periments[4] indicate bulk behavior for $\mathfrak{N}_d \approx 5$. We anticipate no great difficulty in directly extending the calculations to this thickness. For a film $\mathfrak{N}_d$ layers thick, the $\mathfrak{N}_d$ sites of the formally equivalent complex tetragonal lattice lie in a regular array corresponding to a slice for an fcc crystal. Thus there are only $\mathfrak{N}_d - 1$ independent off-diagonal structure coefficients instead of the $\mathfrak{N}_d(\mathfrak{N}_d - 1)/2$ for a general complex lattice with $\mathfrak{N}_d$ sites per unit cell. This implies a computational time roughly $\mathfrak{N}_d$ times that for the monolayer.

It will be interesting to see the repercussions of the changes in electronic structure with film thickness on the characteristic properties of d-band metals, especially magnetic, superconducting, and catalytic behavior. In looking for these various effects it should be remembered that on going from a bulk d-band metal to an ultrathin film deposited on a bulk substrate of a different metal, one changes the d-band electronic behavior in two ways. The first is the change in d-band density of states with thinness; and second is the setting of the Fermi energy by the substrate metal.

I am indebted to Miss E. L. Kreiger for her great aid in carrying out the numerical calculations. Conversations with F. S. Ham have been especially valuable in formulating the film problem. I have enjoyed interesting discussions with B. Segall, D. E. Eastman, W. D. Grobman, U. Gradmann, H. C. Siegmann, M. Campagna, A. J. Bennett, and P. J. Bray on various aspects of film behavior.

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Observation of $\log\sigma \sim T^{-1/2}$ in Three-Dimensional Energy-Band Tails*

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Detailed measurements of the conductivity in controlled-occupancy energy-band tails of isotropic bulk material at low temperatutes (<20 K) are found to be accurately described by the relation $\log\sigma \sim T^{-1/2}$. The only theory that predicts such a relation applies to one-dimensional conduction, not three. It is suggested that these results may reflect the filamentary character of electron transport in random potentials.

A key relation in the behavior of electronic conduction in disordered, nonmetallic materials is the prediction by Mott[1] that the conductivity σ should depend on temperature as $\log\sigma \sim -(T_0/T)^{1/4}$ for hopping among localized states at low temperatures. The same conclusion was reached in more detailed treatments of the problem in the framework of percolation theories.[2,3] The common features of all of these is the assumption that phonon-assisted tunneling (i.e., hopping) is the dominant transport process; then if the density of states is not strongly energy dependent at the Fermi energy, the $T^{-1/4}$ dependence of $\log\sigma$ results. It should be noted that the 4 in the exponent is a consequence of the three-dimensionality of the available conduction space. Thus, disordered layerlike materials should exhibit a dependence like $T^{-1/3}$ and in one-dimensional materials (e.g., polymers) $\log\sigma$ should vary[4] as $T^{-1/2}$. There is extensive controversy, however, concerning the success of the numerous attempts to confirm these relations experimentally. This paper reports a new experimental test of these theories in energy-band tails of disordered semiconductors having three important advantages over any previously used materials: (i) The band tails are describable by quite widely accepted theories, (ii) the Fermi level in the band tails can be controlled, and (iii) the experiments can be done at the very low temperatures required for

hopping processes to dominate ($\lesssim 20$ K).

The difficulties with interpretation of the available results in one and two dimensions are readily seen in the literature on tetracyanoquinodimethan (TCNQ) salts which consist of long chains often closely packed in layers that are, in turn, far apart. The same conductivity data on some of the salts have been claimed to fit the $T^{-1/2}$ relation, thus demonstrating one-dimensional character,[5] and the $T^{-1/3}$ relation, demonstrating the planar behavior.[6] Then the disorder-dominated model itself was criticized,[7] casting doubt on the significance of both of these "fits."

The situation is little better in three dimensions although many more data are available, particularly on amorphous Ge and Si. Notwithstanding several earlier "good fits" of $\log\sigma$ to $T^{-1/4}$, recent work on both a-Ge[8] and a-Si[9,10] show that such fits are critically altered by annealing although the conclusions drawn in these last three papers disagree otherwise. In addition, Mott himself has criticized[11] most of the attempted fits because the measurements always had to be made at temperatures much higher than those in which the hopping mechanism is expected to dominate σ.[12]

The results reported here were obtained on materials having energy-band tails created (and controlled) by high concentrations of impurities in crystalline GaAs. These materials have been described previously[13]; the only aspect to be stressed here is that the available control over the Fermi energy allows preparation of samples having almost any desired total resistance. We can therefore make conductivity measurements down to much lower temperatures than has been possible in any of the other disordered materials cited. This has the dual benefit of giving data in the temperature range most relevant for hopping conduction (< 20 K) and extending considerably the total range of the abscissa in plots of $\log\sigma$ versus $T^{-1/n}$.

Because conductivity results from previous measurements on these materials[14] could be fitted about equally well with exponents of $\frac{1}{2}$, $\frac{1}{3}$, or $\frac{1}{4}$, it was necessary to increase greatly both the accuracy and the detail with which $\sigma(T)$ is measured in order to distinguish among these possible exponents. This has been successful as a result of several improvements in experimental technique. All the data reported here were obtained on six-arm samples of the type used in Hall-effect measurements.[13] The macroscopic homogeneity of the material was verified to be very good, even for these demanding purposes. The data have accuracies of $\sim \pm 2\%$ in conductivity and temperature, values which demanded very low electric fields in the samples and considerable care in temperature stability. At the very lowest temparatures (1.5–2.2 K) the errors might be slightly larger. The data shown by the points in Fig. 1 are representative of our results on several samples differing only in their Fermi energy (and hence T_0). The same data are plotted against both $T^{-1/4}$ and $T^{-1/2}$ as the abscissa.

These data (and others like them) are the essential experimental findings. The two-segment character of the plots with a break near 55 K is presently unexplained, but we note a similar observation for annealed a-Ge.[8] The portions of Fig. 1 at higher temperatures have lines drawn through them for best visual fit but will not be discussed here. The low-temperature results

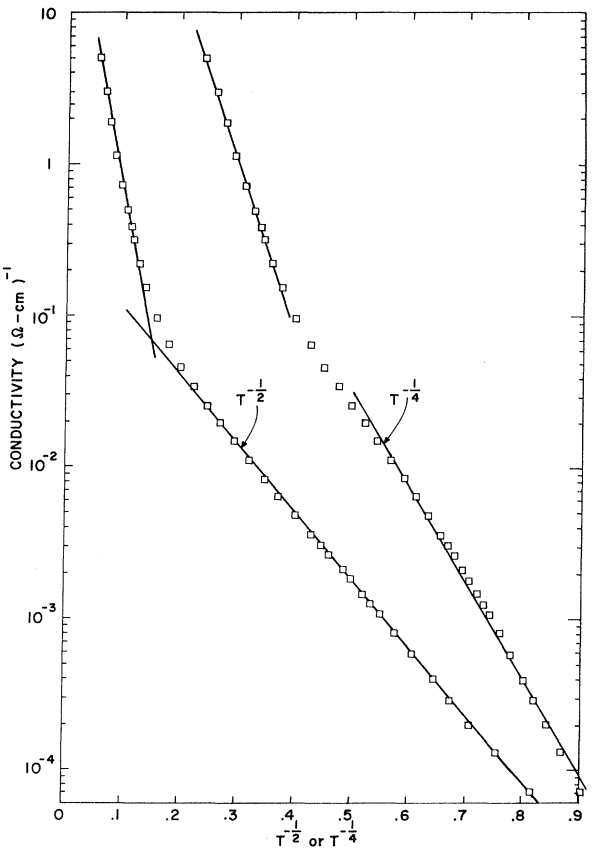

FIG. 1. The temperature dependence of the conductivity of one sample plotted in two ways: one as $\log\sigma$ versus $T^{-1/4}$ and one as $\log\sigma$ versus $T^{-1/2}$. The straight lines through the lower segments are the best, least-squares linear fits to the data. The lines through the upper segments are drawn visually through the data points.

will be stressed because they cover a wider range of the abscissa and because they are most appropriate to hopping conduction.

The accuracy and detail of the low-temperature results make it obvious that $T^{-1/4}$ is *not* a good fit to $\log\sigma$ whereas $T^{-1/2}$ is very good. These unexpected results demand close examination in view of the above-mentioned relation of the exponent of T with the dimensionality of conduction. There has been no physical basis for expecting the conduction in these materials to differ from three-dimensional transport. Thus considerable effort has been made to evaluate quantitatively the closeness of the fit of these plots (and the others not shown). First, numerical least-squares fits to both types of plots were made to determine the magnitude of the root mean square (rms) error given by each. The lines drawn in the lower segments of Fig. 1 were obtained this way. Only the (approximately 15) data points at the lowest temperatures ($\lesssim$20 K) were used so as to avoid the influence of the upper segment. In all cases the plot using $T^{-1/4}$ as the absissa had 4-to-5 times larger rms errors than that with $T^{-1/2}$. Next we asked what exponent gives the *best* fit. Standard curve-fitting techniques[15] may be used to determine the best exponent and its standard deviation. Such an analysis was performed on these data by R. C. Alig of these laboratories with results shown in Table I. The essential conclusions are that the best exponent is indeed $\frac{1}{2}$ within 1 standard deviation and the data do fit such a relation to within ~2%, our estimated accuracy.

In seeking to explain these results, we find the following: First, the pre-exponential factor[3] has a negligible effect on the relative fits. Considered next was Pollak's theory showing that various exponents can arise when one relaxes the usual assumption of an energy-independent density of states.[3] Using that approach and an exponential density-of-states function, Pollak has attempted to fit some of the present data.[16] It does not presently appear, however, that this method leads to a well-defined relation with a single exponent as do the experimental data; in addition, the fitting parameters are not consistent with the other known properties of these materials. For example, one such fit[16] requires that the characteristic width of the band tail be ~0.07 meV, whereas these band tails are known[17] to have widths of order 50 meV. In fact, since $kT \simeq 1$ meV over the range of interest, we believe that density-of-states variations should be negligible quite generally.

TABLE I. Statistical evaluation of best values of x to fit conductivity data with $\log\sigma \sim T^{-x}$.

Sample No.	Value of x for best fit	Standard deviation of x	rms error of data from this fit
I 0.0	0.507	0.010	0.9%
I 0.6	0.515	0.017	1.8%
I 1.33	0.505	0.019	1.6%

Finally, we have examined the possibility that the conduction might actually be quasi one dimensional (1-d) in consequence of the filamentary character of the hopping paths of lowest impedance as first shown by Miller and Abrahams.[18] It is well known that percolation theory of *classical* conduction leads to a single path at low energy[19]; with tunneling conduction a percolation threshold energy does not occur, but isolated paths arise from similar considerations.

There are difficulties with the suggestion of quasi-one-dimensional conduction, but they do not presently seem prohibitive of such a mechanism. First is the question of why previous theories[1-3] did not lead to the prediction of 1-d behavior when they did recognize the existence of filaments. That may be a consequence of the fact that those theories are based on microscopic treatments of the properties of single, representative sites, whereas the actual conduction paths are *macroscopic* chains of sites. In cases for which the "impedances" along a path have a wide range of magnitudes, a small number (the lowest impedances) can dominate the path in the sense of fixing its basic geometry. Then the conduction becomes a percolation problem constrained to such paths.[20] Raising the temperature of such a material can then lower the impedances of a number of unused branches—the microscopic effect—in the network without essentially altering the character of the macroscopic path. On the other hand, a material in which the impedances are nearly equal can respond with frequent cross linking to other similar paths as the temperature increases. This latter description may apply to good quality amorphous Ge and Si which sometimes display a $T^{-1/4}$ relation.

Another difficulty with the suggestion of 1-d conduction is Kurkijarvi's assertion that the extension of the $T^{-1/(d+1)}$ relations to one dimension

is invalid.[4] This objection may not be relevant to the present case, however, since our current paths are not mathematically ideal 1-d systems. Rather, they are paths of minimum impedance selected out of a three-dimensional space.[20] A somewhat similar argument against the relevance of Kurkijarvi's assertion to the TCNQ salts has recently been given in more formal terms.[21] That argument leads to the conclusion that when conduction occurs along multiple, quasi 1-d paths of finite length with weak localization, then $\log\sigma \sim T^{-1/2}$ can be a correct description at low temperatures.[21]

We note in closing that the $\log\sigma \sim T^{-1/2}$ relation has also been found in a system which is an interesting analog to ours: tunnel junctions composed of multiple layers of oxide in which small metal particles are embedded.[22]

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