the longitudinal effect technique, the authors have purposely restricted their investigation to the silicon iron case, so well known through the beautiful work of the ferromagnetism group at the Bell Telephone Laboratories.[2,7,8]

Certain advantageous features of the technique indicate the nature of the problems to which it is peculiarly suited.

1. The entire surface of a domain has a single characteristic intensity and is revealed as a whole rather than being merely outlined; furthermore the relative intensities of the domains indicate without ambiguity the absolute directions of their magnetization.
2. The magnitude of the magnetization at any point on a specimen is subject to rapid quantitative measurement through the optical probe technique.
3. Although a properly polished, strain-free surface is required just as with the powder technique, the need for repolishing between observations is of course completely eliminated.
4. The method is not affected by either high or low temperatures as long as the surface is preserved, so that the study of domain behavior at interesting transition points becomes a distinct possibility.
5. Since the method is by its very nature a dynamic one, certain problems concerning domain dynamics can be undertaken.

There is some question as to how suitable the method will be for studying the truly microscopic domains of polycrystalline samples. The answer probably lies in the degree to which surface imperfections in the image can be eliminated by the photographic "noise-reduction" technique.

We wish to thank H. J. Williams and R. M. Bozorth of the Bell Telephone Laboratories for the loan of the silicon iron crystal and for valuable discussions concerning the investigation. We are also indebted to Dr. Burton Henke of Pomona College for several helpful suggestions.

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The Electrical Conductance of Pressed Powders, in Particular of Zinc Oxide*

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The electrical conductance of a pressed semiconducting material in powder form, representing a multiboundary semiconductor, is investigated. Experiments are described in which the dc conductance of the powder pressed between parallel plates in an evacuated chamber is determined for different pressures and temperatures. A model based on the change of the energy gaps with pressure is developed which accounts for the phenomena observed. Transient changes of conductance with time are observed for which only tentative explanations are suggested. Most of the experimental work refers to zinc oxide.

I. INTRODUCTION

EXTENSIVE work has been done on the electrical properties of powdered and sintered materials. Recently Hausner[1] examined the properties of sintered powders containing some semiconducting constituent. Miller[2] and Hahn[3] made a detailed investigation of sintered zinc oxide powder, whereas Davis[4] examined powders of semiconductive materials, in particular aluminum oxide and zinc oxide pressed between parallel plates.

The work on sintered materials, particularly the work of Miller and his associates, showed the effect of internal grain boundaries; sintering imposes, however, certain conditions on the material resulting from the heating process which, according to the nature and pressure of the gas in which sintering takes place, produces a chemical modification of the grain surface.

The method used by Davis of compressing the powder avoids these chemical changes. Some of his results, however, are not readily accounted for in terms of a general theory. The present investigation was undertaken with the purpose of examining more closely the conditions which arise when pressing a semiconducting powder.

Kantorowicz[5] has investigated the change of electrical conductance of pressed metal powders and has shown that the conductance or reciprocal of resistance

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* This work is the subject of the doctoral dissertation (Northwestern University, 1951) of Colman Goldberg and is there presented in greater detail.

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[1] H. H. Hausner, Electronics **21**(1), 138 (1948).

[2] P. H. Miller, Phys. Rev. **60**, 890 (1941).

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can be expressed by a relation:

$$1/R=G=c_1(p_m)^{\frac{1}{2}}+c_2, \qquad (1)$$

where p_m is the pressure and c_1 and c_2 are constants depending on the elastic properties of the metal.

Holm[6] has given a theoretical derivation of (1). He considers that the current flow through a compressed powder is constricted at the contact points of the powder particles. This accounts for the high resistance of the powder. With increasing pressure the contact areas between the particles become large and the resistance is thus reduced.

Recently Bridgman[7] measured the resistance of semiconducting powders for hydrostatic pressures up to 50 000 kg/cm^2. For zinc oxide he finds that at 25°C and at 100°C the resistance decreases with increasing pressure, whereas at 200°C the resistance increases with increasing pressure.

For tellurium Bardeen[8] has drawn attention to the relationship between the change of conductivity and the change of the energy gap between bands with hydrostatic pressure. Taylor[9] has shown that the energy gap for germanium is increased by applying hydrostatic pressure.

Gyulai and his co-workers[10] have investigated the effect of pressure on the electrical conductivity of rock salt. This work has been discussed and interpreted by Seitz;[11] it will not be discussed further here.

Davis experimented with pressed semiconducting oxides, in particular with aluminum oxide and zinc oxide. He reports that in a general way the conductance of the powder increases with pressure. He further finds that the dc conductance is time dependent in the sense that any sudden change of pressure produces a transient increase in conductance followed by a gradual decrease. He also observed that a reversal of the applied potential is accompanied by a transient increase of conductance.

II. EXPERIMENTAL PROCEDURE

Since most of the work of Davis was done with Al_2O_3, which ordinarily possesses a high resistivity and is hygroscopic, it was thought that his results may be largely due to surface effects of an electrolytic or ionic nature due either to moisture or to a gas film leading to surface conductivity of the type advocated by Cabrera and Mott.[12] In order to minimize such effects, in particular that of moisture, we made our measurements while the powder was in a vacuum. The apparatus used is as follows.

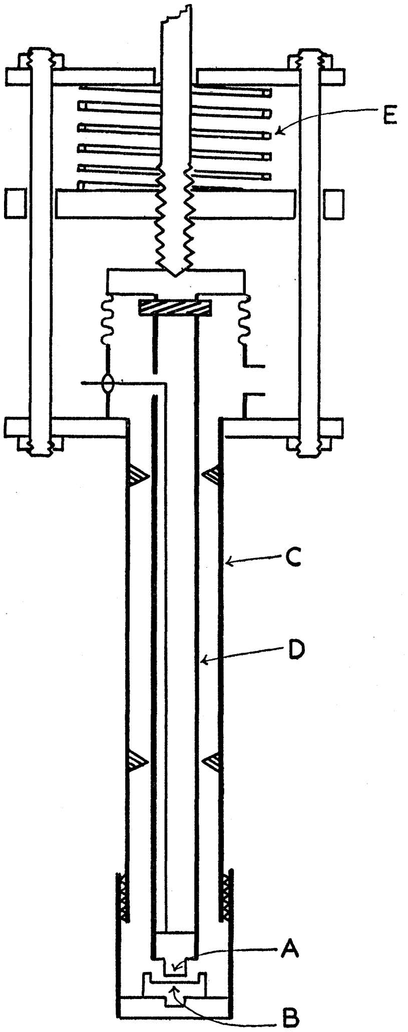

FIG. 1. Schematic diagram of the vacuum chamber for pressing powders.

The powder is placed as a layer between the plates *A* and *B* (Fig. 1) which are the end plates to an outer tube *C* and an inner tubular stem *D* connected by sylphon bellows, so as to form a vacuum-tight enclosure which could be evacuated or filled with a gas to any pressure desired. Plate *A* is insulated and the electrical connection to the outside is made through a glass-metal seal. The leakage resistance between the outer grounded plate *B* and the inner plate *A* was over 10 000 megohms. The lower part of the instrument could be immersed in a bath and maintained at a fixed temperature. The force *f* between *A* and *B* was obtained by means of a screw acting through the intermediary of a spring; the purpose of the spring *E* being to secure a steady force which would not appreciably be affected by "settling" of the powder or by differences in the thermal expansion of *C* and *D*. The compression of the spring gave a ready means for measuring the acting force; the spring

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was calibrated for this purpose. The applied pressure p_m is calculated simply by dividing the force f by A_m, the area of the plate A. Pressures up to 38 000 lb/in.^{2} have been attained. Higher pressures could be attained with an end piece A of smaller diameter. It will be seen that the action on the powder is not a hydrostatic pressure, but is unidirectional.

III. EXPERIMENTAL RESULTS

Using the apparatus described above with aluminum oxide powder it was found that after one hour of evacuation at 150°C the resistance was increased by a factor of more than 1×10^4; it was then so high that accurate measurements could not be made. Although we were thus unable to establish whether the effects observed by Davis were then maintained, it was shown that the major part of the conductivity observed by him was due to surface conditions, probably moisture.[13]

When zinc oxide is held in the evacuated apparatus at a temperature of 150°C in due time a quasi-stationary state is reached for which the resistivity is not too high to permit good resistance measurements. ZnO was thus chosen for all further investigations. In this quasi-stationary state a slow increase of conductance is observed which may be accounted for by a gradual removal of oxygen.[14] At room temperature the rate of this increase of conductance becomes negligible.

Experimenting at room temperature, we found that when a constant potential was applied to the powder and a current was allowed to flow, the conductance decreased with time. In a typical case with 15 volts applied across the compressed powder the conductance decreased 1.8 percent in one hour and 4.4 percent when 100 volts were applied. This is in the sense of the changes observed by Davis but considerably less. If the potential was applied only for the few seconds necessary to make the measurement the conductance remained constant during the time between the measurements. Davis further observed that when a current had been flowing through the powder under the action of an external emf on removal of this emf a current would flow in a direction opposite to that of the original current. This transient was not observed by us, although the apparatus was sensitive enough to detect 0.06 percent of the original current. Thus the transients observed by Davis for a powder held at constant pressure were greatly reduced by the treatment described above, which leads us to believe that these transients were due to surface phenomena which are removed by evacuation and heat treatment.

The effect of changes of pressure on the conductance of zinc oxide may be summarized as follows. (a) When the pressure on the sample is changed there is a sudden change in conductance followed by a slow decrease in conductance, the conductance becoming constant after approximately two hours. (b) At low pressures when the pressure is increased there is a sudden increase of conductance followed by the slow decrease described in (a). The net result of these changes, while at low pressures, is that an increase in pressure causes an increase in conductance. (c) At higher pressures, when the pressure is increased, there is a sudden decrease of conductance followed by the slow conductance decay described in (a). (d) From (b) and (c) it follows that there is a pressure for which the conductance is a maximum. It is found that when the temperature is lowered this maximum occurs at a lower pressure. (e) At pressures above that of the conductance maximum the logarithm of conductance is proportional to the pressure (Fig. 2). The constant of proportionality (the slope of the straight line of Fig. 2) is inversely proportional to P_m. P_m is defined as the maximum pressure that has been applied in the history of the sample in question.

IV. INTERPRETATION OF EXPERIMENTAL RESULTS

We have defined a pressure $P_m=f/A_m$, where f is the force acting on a piston of area A_m. The subscript "m" being used to indicate that we are referring to quantities that are measurable. Actually P_m has no meaning on a microscale. The powder consists of an agglomeration of particles with interstices so that the force f is not being applied to the area A_m, but to a much smaller area a which is the sum of the contact areas for any cross section of the powder. The actual pressure at any particular contact will then depend on its area, its orientation, and the total contact area in the cross section of the contact in question. We introduce the symbol p to represent an average value of this quantity which comprises also a term for the average orientation of the contact areas. The definition of symbols can be summarized by the relation

$$f=p_mA_m=pa. \tag{2}$$

The area a and the pressure p are not measurable quantities. They have physical meaning on a microscale and as used here represent averages only.

According to Holm, the actual contact area a increases as the pressure p_m is increased. This increase is rapid at low pressures, it becomes slower with increasing pressure so that a may be considered to be

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[13] It should be noted that preliminary experiments in which we examined under a protective oil seal Al_2O_3 powder that had been heated in a partial vacuum to 130°C showed reduced conductivity, but all the relaxation phenomena reported by Davis. The low conductivity in vacuum referred to above is only reached gradually in the course of an hour, indicating that the surface conductivity, whatever its nature, is not readily removed. A residual effect of this kind may play a part in some of the phenomena reported for ZnO further on.

[14] Zinc oxide is an excess or donor semiconductor with a stoichiometric excess of zinc, which can alter with the oxygen pressure of the surrounding gas. This can be attributed to removal of oxygen from the lattice or, according to H. Fritsche [Z. Physik **133**, 422 (1952)], to removal of interstitial oxygen. Whichever the nature of the process, it is temperature dependent and very slow at room temperature, which conditions are in agreement with our findings.

approximately constant in the range of higher pressures. [See Eq. (1).] Because of this variation of a with p_m, it can be seen from Eq. (2) that $\partial p/\partial p_m$ is small at low pressures, becoming larger and practically constant as the pressure increases.

For the higher compression rates used the densities of the powder approximated the density values of zinc oxide given in the literature within the limits of error. We did not determine the particle size distribution, so that the actual size of the interspaces was not known.

For a semiconductor we express the conductance as

$$G=G_0e^{-\epsilon/kT}. \qquad (3)$$

We use this classical approximation commonly adopted when ϵ is large compared with kT. From experiments reported further on, the slope of $\ln\epsilon$ *versus* $1/kT$ gave $\epsilon\sim 0.2$ ev for the powders examined by us, which seems to justify the approximation made. For small activation energies an intrinsic conduction term should be added. In our case the activation energy ϵ is half the energy distance between the impurity levels and the conduction band, G_0 depends on the physical dimensions of the sample and includes the geometry of the constrictions. G_0 increases rapidly with pressure for low pressures and becomes approximately constant for high pressures.

The condition for a conductance maximum [Sec. III (*d*)] can be seen from Eq. (3) to be

$$\partial G_0/\partial p_m=(G_0/kT)(\partial\epsilon/\partial p)(\partial p/\partial p_m). \qquad (4)$$

Since $\partial G_0/\partial p_m$ and $\partial p/\partial p_m$ are always positive, the maximum requires a positive $\partial\epsilon/\partial p_m$. In the way of a rough check we determined the sign of $\partial\epsilon/\partial p_m$ by measuring ϵ at different pressures. The ϵ values were derived from measuring the conductance over a range of temperatures. The averaged values were $\epsilon=0.209$ ev for 1200 psi and $\epsilon=0.240$ ev for 10490 psi. The evaluation showed $\partial\epsilon/\partial p_m$ to be positive and of approximately the right magnitude to account for the phenomena observed. It will be noted that $\partial\epsilon/\partial p_m$ is not the same as $\partial\epsilon/\partial p$, which is the quantity with a more direct physical meaning. Unfortunately, $\partial\epsilon/\partial p$ cannot be measured directly, and we are forced to deal with $\partial\epsilon/\partial p_m$; it can, however, readily be seen that the two quantities have the same sign. A positive $\partial\epsilon/\partial p$ means that the gap between the impurity levels, and the conduction band is enlarged as the pressure is increased. Positive values are known to exist. For the particular case of zinc oxide Bridgman reports that ϵ increases with pressure at 200°C and decreases with pressure at 0°C and 100°C. In comparing this with our findings, we must consider that the change of ϵ with pressure depends on impurities, but more important, that our p does not refer to hydrostatic pressure, but to a unidirectional stress and that the lattice deformation differs from that produced by hydrostatic pressure.

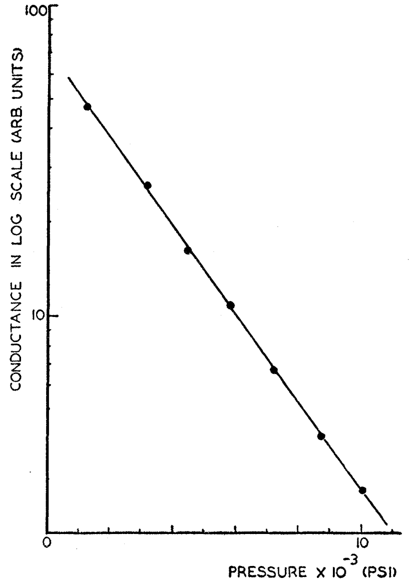

FIG. 2. Conductance in logarithmic scale *versus* pressure, for high pressures.

Since $\partial G_0/\partial p_m$ is positive and decreases with pressure while $\partial p/\partial p_m$ for higher pressures tends towards a constant value and $\partial\epsilon/\partial p$ is little sensitive to pressure changes, Eq. (4) shows that when the temperature is lowered the conductance maximum must occur at a lower pressure, which is in agreement with (*d*) of Sec. III.

The pressure p on the contact area cannot be increased indefinitely. At a certain critical pressure bruising or cracking of particles will occur. This critical pressure will vary with the configuration of the surrounding particles and with the particle size. We introduce the symbol p^* as an average or representative quantity for the maximum pressure which can be applied before breakage of the particle occurs. If the acting pressure on the powder is increased to a value greater than any previously attained pressure the pressure at some contact areas will reach the value for which bruising or crushing of particles occurs and an irreversible increase of the contact area takes place until the contact cross section has increased to a value for which $p=p^*$. If we designate by P_m the maximum acting pressure that has ever been applied to the powder, then

$$p^*a=P_mA_m, \qquad (5)$$

and a, the average contact area, is then a function of P_m.

For $p_m<P_m$ in the high pressure range, for which G_0 may be considered as constant:

$$\ln G=\ln G_0-\epsilon/kT, \qquad (6)$$

and substituting

$$\epsilon(p_m)=\epsilon_0+\frac{\partial\epsilon}{\partial p}\frac{\partial p}{\partial p_m}p_m, \qquad (7)$$

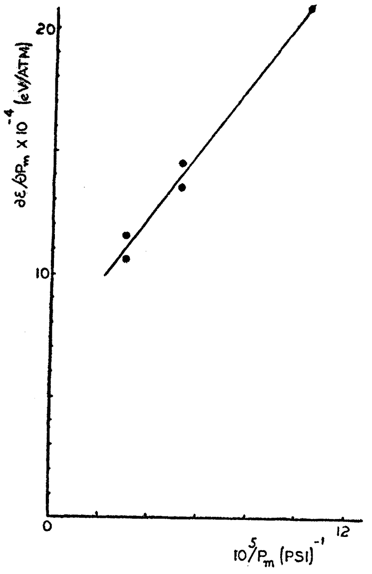

FIG. 3. $\partial\epsilon/\partial p_m$ *versus* $1/P_m$.

we find:

$$\ln G = \ln G_0 - \frac{\epsilon_0}{kT} - \frac{1}{kT}\frac{\partial\epsilon}{\partial p}\frac{\partial p}{\partial p_m}p_m. \tag{8}$$

From Eq. (2) and Eq. (5), it follows that for the high pressure range

$$\partial p/\partial p_m = A_m/a = p^*/P_m; \tag{9}$$

so that we can write:

$$\ln G = \text{const} - \frac{1}{kT}\frac{\partial\epsilon}{\partial p}\frac{p^*}{P_m}p_m. \tag{10}$$

Equation (10) agrees with the experimental result in Sec. III (*e*), in particular with the finding that the constant of proportionality between the logarithm of conductance and pressure is inversely proportional to P_m. Figure 3 shows some of the values of $\partial\epsilon/\partial p_m$ obtained for different values of P_m plotted against $1/P_m$.

The above accounts for most of the experimental findings reported in Sec. III, with exception of the transients which are more difficult to explain. These transients probably result from the superposition of several effects.

The decrease in conductance observed with a constant potential applied to the powder kept at a fixed pressure may be due to residual moisture or to ionic surface conductivity of the type discussed by Mott and Cabrera, to which reference has been made. Such ionic surface conduction would produce phenomena in the nature of electrolytic polarization. Electronic space charges also could play a part. Miller observed some transients with sintered ZnO, the constitution of which, however, differs from that of a powder, and Bridgman observed some at 200°C.

Davis[4] observed that when rock salt crystals were placed under increasing stress a transient increase of current occurred just below the stress for which shattering took place. Pierucci[15] observed a similar effect when cleaving crystals. The transient increase of conductance, which accompanies a change of pressure, may be related to effects of this type. Pierucci interprets his results by assuming that whenever a regrouping of the lattice configuration takes place, some electrons are temporarily lifted into the conduction band before taking their final positions. A general reshuffle of the lattices and grain boundaries will also give rise to a reshuffle of the configuration of space charges.

We do not have a sufficient amount of data available to attempt to give a definite explanation of the transients observed.

V. CONCLUSIONS

The phenomena which we have reported seem to be related to microquantities which we cannot observe in detail, but only interpret in their effect on observable macroscopic quantities. E.g., a significant quantity is $\partial\epsilon/\partial p$, where p is the stress at the contact area. This p is not equivalent to the quantity p_m nor to the hydrostatic pressure applied by Bridgman. Further, the value of ϵ is depending on the impurity content and is thus affected by heat treatment, so that it is likely to vary for different specimens.

Because of this uncertainty we feel that the work reported here is not so much a contribution to the study of the effect of compression on the semiconducting properties of zinc oxide as it is to the study of what happens to a semiconducting powder when it is compressed. This may be of interest to anyone desiring to study the electrical properties of materials that are not obtainable as single crystals but as powders only.

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[15] M. Pierucci, Nuovo cimento 6, 78 (1949).