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Observation of Anderson Localization in an Electron Gas

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Anderson has shown that there is no diffusion of an electron in certain random lattices, and Mott has pointed out that, for electrons in materials in which there is a potential energy varying in a random way from atom to atom, Anderson's work predicts that there should be a range of energies at the bottom of the conduction band for which an electron can move only by thermally activated hopping from one localized state to another. An energy E_c will separate the energies where this happens from the nonlocalized range of energies where there is no thermal activation. Cerium sulfide, investigated some years ago by Cutler and Leavy, is a particularly suitable material testing whether this is so because, in the neighborhood of the composition Ce_2S_3, $\frac{1}{9}$ of the cerium sites are vacancies distributed at random, and the number of free electrons can be varied with only very small changes in the number of vacancies. It is shown that the experimental results find a natural explanation in terms of this model: Conduction is by hopping when the concentration of electrons is low and the Fermi energy E_F lies below E_c; but when the concentration is higher and $E_F > E_c$, conduction is by the usual band mechanism with a short mean free path. The thermoelectric power is examined in both ranges, and the Hall mobility in the hopping region ($E_F < E_c$) seems in fair agreement with the theory of Holstein and Friedman.

I. INTRODUCTION

FIVE years ago one of us in cooperation with Leavy made measurements of the electronic transport in high-resistivity cerium sulfide.[1] The particular interest of this substance is that at the composition Ce_2S_3 it is an insulator, but at this composition it differs from the structure of Ce_3S_4 by the presence of vacancies at $\frac{1}{9}$ of the cerium sites and is thus conveniently written $Ce_{3-x}S_4$ with $x=\frac{1}{3}$. These vacancies are distributed at random, and thus the addition of a small number ν of cerium atoms per molecule of Ce_2S_3 adds 3ν electrons to the cerium d band without affecting appreciably the much larger number of vacancies. One can therefore study the behavior of a small number of free electrons introduced into a band in which there are no corresponding trapping centers. Instead, there is a rapidly fluctuating random field due to the negative charges on the vacancies, which may be thought of as superimposed on a uniform distribution of positive charge. The kind of potential energy expected is illustrated in Fig. 1.

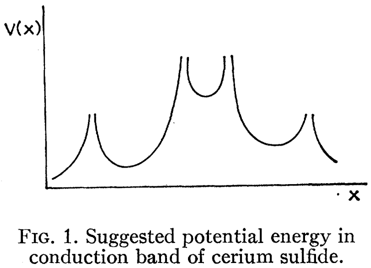

FIG. 1. Suggested potential energy in conduction band of cerium sulfide.

The aim of this paper is to interpret these observations in terms of the concept of localization of electron states which derives from Anderson[2] and has been developed by one of us.[3,4] The theoretical framework is set out in Sec. II.

II. LOCALIZATION IN A DISORDERED LATTICE

In the model of noninteracting electrons, each electron is to be thought of as moving in the d band of cerium sulfide under the influence of the random field of Fig. 1. One expects the density-of-states curve (Fig. 2) to be broader than it would be without the random field, and with a tail in which the states are localized.[3] We denote by E_c the energy separating states which are localized from those which are not. Then if the Fermi energy E_F lies below E_c, the conductivity σ tends to zero with T; if E_F lies above E_c, σ tends to a finite value (Fig. 3). For energies $E<E_c$, conduction is by hopping and the mobility contains an activation energy $W(E)$, which is expected to tend to zero as $E \rightarrow E_c$.

We show in Fig. 4 resistivity curves from CL. As the electron concentration in a sample is decreased, as indicated by an increasing resistivity at a given tem-

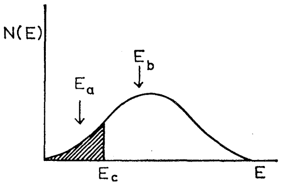

FIG. 2. Suggested density of states. Localized states are shaded. E_a is the Fermi energy for low concentrations of electrons for which conduction is by hopping, E_b for high concentration.

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[1] M. Cutler and J. F. Leavy, Phys. Rev. **133**, A1153 (1964), hereafter CL.

[2] P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

[3] N. F. Mott, Advan. Phys. **16**, 49 (1967).

[4] N. F. Mott, Phil. Mag. **17**, 1259 (1968).

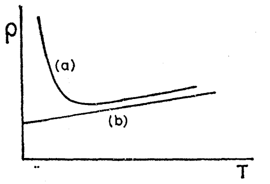

FIG. 3. Suggested plots of resistance against T for $E_F=E_a$ and $E_F=E_b$, respectively.

perature, there is a clear indication of a transition from band conduction to transport by hopping. In the following sections, the behavior of the transport coefficients in the hopping domain will be examined in detail.

Evidence that the impurity band in heavily doped germanium can have nonlocalized states in the middle and localized states at the top or bottom has been presented by Mott and Davis[5] based on the experimental work of Davis and Compton.[6] The situation here is rather similar except that there is no possibility of a "Mott transition" since the number of electrons is much smaller than the number of positively charged ions. A Wigner[7] transition is in principle possible, but we think that the density of the electron gas for $E_F>E_c$ is above that at which the transition is predicted.

III. TRANSPORT COEFFICIENTS

It is convenient to have a single expression for the electrical conductivity σ and the Seebeck coefficient S which describes the behavior of both the localized states at $E<E_c$ and the band states at $E>E_c$. This is derived below.

A familiar form for σ for the case of isotropic conductivity in a band is[8]

$$\sigma=-e^2\int\frac{1}{3}\tau v^2\left(\frac{\partial f}{\partial E}\right)N(E)dE, \tag{1}$$

where $N(E)$ is the density of states, f is the Fermi-Dirac function, and τ is the scattering time. For the present purpose, it is convenient to use the relationship $\partial f/\partial E=-f(1-f)/kT$ and to define a scattering distance (mean free path) by $L^2=\frac{1}{3}(\tau v)^2$, which results in

$$\sigma=\int\frac{e^2L^2}{\tau kT}f(1-f)N(E)dE. \tag{2}$$

A corresponding expression for the Seebeck coefficient in band conduction is

$$S\sigma=-\frac{k}{e}\int\frac{e^2L^2}{\tau kT}\left(\frac{E-E_F}{kT}\right)f(1-f)N(E)dE. \tag{3}$$

In these formulas $1/\tau$ will be of order $h/mL^2\sim10^{15}$ sec^{-1} for mean free paths of the order of the interatomic distance.[9]

Let us now consider hopping transport. The drift of electrons in a gradient of temperature or potential occurs by a sequence of transitions between adjoining localized states of varying energy. If one considers two states 1 and 2 at the same energy E, the transfer of electrons between them (normally through one or more sequences of intermediate states at other energies) can be characterized by a mean-squared distance L^2 along the direction of the gradient (x direction) and a mean frequency τ^{-1} which will be determined by the overlap integral and the energies of the spatially intermediate states. τ^{-1} will have an activation energy determined by the highest intermediate energy, and will be of the form $1/\tau=(1/\tau_0)e^{-W(E)/kT}$, where $1/\tau_0$ is a phonon frequency ($\sim10^{13}$ sec^{-1}).

The current between states 1 and 2 due to an electric field F and a temperature gradient dT/dx is

$$j_{12}=(ed/\tau)[f_1(1-f_2)\,e^{-eFd/2kT}-f_2(1-f_1)\,e^{eFd/2kT}], \tag{4}$$

where d is the x component of the distance between the two states, and τ its particular mean time. f_1 and f_2 differ from $f(T)$ at the average position of the two states by $\pm(dT/dx)(df/dT)(\frac{1}{2}d)$. On substituting for f_1 and f_2, expanding the exponentials, and retaining only

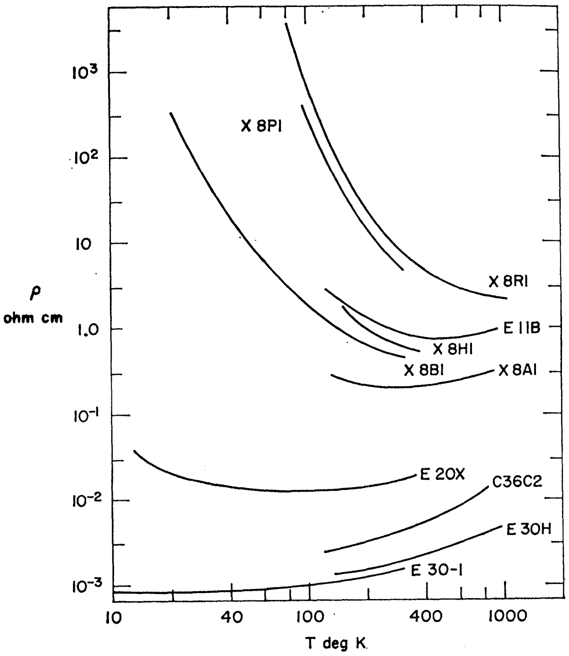

FIG. 4. Experimental curves from CL for resistivity versus temperature for cerium sulfide samples with various compositions.

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[5] N. F. Mott and E. A. Davis, Phil. Mag. **17**, 1269 (1968).

[6] E. A. Davis and W. D. Compton, Phys. Rev. **140**, A2183 (1965).

[7] E. P. Wigner, Trans. Faraday Soc. 34, 678 (1938).

[8] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, Oxford, 1960), Chap. 7.

[9] M. H. Cohen and H. Fritzsche (to be published).

TABLE I. Characteristics of the samples.

Sample	$20X$	$A1$	$B1$	$H1$	$11B$
(CL designation)	$E20X$	$X8A1$	$X8B1$	$X8H1$	$E11B$
$\sigma(300°\mathrm{K})$ (mho/cm)	52	5.4	2.32	1.54	1.30
T_c(°K)	100	300		400	
$kT_c(10^{-3}\,\mathrm{eV})$	8.6	25.8		34.4	
$W(10^{-3}\,\mathrm{eV})$	3.2[b]	8.6	15.3	31.6	26.4
$(dW/dE)_{E_F}$	−0.078	−0.67	−1.06	−1.10	−1.47
$(d\ln\mu_0 N/dE)_{E_F}(\mathrm{eV}^{-1})$	34.6	15.6	14.1	11.1	3.8
Parameters at 200°K					
σ(mho/cm)	83.5[a]	4.55	1.74	1.00	0.715
$\ln\sigma$	4.42[b]	1.52	0.555	0.0	−0.335
$dE/d\ln\sigma$ $(10^{-3}\,\mathrm{eV})$	25.6	15.5	13.2	13.3	11.2
dE/dW	−12.85	−1.49	−0.945	−0.910	−0.680
$dW/d\ln\sigma(10^{-3}\,\mathrm{eV})$	−1.99	−10.4	−14.0	−14.6	−16.5
$E_F{}^0(10^{-3}\,\mathrm{eV})$	37.8	−16.3			−32

[a] Since T_c is less than 200°K for this sample, the curve was extrapolated from the hopping range (below 100°K) to obtain this value.
[b] See note added in proof in Sec. IV.

terms linear in dT/dx and F, one obtains

$$j_{12}=\frac{e^2d^2}{\tau kT}f(1-f)F+\left(\frac{k}{e}\right)\frac{e^2d^2}{\tau kT}\left(\frac{E-E_F}{kT}\right)f(1-f)\frac{dT}{dx}. \quad (5)$$

On summing over all states at a given energy, d^2/τ is transformed to $(L^2/\tau)N(E)$, so that expressions (2) and (3) have the appropriate form for hopping states as well as band states. Thus, for $E>E_c$, L^2/τ corresponds to the diffusion constant for an electron gas, while for $E<E_c$ it corresponds to the diffusion constant for a random walk in which the average time between hops contains an activation energy.

In addition to σ and S, we need to consider the behavior of the Hall coefficient in the hopping domain. We shall examine it in the light of the analysis of Holstein and Friedman,[10] which indicates that the Hall mobility should have an activation energy which is smaller than that of the drift mobility by a factor of $\frac{1}{3}$.

IV. ANALYSIS OF EXPERIMENTAL DATA

The factor $f(1-f)$ in the integrals in Eqs. (2) and (3) for σ and S acts at low temperatures like a delta function with an area and width equal to kT. If $E_F<E_c$, but $E_c-E_F<kT$, the factor $f(1-f)$ permits contributions from band states with $E_F>E_c$. These tend to dominate the transport because of the relatively high mobility of band states. Thus, those samples in Fig. 4 which have a minimum in the $\rho(T)$ curve reflect this kind of situation: At high T, $E_c-E_F<kT$, and band conduction dominates. At low T, $E_c-E_F>kT$, and the main process is hopping. The temperature at which ρ is a minimum, denoted by T_c, is listed in Table I for those samples where it is observed. kT_c, also listed in the table, is a rough measure of the value of E_c-E_F. Transport at temperatures such that $T>T_c$ has been explained fairly well in CL in terms of conventional band theory. We consider here the data for $T<T_c$ in the light of the hopping mechanism.

When $kT\ll E_c-E_F$, Eqs. (2) and (3) reduce to the "metallic" formulas

$$\sigma=\sigma(E_F)=e\mu(E_F)N(E_F)kT, \quad (6)$$

where

$$\mu(E)=\mu_0(E)\exp[-W(E)/kT] \quad (7)$$

and

$$\mu_0=eL^2/\tau_0 kT. \quad (8)$$

Since the factors kT in Eqs. (6) and (8) cancel, the activation energies listed in CL should be equal to $W(E_F)$, assuming that dE_F/dT is negligible. This seems to be a good assumption, since $N(E_F)$ must be relatively large in the first place for $\sigma(E_F)$ to be appreciable. These activation energies are listed in Table I.

The corresponding metallic formula for S is, writing $E=E_F$ in both formulas,

$$\begin{aligned}S&=-(\pi^2k^2T/3e)d\ln\sigma(E)/dE\\&=-\tfrac{1}{3}\pi^2(k/e)[kTd\ln(\mu_0N)/dE-dW/dE]. \quad (9)\end{aligned}$$

Thus, S should be a linear function of T whose slope and intercept yield values of $d\ln(\mu_0E)/dE$ and (dW/dE) for $E=E_F$. This is found to be true. Some typical linear plots of $S(T)$ are shown in Fig. 5, and the resulting parameters are listed in Table I for all samples for which this analysis could be made.

The above results can be tested for self-consistency in the following way: The parameters derived from $S(T)$ can be used to calculate $(d\ln\sigma/dE)_{E_F}$ at any particular temperature. Dividing this by $(dW/dE)_{E_F}$ yields $(d\ln\sigma/dW)_{E_F}$ at that temperature, which can be compared with a curve for $\ln\sigma$ versus W at that temperature, derived from the resistivity data. We have

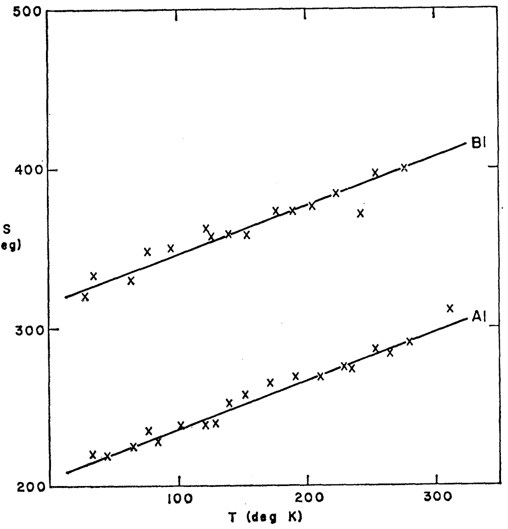

FIG. 5. Some typical plots, showing linear dependence of S on T for samples $A1$ and $B1$.

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[10] T. Holstein and L. Friedman, Phys. Rev. 165, 1019 (1968).

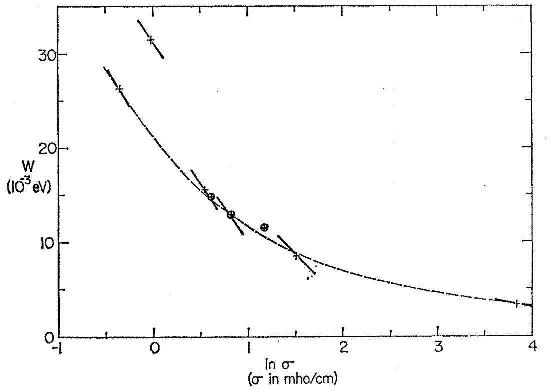

FIG. 6. Plot of W versus $\ln\sigma$. Short straight lines indicate the calculated value of $dW/d\ln\sigma$. Uncircled points are from data of CL, and points marked with circles are from new, recent measurements.

made such calculations at $T=200$°K, and show in Fig. 6 the points for $\ln\sigma$ versus W as well as $(d\ln\sigma/dW)_{E_F}$, indicated by short straight lines. These calculated slopes agree reasonably well with a smooth curve drawn through the points, considering the amount of scatter in the original data.

This measure of consistency encouraged an attempt to reconstruct a curve for $W(E)$ as a function of E, which was done as follows: using $\ln\sigma$ and $(d\ln\sigma/dE)_{E_F}$ for various samples at $T=200$°K, graphical integration yielded a curve, shown in Fig. 7, for $\ln\sigma$ versus E, where the zero of the E scale (on the left side of the figure) is arbitrary. On combining this with the data for W versus $\ln\sigma$, points are obtained for a curve $W(E)$. As a check on this, short straight lines are added corresponding to the expected slopes dW/dE, which are again seen to be in reasonable agreement with the smooth curve drawn through the points.

The analysis based on band conduction in CL leads to sufficient information to deduce the behavior of the Fermi energy in samples for which data on $S(T)$ exist for $T>T_c$. If one assumes that the "normal" density of states (Fig. 8) can be used, values of the Fermi energy $(E_F{}^0)$ at $T=200$, listed in Table I, can be deduced. It is interesting to compare the dependence of $E_F{}^0$ on σ with the curve in Fig. 7. The scale of $E_F{}^0$ (on the right side of the figure) was adjusted to match E for sample $20X$, and it is seen that the points for the other two samples for which $E_F{}^0$ could be determined lie near the curve for $\sigma(E)$. This agreement is perhaps more than what is to be expected, since the change in $N(E)$ caused by the disorder should pull E_F down below $E_F{}^0$ in samples with lower electron concentrations. Perhaps the observed agreement indicates that this effect is relatively small in this range of E.

Note added in proof. A more accurate plot of $\sigma(E)$ yields a curve which lies below the values of F_{f0}, as originally expected. This new curve, and the corresponding one for $W(E)$, is otherwise similar to the ones in Fig. 7. The improvements consisted in correcting an error in the plotted value of $\ln\sigma$, for sample $20X$, and in using $W=1.14\times10^{-3}$ eV instead of 3.2×10^{-3} eV. The former corresponds to the activation energy in the same range of T as was used in taking A and B from $S(T)$ (20–50°K) rather than a lower range of T which yields the latter value. (See Fig. 3 of CL.)

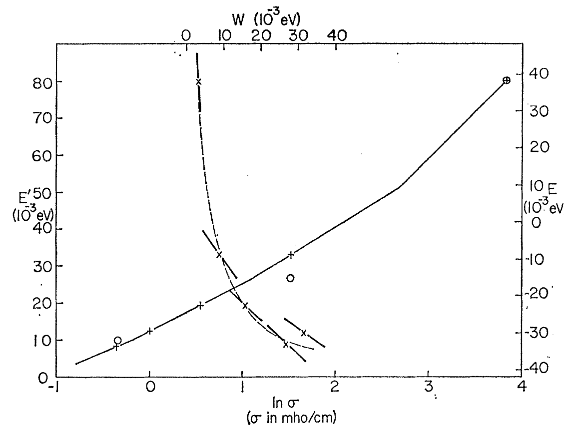

FIG. 7. Calculated curves for $E'(\sigma)$ and $W(E')$ from the data in Table I. The solid line is the result of a graphical integration to get E' as a function of $\ln\sigma$. The dashed curve shows the dependence of W on E', and the straight lines provide a comparison with the slope calculated for each point. The circles represent calculated values of $E_F{}^0$ (scale on the right) versus $\ln\sigma$. The zero of the right-hand scale was set to make the points for E and $E_F{}^0$ coincide for sample $20X$.

The two highest resistivity samples of CL ($X8P1$ and $X8R1$) differ from the others in that $d|S|/dT$ is negative rather than positive. This is believed to be the effect of an excessively small $\sigma(E_F)$ as compared to σ at higher energies, with the result that transport is dominated by thermally excited electrons at energies well above E_F.

To show that this would lead to the observed slope in $S(T)$, consider a simplified model in which $\sigma(E)$ is assumed to be zero for E less than some value E_x, and suppose that $E_x-E_F\gg kT$. In that case, the factor $f(1-f)$ in Eqs. (2) and (3) reduces to a Boltzmann factor $\exp[(E_F-E)/kT]$, and the lower limit of the integral becomes E_x. If one makes a Taylor's expansion of $\sigma(E)$ at $E=E_x$, one obtains, after some straightforward mathematical operations,

$$\sigma=\sigma(E_x)\,e^{-(E_x-E_F)/kT}[1+kTd\ln\sigma/dE+\cdots] \quad (10)$$

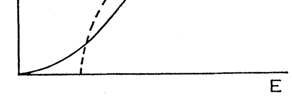

FIG. 8. Sketch of curves for the undistorted density of states (dashed line) and density of states distorted by potential fluctuations in the lattice.

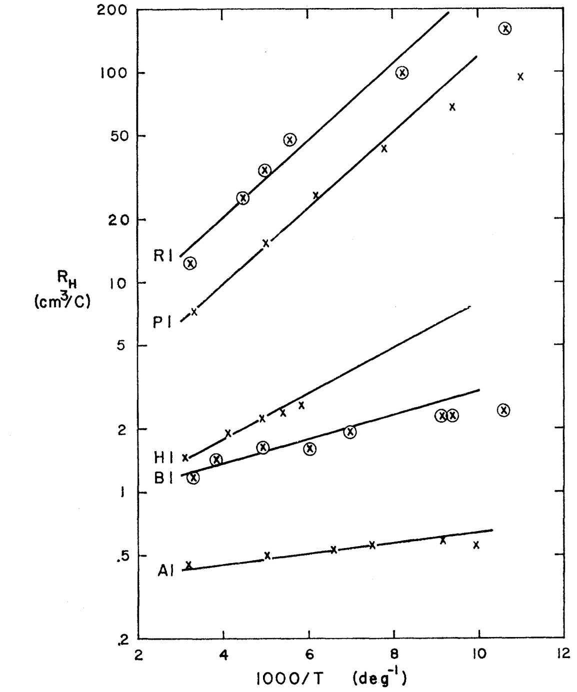

FIG. 9. Hall coefficient data from CL plotted with straight lines having $\frac{2}{3}$ the slope of the corresponding resistivity curves.

and

$$S=\frac{k}{e}\frac{E_x-E_F}{kT}+\frac{1+2kTd\ln\sigma/dE+\cdots}{1+kTd\ln\sigma/dE+\cdots}, \tag{11}$$

where the derivatives are taken at $E=E_x$.

It is clear from the above expressions that σ will continue to have an activation energy which includes the excitation energy E_x-E_F as well as W, while the first term in the expression for S can cause the observed change in slope. Since the assumed sharp cutoff in E at E_x is probably unrealistic, and E_F may now be a function of T, we have not attempted to analyze the experimental results in terms of Eqs. (10) and (11).

Finally, we compare the Hall data in CL with the theory of Holstein and Friedman.[10] This theory predicts that the activation energy for the Hall mobility should be $\frac{1}{3}$ the activation energy in σ, and the other $\frac{2}{3}$ should appear in R_H. In view of the larger scatter in the experimental points for R_H as compared to σ, a good way to make this comparison is to plot straight lines having $\frac{2}{3}$ the slope of the corresponding σ curves, using the experimental points for R_H. This is done in Fig. 9. It is seen that the experimental curve has the predicted slope, but there is an appreciable tendency for the slope to decrease at lower T. This may indicate a deviation from the theoretical behavior at low temperatures; a reason for this is suggested in Sec. V.

V. DISCUSSION AND CONCLUSIONS

It is seen that transport behavior of cerium sulfide can be accounted for very well in terms of the hypothesis that localized states occur at energies below a critical energy E_c, and for these energies conduction is by thermally activated hopping. The transport theory for hopping has been extended to permit a discussion of the behavior of the Seebeck coefficient, and the analysis has permitted a deduction of relatively crude curves for the behavior of $\sigma(E)$ and $W(E)$ as functions of E in the hopping range $E<E_c$.

The Fermi energy of sample $20X$, used to fix the right-hand scale in Fig. 7, is expected to be very close to E_c. The estimate of $E_c-E_F\sim kT_c$ leads to a difference equal to 0.0086 eV, so that one might fix E_c approximately at 0.047 eV in this figure. (It should be noted that the changes in kT_c with conductivity are considerably smaller than the change in E_c-E_F given by this figure, so we must assume that the estimate of E_c-E_F provided by kT_c may be off by a factor of 2 or more, if the curves in Fig. 7 are to be believed.)

Some of the results of CL, in particular, the behavior of ρ and S at $T<80°$K for sample $B1$, have not been discussed. A decrease in the activation energy of ρ at lower T is observed which may be indicative of a phenomenon predicted by one of us,[11] in which tunneling to more distant sites with a lower value of W is to be expected to be favored in hopping as T becomes very low. It seems possible that the tendency for R_H to fall below the predicted slope is connected with the same phenomenon. Because of the paucity of data, further measurements are being made and the low-temperature behavior is currently being investigated.

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[11] N. F. Mott, J. Non-Crystalline Solids 1, 1 (1968).