Electrical-conductivity and Hall-effect measurements in semiconducting powders. Study of percolation effects

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We report Hall and conductivity measurements on ZnO-ZnS powder mixtures over the range (25–100)-wt.% ZnO. The conductivity shows "classical" percolation behavior according to the equation $\sigma = \sigma_0 (X - X_c)^S$ where X is the volume fraction of ZnO. The values of X_c and S are found to be $X_c = 0.135 \pm 0.020$ and $S = 1.7 \pm 0.2$. Though there is considerable scatter in the Hall coefficient, it remains approximately constant over the range of the measurements. This is reflected in the fact that we obtain the same exponent S from a plot of Hall mobility versus $X - X_c$ as is given by the conductivity.

I. INTRODUCTION

There has recently been a growth of interest in electrical conduction in systems containing random mixtures of conducting and nonconducting species. Several different theoretical approaches have been described using (a) highly idealized models of a solid medium,[1-6] (b) the so-called effective-medium theory,[7] and (c) percolation models of incomplete lattices of conductors.[8-13] The two former models have been extended to include calculation of the Hall effect. As there are significant differences between the predictions of these theories it is important to test their validity against a wide range of experiments on real systems.

A number of experimental investigations have been reported, principally on powder mixtures,[14,15] granular metal films,[16-27] metal-ammonia solutions,[28-31] and "alloys" of rare-earth metals with rare gases,[32-35] though a novel system of conducting and nonconducting sugar granules was studied by Clerc *et al.*[36] and similar measurements have been reported by Fitzpatrick *et al.*[37] on mixtures of aluminum and plastic spheres. These studies have yielded a disconcertingly wide range of results.

As part of a program on the electro-optical properties of powder semiconductors we have measured Hall effect and electrical conductivity in a system of mixed conducting (ZnO) and insulating (ZnS) powder grains. Our conductivity results are consistent with the percolation theory of conduction in such a system. The Hall-effect results support the prediction of effective medium theory that the Hall coefficient away from the percolation limit, is insensitive to the volume fraction of conducting material.

The most convincing theoretical approach to the calculation of conductivity in a powder system is in terms of percolation theory. This predicts a dependence of the form

$$\sigma = \sigma_0 (X - X_c)^S , \tag{1}$$

where X is the volume fraction of the conducting species and X_c is the percolation limit below which the conductivity falls to a very small value. The details of behavior, i.e., the values of X_c and S in Eq. 1 depend somewhat on the choice between "site" and "bond" percolation, however, as our experimental system provides a clear example of site percolation, we shall consider only this. Kirkpatrick[10] finds $S = 1.5 \pm 0.2$ for three-dimensional (3-D) site percolation for all values of X from X_c to unity (as can be seen by careful examination of his Fig. 4) and Straley[13] obtains $S = 1.75 \pm 0.1$ from a similar calculation. On the other hand, Adler *et al.*[9] calculate $S = 2$ for site percolation for all $X > X_c$, although a value of $S = 1.7$ is required to give the correct slope at $X = 1$ [cf. Kirkpatrick's Equation (6.22)]. There has also been some discussion of the value to be expected for X_c. The usual computer calculations on lattices of conductors determine the parameter p_c, which is the fraction of sites present at the percolation limit. This depends on the type of lattice but Scher and Zallen[8] suggested that for a number of regular 3-D lattices of touching spheres, these all reduce to approximately the same value of $X_c = 0.15$ ($X_c = fp_c$, where f is the appropriate packing factor). Kirkpatrick suggests a value of $X_c \simeq 0.25$ for a mixture of random shapes but, as discussed also by Saeger and Pike,[12] the value $X_c \simeq 0.15$ appears probable for a powder mixture of more or less regular grains. A similar value also emerges from the correlated bond model used by Webman *et al.*[30] to interpret experimental results on metal-ammonia solutions.

Experimental confirmation of percolation behavior has been obtained on a number of different systems but there is a rather wide variation in the values of X_c (or p_c) obtained (see Table I). For

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TABLE I. Survey of experimental results on electrical conductivity in 3-D percolation systems. Results marked with an asterisk were not quoted in the reference but have been derived from the data given.

System	X_c	S	Ref.
Hot-pressed C black		1.38	16, 17
C black in wax	0.07		18
Sintered Ag-Al_2O_3	0.2		19
Bakelite-Ag compact	0.37		19
W-Al_2O_3	0.47 ± 0.05	1.9 ± 0.2	20
Au-Al_2O_3	≅0.5		21
Ni-SiO_2	≅0.6		21
Al-SiO_2	0.58		22
La-SiO_2	≅0.45		23
Mo-SiO_2	≅0.75		23
Cr-SiO_2	0.6	≅1.5	16, 24
Cr, Au, NiCr-SiO, SiO_2	0.5-0.6		25
Silver paint	0.1, 0.25	1.45	16, 17, 26
Fe in polyimide	0.19		27
Ni-polyethylene powders	0.15-0.5		14
Al-plastic spheres	0.15	1.4*	37
Sugar ellipsoids	≅0.16*	1.9 ± 0.1*	36
ZnO-ZnS powders	0.135 ± 0.020	1.7 ± 0.2	Present work
RbKr alloys	0.14	2.0 ± 0.5	32
CsXe alloys	0.17	2.0 ± 0.5	32
CuAr alloys	≅0.14	1.6	33, 34
NaAr alloys	0.15 ± 0.01		35
Li, Na-NH_3 solutions	≅0.15	≅1.6	30, 31
Na_xWO_3	0.16 ± 0.03	1.8 ± 0.2	38
M_xWO_3	0.17 ± 0.02	1.6	31

dispersions of conducting particles in continuous media (e.g., carbon black in wax or metal cermets), X_c may range from 0.07 to 0.75 while Malliaris and Turner[14] showed that for mixtures of nickel and polymer grains, X_c varied considerably according to the relative sizes of the conducting and nonconducting grains. There have been rather fewer determinations of S. Abeles *et al.*[20] obtained $S = 1.9 \pm 0.2$ for a W-Al_2O_3 cermet (though coupled with $X_c = 0.47 \pm 0.05$). Experiments showing the combination $X_c \simeq 0.15$ with $S \simeq 1.7$ appear to be those on rare-earth-rare-gas alloys, metal-ammonia solutions, tungsten bronzes, and on sugar granules. This latter system is similar to our own and gives similar results.

The situation with regard to Hall measurements on these inhomogeneous systems is also somewhat unclear. The effective medium theory of Cohen and Jortner[7] and the composite sphere model of Mathew and Mendelson[6] both suggest that the Hall coefficient R should increase slowly as X decreases from $X = 1$, though in the region of the percolation limit R may diverge. Swenumson and Thompson[29] used a computer simulation to interpret experiments on Li-NH_3 solutions[28] and were able to confirm the predictions of effective medium theory. They showed that the behavior near the percolation limit depended strongly on the conductivities and mobilities of the two components but the choices they considered are not appropriate to our case. Other experimental evidence of a slow variation of R with X was obtained by Goldin and Juretschke[39] for porous copper and by Juretschke and Steinitz[15] for transition-metal diborides in the form of pressed powders.

II. RESULTS

The ZnO powder used in our measurements was electrophotographic grade, having a mean particle diameter of about 0.3 μm (estimated from specific surface area measurements and checked with a

disc centrifuge). The insulating ZnS powder was specially prepared to have a closely matched grain size. This was achieved by forming a fine-grain (~100 Å-diam) precipitate by adding thioacetamide to a solution of $ZnSO_4$ in excess ammonia, then firing in nitrogen at a carefully controlled temperature. The mean grain diameter was measured as 0.27 μm. The powders were mixed by ball milling in a 4-vol%-polyvinyl alcohol (PVA)-alcohol solution for two h, having checked that this treatment did not affect the electrical properties of the ZnO.

Layers were prepared for measurement by spinning the milled solution onto a glass substrate on which the appropriate electrode pattern had previously been evaporated. The thickness was built up to 4 μm by repeated spinning at 4000 revolutions per minute using a standard volume of solution and the PVA was then baked off at 400 °C. A selection of ZnO layers was sectioned and examined with a scanning electron microscope (SEM) from which the thickness was found to be 4 ± 1 μm and all our results analyzed on the assumption of a constant thickness of this value. Nonuniformity within a layer was also found to be of order ± 1 μm. By measuring the total weight of the layer, its thickness and area, the average packing density could be determined. A value of 0.45 ± 0.05 was obtained from a number of ZnO layers and this was used to determine the ZnO volume fraction X for the mixed layers (knowing the ZnO to ZnS ratio).

The SEM results were also useful in revealing the shape of individual powder grains. Scher and Zallen's[8] empirical value of $X_c \simeq 0.15$ is based on the assumption of spherical "grains" and, as pointed out by Pike and Seager,[11] is not valid for strongly anisotropic shapes. While the grains in our experiment are certainly not spherical and show evidence of crystal facetting, they are not markedly anisotropic and are much more nearly spherical than the stick model considered by Pike and Seager. We may reasonably expect Scher and Zallen's prediction to be a good first approximation.

Electrical measurements (dc) were made on clover-leaf-shaped samples using the standard van der Pauw method and a circuit specially designed for high-resistance samples.[40] The sample voltage was measured with a Keighley 610C electrometer and displayed on a chart recorder. For Hall measurements the magnetic field was swept repetitively between ± 17 kG and plotted alongside the measured Hall voltage. ZnO powder in air is highly resistive (~10^7 Ω cm) due to oxygen adsorption which creates surface barriers at grain-grain contacts, but it may be desorbed by illumination with band-gap light ($\lambda = 383$ nm).[41] For this reason all measurements were made in a vacuum chamber fitted with a quartz window, the sample being irradiated with a uv lamp and the pressure maintained at about 10^{-5} Torr. Under these conditions the resistivity of a ZnO sample was reduced to about 2 Ω cm.

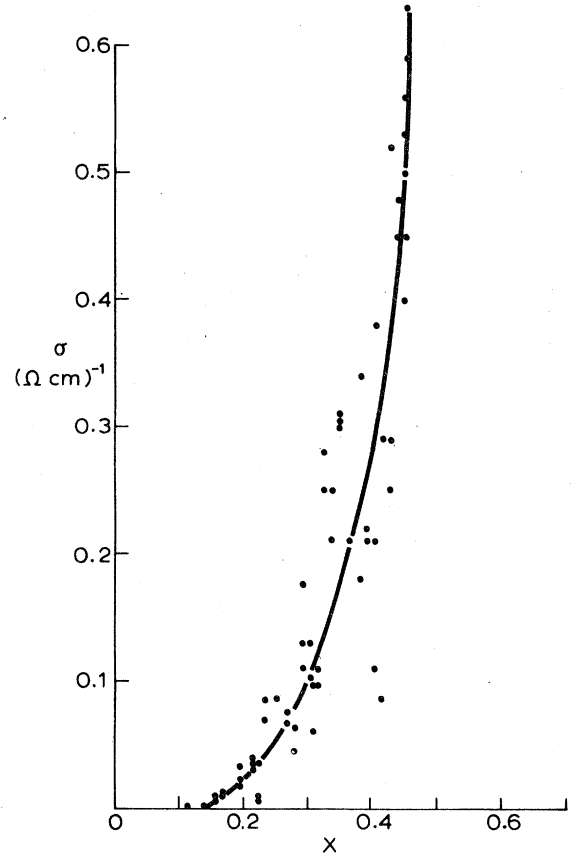

FIG. 1. Plot of conductivity of ZnO-ZnS mixed powders against volume fraction of ZnO showing the existence of a percolation limit of $X_c \simeq 0.13$.

Measurements on a range of ZnO layers gave values of carrier concentration and effective Hall mobility of $n = (3.0 \pm 0.5) \times 10^{17}$ cm^{-3} and $\mu_{eff} = 11 \pm 2$ cm^2/V sec. Layers of ZnS were also tested and found to be of very high resistance, as expected. A large number of mixed layers having the ZnO-to-ZnS ratio varying from 0.25 to 1.0 was then measured and the conductivity plotted against volume fraction of ZnO in Fig. 1. The critical volume fraction X_c was determined as 0.135 ± 0.015 (assuming a packing factor of 0.45), while allowing for the uncertainty in packing factor we obtain $X_c = 0.135 \pm 0.020$. Using this value of X_c the results are replotted in Fig. 2 against $X - X_c$ and show a power law dependence with exponent $S = 1.7 \pm 0.1$, the solid line in Fig. 2 being a least-squares fit to the measured points. The uncertainty

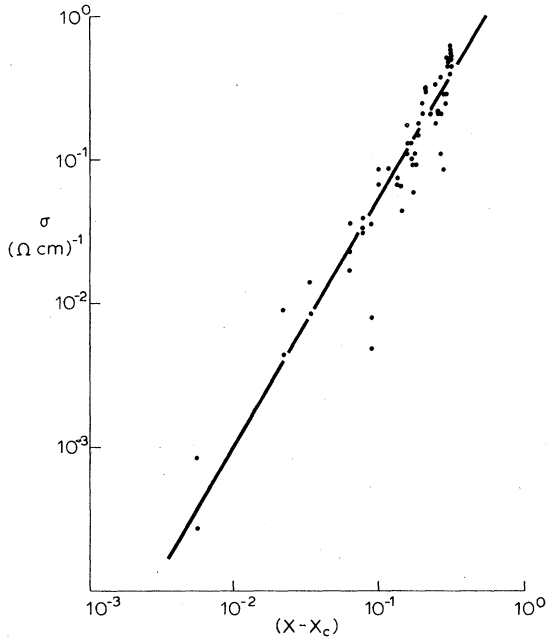

FIG. 2. Logarithmic plot of conductivity against $X - X_c$ for $X_c = 0.135$. The slope of the fitted straight line is $S = 1.7 \pm 0.1$.

in X_c increases the error so we obtain finally $S = 1.7 \pm 0.2$.

In the analysis of the conductivity data, σ depends on layer thickness which is not known with very high precision, whereas the effective Hall mobility is independent of thickness and is therefore subject

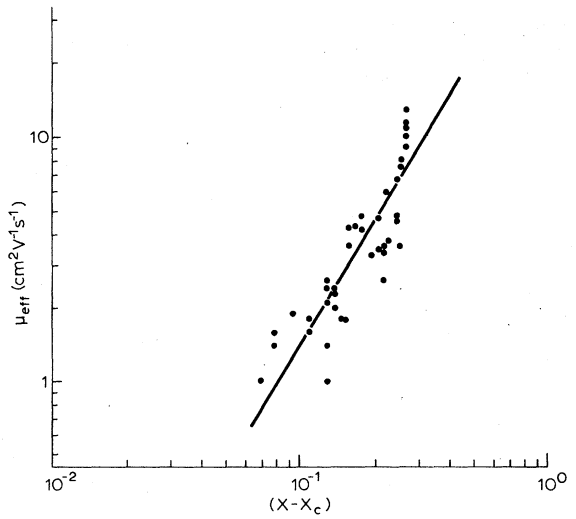

FIG. 3. Logarithmic plot of Hall mobility μ_{eff} against $X - X_c$ for $X_c = 0.135$. The slope of the line is $S = 1.7 \pm 0.3$.

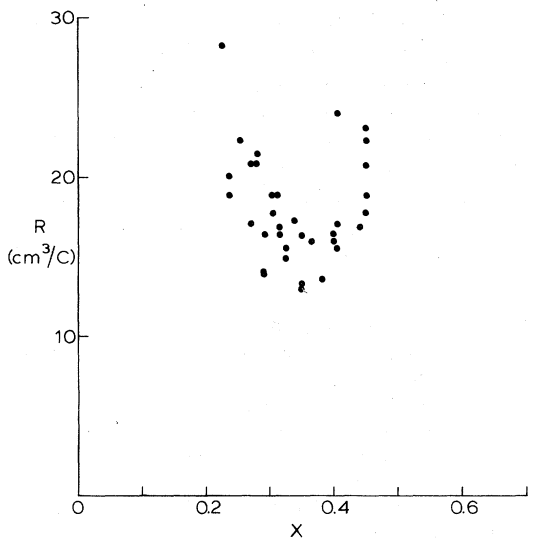

FIG. 4. Hall coefficient R plotted against volume fraction of ZnO.

to less random scatter. The plot in Fig. 3 of μ_{eff} against $X - X_c$ using $X_c = 0.135$ as before gives $S = 1.7 \pm 0.3$, the larger uncertainty in S resulting from the much smaller range of X over which Hall measurements were possible.

The plot of Hall coefficient R vs X in Fig. 4, though showing considerable scatter, shows no evidence for any trend. In fact, we might conclude from Fig. 4 that, within the accuracy of our measurements, R is independent of X over a range corresponding to a conductivity change of a factor 20. It is tempting to extrapolate this result to $X = 1$ (i.e., over a further factor 5 in σ) and suggest that the carrier concentration derived from Hall measurements is equal to that of a single crystal of the conducting grain material. However, it appears likely that accumulation layers may be created on the surfaces of the ZnO grains as a result of uv irradiation[41] and this throws doubt on the interpretation of the measured Hall coefficient. The apparent constancy of R is nevertheless an interesting result and, allowing for the experimental uncertainty, is consistent with the small change predicted by effective medium theory.

In summary, we have shown that the conductivity of our mixed ZnO-ZnS powders follows the predictions of site percolation theory for a 3-D system. This is interesting in that our layers are only some 10–15 grains thick. The value we obtain for the critical volume fraction X_c agrees with Scher and Zallen's[8] prediction well within the uncertainty of our measurements and the exponent S in Eq. (1) lies within the expected range 1.5–2.0. This "classical" percolation behavior prob-

ably depends on the fact that we are dealing with a mixture of grains having very similar size and mechanical properties, as was also the case in the work of Clerc *et al.*[36] Finally, we find that over the range $0.25 < X < 0.45$ the measured Hall coefficient remains roughly constant and a logarithmic plot of Hall mobility against $X - X_c$ yields the same exponent S as is obtained from the conducitivity data.

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