Ref. 7, and, on that basis, the tentative conclusion was that  $m^*/m = 3.12$ . The data in Fig. 6, which are somewhat more accurate, lead to essentially the same results. As a result of the complexity of the actual physical situation, however, the true value of  $m^*$  is open to question; we discuss this in further detail in Sec. IV.

Extension of the measurements of  $S$  to temperatures of the order of 1000°K, together with theoretical curves, are shown in Fig. 7. The data agree over this wider temperature range with theoretical curves based on  $m^*/m = 3.1$  and  $R=0$ , even at lower values of  $n$  where there are departures from complete degeneracy. [The appropriate theoretical expressions involving Fermi-Dirac integrals were used instead of Eq. (4) in the latter region.<sup>13</sup>] However, even in the latter region, an alternate choice of  $R=2$ ,  $m^*/m = 1.04$ , would give almost equally good agreement, so that the choice of this particular combination of  $m^*$  and  $R$  is not dicatted by the results for the Seebeck coefficient. For an empirical description, however, the former choice has an element of self-consistency since it would also describe some of the behavior of  $\rho(T)$ .

The measurement of  $S$  was extended to temperatures below 100°K in order to clarify the anomaly noted in Fig. 5. The curves, plotted in Fig. 8, show humps typical of phonon drag effects. This effect appears most strongly in samples with large  $n$ . The accuracy of the data decreases as one goes below 40°K since copper-constantan thermocouples were used in an apparatus in which the temperature gradient in the thermocouple wires could not be carefully controlled. However, the accuracy

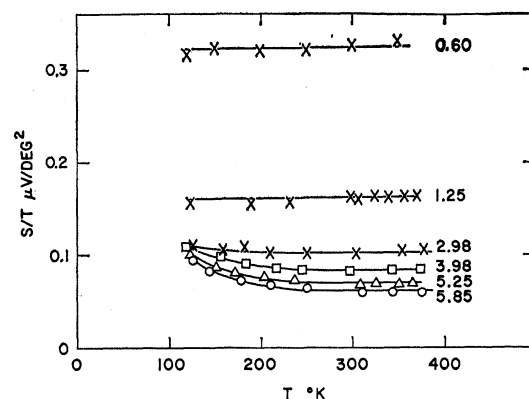


FIG. 5.  $S/T$  between 100 and 400°K, for different values of  $n$ , in units of  $10^{21}/\text{cm}^3$ .

is good enough to show correctly the main features of the behavior of  $S$ .

The temperature range in which the peak of the hump occurs and the dependence on temperature above the peak temperature are both characteristic of phonon drag effects.<sup>14</sup> At higher temperatures, according to theory the increment in Seebeck coefficient due to phonon drag varies as  $1/T$ . Thus one should have the equation

$$S = C_1 T + C_2/T \quad (5)$$

at temperatures above the one at which the peak occurs. The experimental data obey this equation quite well for those samples in which the hump is pronounced. Evaluation of  $C_1$ , according to this equation for samples with largest  $n$ , led to somewhat smaller values of the coefficient  $S/T$  in Eq. (4). These are plotted as open circles in Fig. 6. The disappearance of the phonon drag effect at low  $n$  is consistent with the fact that the vacancy concentration becomes large. Phonon and elec-

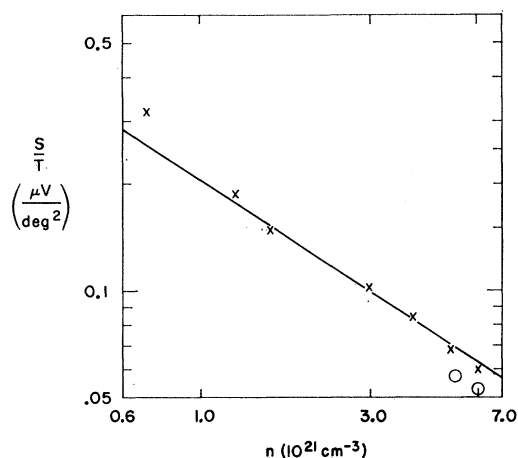


FIG. 6.  $S/T$  as a function of  $n$ . The circles are points corrected for phonon drag.

tron collisions with lattice imperfections prevent phonon drag by providing an alternate mechanism to umklapp processes for fulfilling the Bloch condition at low temperatures.

### III. SCATTERING BY VACANCIES

The usual theory for the effects of impurities or vacancies in metals assumes a strongly shielded ion whose effective charge is the excess over the normal value at the site. The screening distance  $r_t$  is given approximately by the Thomas-Fermi formula

$$r_t = [E_f / 6\pi n e^2]^{1/2} \quad (6)$$

and has a value of about 1 Å for  $Ce_3S_4$ .<sup>15</sup> There are some

<sup>14</sup> D. K. C. MacDonald, *Thermoelectricity* (John Wiley & Sons, Inc., New York, 1962).

<sup>15</sup> J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, 1960).

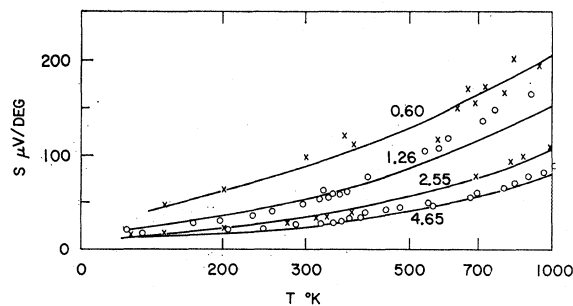


FIG. 7.  $S(T)$  at high  $T$ , for different values of  $n$  (in units of  $10^{21}/cm^3$ ). Curves are based on theoretical equations for  $m^*/m=3$ ,  $R=2$ .

questions about the effective mass and the use of a dielectric constant in Eq. (6), which will be discussed later. It has been noted by Friedel that there can be a significant deviation from the usual screening formula in the case where a negatively charged ion is shielded by electrons.<sup>16</sup> If one has a positive charge, the high field near the impurity causes a high density of screening electrons in its immediate vicinity; however, with a negative charge, the electron concentration in the high-field region cannot be reduced below zero. In the case of cerium sulfide, one has a large negative point charge in a lattice with a low average electron density. Electrons are almost entirely excluded over a region considerably larger than  $r_t$ , and the screening is provided by the remaining positive charge of the lattice ions.

Consider the perfect lattice in  $Ce_3S_4$ . Each  $Ce^{3+}$  ion is surrounded by eight  $S^{2-}$  ions at a distance of 3.0 Å, and each  $S^{2-}$  ion has six nearest neighbors.<sup>3,4</sup> Vacancies occur only at cerium sites. Using the standard procedure of taking the difference between the charge of the imperfection and the normal charge, one obtains an effective

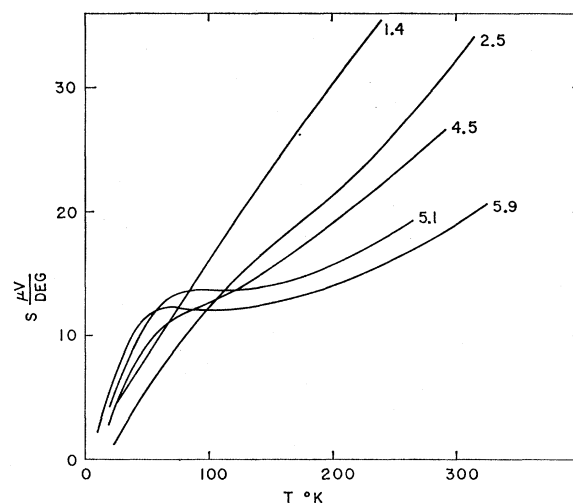


FIG. 8.  $S(T)$  at low  $T$ , for different values of  $n$  (in units of  $10^{21}/cm^3$ ). The numerous experimental points are not shown. They were all within 1  $\mu V/deg$  of the drawn curves.

<sup>16</sup> J. Friedel, *Advan. Phys.* 3, 446 (1954).

charge of 3- for a vacancy. On the other hand, a perfect crystal has  $\frac{1}{3}$  of an electron per cerium ion. Since the electronic wave function is concentrated near the cerium ions, as compared to the sulfur ion, one can assume that one obtains an excess charge of  $+\frac{1}{3}$  for every cerium ion site in a region in which electrons are completely excluded. If one assumes that electrons are excluded completely from discrete neighboring ion positions out to a distance sufficient to neutralize the effective charge of the vacancy, they are excluded from the eight nearest-neighbors cerium sites which are at an equal distance of 4.0 Å. There are four next-nearest cerium sites at 4.81 Å which would be the nearest sites beyond the region of electron exclusion. If one adopts a continuum model for the positive charge, then the radius  $r_e$  of a sphere of exclusion, which has a net positive charge of +3, will be 4.86 Å. This coincides with the result for discrete positive charges.

Of course, electrons would not be completely excluded from  $r < r_e$ . If the potential energy at a distance  $r$  is  $V(r)$ , then value for the electron concentration at distance  $r$  is

$$n(r) = (\pi/3)[8m^*/\hbar^2]^{3/2}[E_f - V(r)]^{3/2}, \quad (7)$$

using the Thomas-Fermi approximation. One can obtain a solution for  $V(r)$  by solving the Poisson equation

$$\nabla^2 V = (4\pi e^2/K)[n_p - n(r)], \quad (8)$$

where  $K$  is the static dielectric constant, equal to 19.<sup>9</sup> Equations (7) and (8) have no exact analytic solution, but two approximate solutions are of interest.

One approximation is obtained by assuming that  $n(r) = 0$  for  $r < r_e$ ; i.e., there is complete exclusion of electrons from a sphere large enough for the vacancy to be balanced by the smeared positive charge density  $n_p$ . The solution for this approximation is

$$\begin{aligned} V/V_0 &= (r/3r_e) - (1/2) + r^2/r_e^2, & r < r_e; \\ V/V_0 &= 0, & r > r_e; \end{aligned}$$

where

$$\begin{aligned} V_0 &= 9e^2/Kr_e = 1.39 \text{ eV}, \\ r_e &= [9/4\pi n_p]^{1/3} = 4.85 \text{ Å}. \end{aligned} \quad (10)$$

This approximation tends to be accurate if  $E_f \ll V_0$ .

The other approximation is based on the assumption that  $V \ll E_f$ , so that the term  $[E_f - V(r)]^{3/2}$  in Eq. (7) is expanded to  $E_f(1 - 3V/2E_f)$ . This leads to the usual expression for a shielded Coulomb potential:

$$V/V_0 = (r_e/3r) \exp(-r/r_0), \quad (11)$$

where

$$\begin{aligned} r_0 &= r_e [2E_f/3V_0]^{1/2} \\ &= [KE_f/6\pi n_p e^2]^{1/2}. \end{aligned} \quad (12)$$

The approximation of Eq. (11) and (12) becomes accurate when  $E_f$  is equal to or larger than  $V_0$ .

The derivation of Eqs. (11) and (12) is identical with that of the usual Thomas-Fermi screening formula

except that the static dielectric constant was used. This is correct for a fixed charge in a polar lattice, to the extent that one can assume that the macroscopic static dielectric constant is appropriate for the small region in question.

In the case where the conduction band is nearly empty, one would divide  $e^2$  in the usual screening distance  $r_t$  of Eq. (6) by the high-frequency dielectric constant (6.25 for  $\text{Ce}_3\text{S}_4$ ), and use the effective mass to determine  $E_f$ . In the present case, where the band is about 20% full,<sup>7</sup> the questions of the appropriate values for the dielectric constant and the mass in the screening distance become more ambiguous, assuming even that we have the appropriate information about the band structure. The questions of the appropriate effective mass and dielectric constant for shielding become complicated when the energy of plasma oscillations become comparable to band and interband energies. These questions, discussed by Pines,<sup>17</sup> go much farther than what is necessary for our crude model. The significant facts in the present case, are that the static dielectric constant plays a role, and that in using Eq. (12), the appropriate values for the mass and the dielectric constant are not very well defined. We will use the macroscopic static dielectric constant ( $K=19$ ) in the following discussions. The conclusions to be drawn do not, however, depend sensitively on the values used for these quantities.

The value of  $E_f$  depends on the choice of a value for  $m^*$ . If one uses  $m^*/m = 3.1$ , then  $E_f = 0.40$  eV, and Eqs. (9) and (10) provide the better approximation to the solution. In this case,  $V(r)$  is equal to  $E_f$  at  $r_1 = 3.2$  Å, and  $V$  drops to zero at  $r_e = 4.85$  Å. The solution is most accurate near  $r = r_1$ , and, of course, the correct solution for  $r > r_e$  would have a small  $V(r)$  which drops off exponentially with increasing distance. There are reasons, discussed in Sec. IV, to believe that  $m^*/m$  may be appreciably smaller than 3, and it may be closer to unity. If  $m^* = m$ , then  $E_f = 1.20$ , and Eqs. (11) and (12) are a good approximation to the correct solution, with  $r_0 = 3.8$  Å. In this case, one finds that the distance  $r_1$ , at which  $V(r) = E_f$ , is equal to 1.29 Å.

The purpose of presenting such detailed results for the potential near a vacancy is to have a clear starting point in considering the implications for the mobility and potential distribution as the vacancy concentration  $N_v$  in the crystal is increased. These considerations necessarily involve increasingly qualitative deductions.

Two immediate conclusions are noteworthy:

(1) If the vacancies are not close to each other, the electron concentration remote from vacancies is  $n_p = 6.25 \times 10^{21}/\text{cm}^3$ , rather than the average electron concentration  $n$ .

(2) The diameter of the region near the vacancy in which the potential is strongly disturbed ( $\sim 9$  Å) is

<sup>17</sup> D. Pines, *Solid State Physics*, edited F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, p. 367.

considerably larger than the de Broglie wavelength of an electron (1.75 Å).

The preceding conclusions indicate that the Born approximation is not valid. Also, the use of the Thomas-Fermi expression for  $n(r)$  is open to question. In view of the many approximations in formulating the expression for  $V(r)$ , it seems best to examine vacancy scattering by working back from the experimental data to calculate the scattering cross section. The appropriate expression in the limit of noninteracting vacancies is

$$\mu = (n/n_p)e/\hbar k_f N_v S_v, \quad (13)$$

where  $k_f$  is the wave vector at the Fermi surface corresponding to a carrier density  $n_p$ , and  $S_v$  is the scattering cross section per vacancy.<sup>18</sup> The value of the effective mass does not enter here. Using the experimental data for  $\mu_0$ , calculated results, expressed in terms of a scattering radius  $r_s$ , where  $S_v = \pi r_s^2$ , are shown in Fig. 9. We also show, for reference, the behavior of the mean free path  $\lambda_s$ ; this is calculated from Eq. (13) with the omission of the factor  $n/n_p$ .

In the limit of small vacancy concentration  $N_v$ , where the vacancies are far apart, these results can be expected to represent the effect of individual vacancies. Figure 9 also shows the corresponding distance  $r_v$ , which is the radius of the average spherical volume per vacancy. We may take data for  $r_v > 7$  Å, that is,  $n > 4 \times 10^{21}/\text{cm}^3$ , as representing, reasonably well, situations with non-overlapping vacancy regions. With the exception of the point for the lowest  $N_v$  with  $r_s = 7.6$  Å, the values  $r_s \approx 4.4 - 5.1$  Å agree roughly with the size of the region of strong potential perturbation, so that the vacancies would seem to act like hard spheres with  $r_s \cong r_v$ . The point at lowest  $N_v$  is unreliable by itself. The vacancy concentration is very low here, so that the accuracy of determination of  $N_v$  from density measurements was poor. Also, a small contribution in another scattering process, such as residual spin scattering not associated with vacancies, could possibly have a relatively large effect on the value of  $\mu_0$ . We will discuss possible effects of spin scattering in Sec. IV. However, it should be pointed out here that if spin scattering occurs, it may also have the effect of adding to the scattering cross section per vacancy an increment which is an appreciable fraction of the total. Therefore, the apparent agreement of  $r_s$  with  $r_v$  cannot presently be used to reach a definite conclusion about the nature of the scattering process.

One notes in Fig. 9 that  $r_v$  decreases as  $N_v$  increases and  $n$  decreases. For  $n < 4 \times 10^{21}/\text{cm}^3$ ,  $r_v$  is close to the minimum value of 4.75 Å and is comparable to  $r_0$  or  $r_e$ . There is a significant overlap between adjoining vacancy regions. As a result, regions in which  $n(r)$  is constant and equal to  $n_p$  disappear, and most of the electrons are continually in regions of large potential perturbations.

<sup>18</sup> We are indebted to Dr. Walter Kohn for this formula.

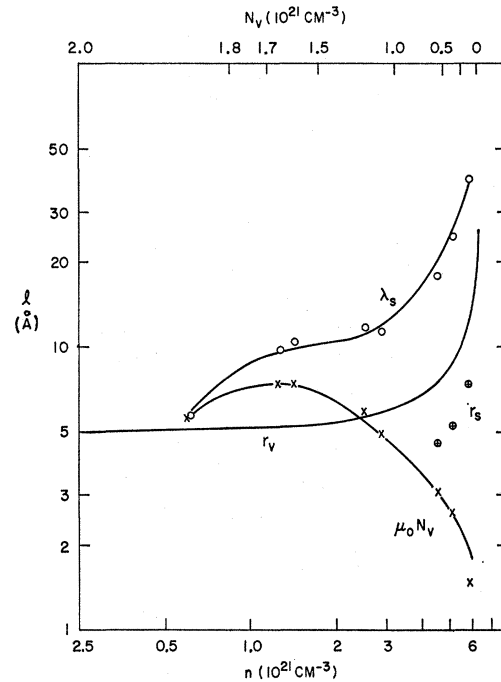


FIG. 9. Behavior of scattering radius  $r_s$ , mean free path  $\lambda_s$ , and  $\mu_0 N_v$  [in units of  $(\text{cm}^2/\text{V sec})(10^{21}/\text{cm}^3)$ ] as a function of  $n$  and  $N_v$ , as determined from  $\mu_0$ .  $r_v$  is the radius of the average spherical volume per vacancy.

It is to be expected that the character of the wave functions appropriate for describing transport would be drastically altered if the potential fluctuations are comparable to the Fermi energy. Since these wave functions will reflect to some extent an average potential, including the presence of the vacancies, one can expect the cross section per vacancy to diminish. For this region, the formula of Eq. (13) is not appropriate. A more proper indication of the scattering in the region of  $n < 4 \times 10^{21}/\text{cm}^3$  is the behavior of  $\mu_0 N_v$ , which is plotted in Fig. 9. One sees an increase in the quantity by a factor of 3 on going to large values of  $N_v$ . The decrease at lowest  $N_v$  is probably caused by incipient barriers, discussed below.

It seems, then, that the character of the electronic transport strongly affected by large potential fluctuations which occur in the crystal over most of the experimental range ( $n < 4 \times 10^{21}/\text{cm}^3$ ). In the low  $n$  range, an approximate solution for  $V(r)$  of the type obtained in Eqs. (11) and (12) would be modified by introducing new boundary conditions representing effects of neighboring vacancies. In the spirit of the model, one would require that  $dV/dr = 0$  at  $r = r_v$ , leading to a situation where  $n$  is everywhere smaller than  $n_p$ . Analysis of this type of problem has been discussed by Friedel.<sup>16</sup>

A pertinent aspect of the physical situation at large  $N_v$  arises from the random positions of the vacancies. There will be fluctuations in the distance between neighboring vacancies. Also, the minimum value of  $n(r)$

on lines between adjoining vacancies will be smaller than in other directions. These regions will act as passes between regions of lower potentials and can be expected to affect the impedance when the average electron concentration is small enough. This is the situation which seems to develop for samples with compositions approaching  $\text{Ce}_2\text{S}_3$  which are considered in Ref. 8. As  $n$  is decreased, the energy of the barrier regions increases and first becomes evident from regions of negative slopes in  $\rho(T)$  which occur at low temperatures. There is some evidence of upturning in  $\rho(T)$  near  $T=10^\circ\text{K}$  in the higher resistivity range of the samples considered in this paper, which seems to represent the beginnings of this effect. We observe in Fig. 3 a very shallow minimum in  $\rho(T)$  for  $n=1.42\times 10^{21}/\text{cm}^3$ ; and the effect is indicated in other samples, for which detailed curves were not obtained, by the excess in  $\mu_\nu$  above  $\mu_0$  in Fig. 2. This probably accounts for the decrease in  $\mu_0 N_\nu$  at low  $N_\nu$  in Fig. 9.

#### IV. DISCUSSION

The large potential fluctuations which occur over most of the experimental range ( $n < 4\times 10^{21}/\text{cm}^3$ ; for brevity, we will refer to this as the low- $n$  region) raise doubts about the validity of a literal interpretation of the parameters used to fit experimental results to the equations of conventional transport theory. Consequently, they should be regarded as an empirical description. The fact that this description works so well is of considerable interest, however, and suggests that the equations of the conventional theory contain elements of truth which go beyond the constraints of the model. One aspect of it, the fact that the contribution to the resistivity caused by increasing temperature is proportional to the absolute temperatures, seems readily understandable since this has to do with the nature of the lattice vibrations rather than the nature of the electrons. On the other hand, one can understand now why  $\mu_T$  does not depend on  $n$  in the way required by the conventional theory. The fact that the Seebeck coefficient varies as  $n^{-2/3}T$ , and the fact that one can use Fermi-Dirac integrals based on this behavior ( $m^*/m=3$ ,  $R=0$ ) to account for deviations from degenerate statistics in the transport is not readily anticipated. Investigation of the theory for transport of electrons in crystals with large potential fluctuations is needed for an evaluation of the significance of these observations.

In the limit of low-vacancy concentration (high- $n$  region), one should be able to make use of conventional transport theory for a literal interpretation of our results. It has been shown that the magnitude of the low-temperature mobility  $\mu_0$  can be accounted for, at least roughly, by the large distance required to screen the charge of the vacancies. We next reconsider the question of the appropriate value for the effective mass.

In Ref. 7, a value of  $m^*=3.1m$  was tentatively deduced from the fact that  $S/n^{2/3}$  was constant over a wide range of  $n$ . We now see that Eq. (4) cannot be

applied literally in the low- $n$  region, where conventional theory would normally be applied most safely to deductions about the density-of-states effective mass. Now, if one is restricted to considering  $S$  in the high- $n$  range, with  $n > 4\times 10^{21}/\text{cm}^3$ , there is greater ambiguity in a deduction of the effective mass. For one thing, the possible effects of distortions of the Fermi surface create more uncertainty in interpretation. In Ref. 7, experimental results for Hall measurements were reported with the results  $R_H n e < 1$  for large  $n$ . Although the interpretation of the behavior of Hall coefficient for this range may be affected by the complexity of the transport now brought to light, the conclusions about the behavior at large  $n$  still stand. Since  $R_H n e$  is significantly smaller than unity in the latter region, it seems likely that the Fermi surface has concave regions in addition to convex ones.

If one wishes, nonetheless, to deduce a value of  $m^*$  from  $S$  in the high- $n$  range, there is greater uncertainty about the appropriate value for  $R$  in Eq. (4). The energy dependence for scattering by vacancies is not evident, although a hard-sphere model suggested by the results in Fig. 9 would still require that  $\lambda_s$  be independent of energy, and  $R=0$ . On the other hand, the requirement that  $n < n_a/4$  is not clearly met, so that it is not evident, according to Eq. (2), whether  $f < 1$ , giving  $R=0$ , or  $f=1$ , giving  $R=2$ , or something in between. Of course, knowing the values of  $R$  for both the vacancy and lattice scattering, one would have to take an appropriately weighted average. The resistivity at room temperature contains about equal contributions from both types of scattering, and the values of  $S$  in Fig. 6 reflect essentially this situation. Thus, all that can be said is that  $R$  lies between 0 and 2, so that  $1 < m^*/m < 3$ .

Another indication of the value of  $m^*/m$  is obtained by comparing the mobility  $\mu_T$ , due to lattice scattering with high  $n$ , with literature values for other substances, in the light of Eq. (2). When this is done, it is found that the use of  $m^*/m=3$  for  $\text{Ce}_3\text{S}_4$  gives abnormally large values for  $\mu_T$ , as compared with other conductors, including silver and III-V semiconductors. In making comparison with metals, we assume that  $f=1$ , and that the product  $M a^2 \theta^2 / C^2$  is the same for both substances. By taking into account the difference in  $n/m^{*3}$ , one obtains a scaled value for the mobility, which will be denoted as  $\mu_s$ . As determined by data for silver,  $\mu_s$  is equal to  $0.1\mu_T$ . Since  $f \lesssim 1$  for  $\text{Ce}_3\text{S}_4$ , and  $M a^2$  cannot be far different for the two substances, one must account for the difference by the abnormally large value of the Debye temperature  $\theta$  ( $\sim 660^\circ\text{K}$ ) in cerium sulfide, an abnormally small coupling constant  $C$  (one-third the value for silver), or a value of  $m^*/m \cong 1$ . The value of  $\theta$  predicted by Lindemann's rule ( $296^\circ\text{K}$ ), as well as the spectroscopic data of Kurnick and Meyer<sup>19</sup> precludes the first explanation. The second alternative seems unlikely, so that there is support for the belief that  $m^*/m$

<sup>19</sup> S. W. Kurnick and C. Meyer, Phys. Chem. Solids (to be published).



is close to unity. In a similar manner, data for indium antimonide or other III-V semiconductors give values of  $\mu_s$  smaller than that for  $Ce_3S_4$  by a factor of 30 or more, if one assumes  $m^*/m=3$ , but in better agreement with  $m^*/m=1$ .

Other information relating to the estimated value of  $m^*/m$  is provided by the data of Kurnick and Meyer for the free carrier optical absorption in cerium sulfide.<sup>19</sup> They deduce  $m^*/m=1.3$ . However, this is based on the use of conventional theory in a situation ( $n\sim 10^{19}/cm^3$ ) where its applicability is open to question.

The low-temperature anomalies in  $S(T)$  and  $\rho(T)$  occur most strongly in the limit of small vacancy concentration, so that the possible causes can be considered in the light of conventional theory for electron transport. Although there seems to be a correlation between the magnitude of the anomalies of  $S$  and  $\rho$  in their dependence on both  $n$  and  $T$ , this may not necessarily reflect a common mechanism since different mechanisms may be separately suppressed by an increasing vacancy concentration and may have similar characteristic ranges of temperature. Phonon drag at low temperatures is fairly common, and, as noted above, one expects it to be suppressed by the presence of lattice imperfections.

The resistivity anomaly is more interesting. The appearance of the curves for  $\rho(T)$  suggests that an added scattering mechanism exists which increases in magnitude with increasing temperature and which saturates at about 100°K. The value of  $\Delta\rho$ , which is defined as the difference between the extrapolated resistivity at  $T=10^\circ K$  and the measured value, decreases as  $n$  is decreased and  $N_v$  increases. This indicates that the mechanism causing the anomaly tends to disappear at large  $N_v$  (smaller  $n$ ), since the mobility corresponding to it apparently increases by a large factor.

There seem to be at least two possible mechanisms. One is that there are localized modes of lattice vibrations associated with the vacancies which have a relatively low characteristic temperature ( $\sim 100^\circ K$ ). Localized lattice vibrations have recently been receiving attention as a cause of anomalies in thermal conductivity of insulators.<sup>20</sup> We cannot say much about the hypothesis. It seems reasonable to expect that they would be more effective in adding to the scattering at low values of  $N_v$ , since there is a larger region between vacancies in which they can act.

Another possible cause of the anomaly is scattering by random spin states of the  $(4f)^1$  electrons of the cerium ions. Guthrie and Appel have suggested that spin scattering plays a role in paramagnetic rare-earth sulfides.<sup>21</sup> It does not seem necessary to invoke spin scattering to explain the values of  $\mu_0$  and  $\mu_T$ , since their magnitudes can be accounted for by the vacancies and lattice vibra-

tions. However, spin scattering may provide a reasonable explanation for the resistivity anomaly and may also contribute to the residual resistivity at the lowest temperatures.

Spin scattering has been proposed by Kasuya<sup>22</sup> as a mechanism for electrical resistivity, and the problem has been discussed by other authors.<sup>23-27</sup> We will consider tentatively the general conclusions suggested by the  $\rho(T)$  curves, assuming that spin scattering is the cause. The break in  $\rho(T)$  for the samples with  $n > 5 \times 10^{21}/cm^3$  suggests that  $T \cong 100^\circ C$  may represent the occurrence of an antiferromagnetic type of ordering.<sup>28</sup> The magnitude of  $\Delta\rho$  corresponds to a mobility of 16  $cm^2/V$  sec arising from magnetic scattering, which is equivalent to a scattering cross section of about  $10^{-16} cm^2$  for  $Ce^{3+}$  ions. Since spin order may be incomplete at the lowest temperature, an upper limit to the effect of spin scattering is given by the extrapolated resistivity at  $T=0$ , and the corresponding mobility is  $\mu_x \cong 0.8 cm^2/V$  sec.

According to the theory given by De Gennes and Friedel, the scattering cross section is proportional to  $m^*S'(S'+1)$ , where  $S'$  is the spin quantum number.<sup>23</sup> However, a more accurate consideration of the spin transitions given by Brout and Suhl suggests that  $S'(S'+1)$  should be replaced by  $S'^2 \cos^2(\mathbf{S} \cdot \mathbf{J})$ , which is equal to  $S'^2 J/(J+1)$  or  $5/28$  for  $Ce^{3+}$ .<sup>26</sup>  $J$  is the total angular momentum. Smidt and Daane have shown that  $\Delta\rho$  is proportional to  $S^2 \cos^2(\mathbf{S} \cdot \mathbf{J})$  for heavy rare-earth metals and alloys.<sup>27</sup> Using the slope of their curve as an indication of the strength of spin scattering of the  $Ce^{3+}$  ions in cerium sulfide, with appropriate corrections for the different values of  $n$  and density of scattering centers, we find that there is agreement with  $\Delta\rho$  if one takes  $m^*/m=2.5$  for cerium sulfide. This agrees fairly well with other information. Comparison with  $\mu_x$  gives poorer agreement, with  $m^*/m=4$ . However, the validity of the comparisons is open to some question since the differences arising from the different electronic band structures introduce an unknown factor. The fact that  $\Delta\rho$  decreases with increasing  $N_v$  can be ascribed to the increasing lattice disorder which would inhibit spin ordering at low temperatures.

If spin scattering occurs, some disorder can be expected to remain and contribute to scattering at the lowest temperatures in the experimental range. Much of the residual spin scattering would be related to the

<sup>22</sup> T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 58 (1956).

<sup>23</sup> P. G. De Gennes and J. Friedel, Phys. Chem. Solids **4**, 71 (1958).

<sup>24</sup> B. R. Coles, Advan. Phys. **7**, 40 (1958).

<sup>25</sup> G. S. Anderson and S. Legvold, Phys. Rev. Letters **1**, 322 (1958).

<sup>26</sup> R. Brout and H. Suhl, Phys. Rev. Letters **2**, 387 (1959).

<sup>27</sup> F. A. Smidt, Jr., and A. H. Daane, Phys. Chem. Solids **24**, 361 (1963).

<sup>28</sup> The possibility of ferromagnetic behavior at liquid-helium temperatures was eliminated by a rough check on the magnetic susceptibility. We are indebted to Dr. R. H. Hammond for providing this information.

<sup>20</sup> J. A. Krumhansl, Bull. Am. Phys. Soc. **8**, 207 (1963), paper GA4; M. Wagner, *ibid.* paper GA5; G. T. Walker, *ibid.* paper GA6.

<sup>21</sup> G. Guthrie and J. Appel, Bull. Am. Phys. Soc. **8**, 224 (1963).

vacancy concentration, but some may not. The former part would add to the contribution of the electrostatic potential to the scattering cross section per vacancy. Residual random spin scattering not associated with vacancies would provide a background contribution to the scattering which would cause  $S_v$  to apparently increase at small  $N_v$ , possibly accounting for the larger  $S_v$  at our smallest  $N_v$ .

We cannot tell at present to what extent spin scattering might contribute to  $S_v$  calculated in the previous section. It could conceivably account for all of it, but we do not think that this is likely. In such a case,  $\mu_x$  would represent scattering by disordered spins; the fact that  $\mu_x$  is independent of  $N_v$  is consistent with this idea. However, one must suppose that the range of the disordering influence of each vacancy is larger ( $\sim 7.5 \text{ \AA}$ ), and the strength of scattering by  $\text{Ce}^{3+}$  ions compares more poorly with the data for the heavy rare-earth ions. In view of the large screening distance at the vacancies, it seems most likely that the electrostatic scattering accounts for at least a large part of the residual resistivity.

It would be very desirable, of course, to establish whether magnetic scattering plays a role in the transport and to determine its importance in relation to other scattering mechanisms. Guthrie and Appel have suggested a study of an analogous nonparamagnetic compound, lanthanum sulfide, which would have no electrons in  $4f$  states.<sup>21</sup> Other obvious possibilities are the study of the magnetic susceptibility or magnetoresistance of cerium sulfide samples which have low concentrations of vacancies. Magnetic susceptibility measurements would be a means for testing whether spin ordering occurs, as is suggested by the  $\rho(T)$  curves. Magnetoresistance measurements may not only establish whether the resistivity can be reduced by aligning the spins in an external field, but could also provide a means for measuring their contributions relative to other scattering mechanisms.

## V. CONCLUSIONS

A study of resistivity and Seebeck coefficient over a wide range of composition and temperature provides

data which can be described in large measure by the formulas of transport theory for metallic conductors. An examination of the electrostatic fields caused by the vacancies shows that most of the electrons are in regions widely fluctuating potentials except in the limit of low-vacancy concentrations. As a result, the transport equations must be regarded largely as providing an empirical description over most of the range of composition. Considerations of the data for low-vacancy concentrations show that the effective mass ratio  $m^*/m$  lies between 1 and 3. Measurements below liquid-air temperatures show anomalies, both in the Seebeck coefficient and in the resistivity, which occur most strongly at low-vacancy concentrations. The former is typical of phonon drag effects. The latter may be caused by spin scattering, but other possible causes such as scattering by localized modes of lattice vibrations are not excluded. The large residual resistivity at liquid-helium temperatures can be accounted for by scattering by vacancies, since there is weak screening, and one can expect a large scattering cross section. However, spin scattering could account for part of the residual resistivity and possibly a large fraction of it.

The physical situation in cerium sulfide is an interesting one, and one for which there is no adequate theory of transport. The wide fluctuations in potential seem to present an extreme case of the type of situation which occurs in single-phase metallic alloys. Our original view was that one could study cerium sulfide to determine what happens in a metal when the conduction band is gradually emptied. It is apparent now that one cannot empty the band without at the same time destroying it by the introduction of point defects which have poorly screened effective charges. Thus, it is similar to typical metals, except that the perfect lattice has a much lower density of electrons, with a consequently large screening distance, and one can go all the way in the same phase to a zero density of electrons.

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