These results agree with earlier measurements but are thought to be more accurate.

From the theory developed above it is seen that the present circuit cannot be used to measure nuclear time intervals much less than 10^{-7} sec., because of the then relatively large effect of variations in pulse formation.

In conclusion the author wishes to express his thanks to Professor H. L. Schultz and Professor E. R. Beringer for suggesting this problem and allowing the author the use of their equipment. It is also a pleasure to acknowledge a fellowship grant from the Swarthmore College Chapter of Sigma Xi during part of this work.

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Observation of the Ferro-Electric Barkhausen Effect in Barium Titanate

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Conductivity pulses were observed immediately after a single crystal of barium titanate was placed in an electric field, but died out in a few seconds. Several experiments were designed to test the hypothesis that these pulses were caused by the Barkhausen effect. From the experiments, the volume of a Barkhausen region and the apparent velocity of a domain wall could be estimated.

WHEN a single crystal of barium titanate grown by B. Matthias[1] was placed between electrodes and inserted in the equipment used by Wooldridge, Ahearn, and Burton[2] for the observation of alpha-conductivity in diamond, it was found that conductivity pulses appeared immediately upon application of an electric field, even when no alpha-radiation was present. These pulses were quite large, and did not die out for some seconds after application of the field. They were almost all in the same direction; this direction reversed when the direction of the applied field was reversed. Perhaps one pulse in a thousand was in the wrong direction.

In order to observe this effect, it is necessary that the crystal be in a vacuum (about 10^{-2} mm). At atmospheric pressure, application of the required field gives rise to a large amount of noise, which drowns out the effect described above. This noise is readily distinguishable experimentally from the effect in question, since the former does not die out with time.

Polarizing microscope studies[3] had shown that the barium titanate crystal used had domain structure, and that, upon application of an electric field, favorably oriented domains grew at the expense of less favorably oriented ones. It therefore seemed reasonable to assume that the pulses observed were a manifestation of the ferro-electric analog to the well-known Barkhausen effect.[4] This analog has been observed for rochelle salt by Mueller,[5] and has been postulated to account for discontinuities in hysteresis loops[6] of potassium dihydrogen phosphate and barium titanate.

In order to identify the effect conclusively, we undertook the following series of essentially qualitative experiments: (a) a measure of the largest conductivity pulses, (b) a measure of the total charge transferred by all the pulses following an application of field, (c) a measure of the duration of the individual pulses, that is, the length of time during which charge is moving, and (d) a search for a Curie point (suggested to the authors by G. C. Danielson), that is, a

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* Now at University of Tennessee, Knoxville, Tennessee.

[1] B. Matthias, Phys. Rev. **73**, 808 (1948).

[2] D. E. Wooldridge, A. J. Ahearn, and J. A. Burton, Phys. Rev. **71**, 913 (1947).

[3] B. Matthias and A. von Hippel, Phys. Rev. **73**, 1378 (1948).

[4] H. Barkhausen, Physik. Zeits. **20**, 401 (1919).

[5] H. Mueller, Phys. Rev. **47**, 175 (1935).

[6] A. von Arx and W. Mantle, Helv. Phys. Acta **17**, 299 (1944); B. Zwicker and P. Scherrer, Helv. Phys. Acta **17**, 346 (1944); A. de Bretteville, Jr., Phys. Rev. **73**, 807 (1948).

temperature at which the effect disappears more or less abruptly.

When the detailed study of the phenomenon was begun, it was found that more reliable results were obtained by reversing the field than by changing from zero to some finite value. Accordingly, when voltages are given in what follows, it is to be understood that the voltage across the crystal is changed from a plus to a minus (or vice versa) voltage of the size given.

Since the response of the amplifier is slow, the amplifier functions as an integrating device, and hence the pulse height is a measure of the total charge transferred during a pulse. From the known characteristics of the circuit used, it was computed that the largest pulses were equivalent to the transfer of 8.5×10^6 electrons all the way across the crystal. From this, we can compute the effective volume of a Barkhausen region, that is, the volume of crystal within which the direction of spontaneous polarization would have to reverse in order to give the observed motion of charge.

Let P be the polarization existing within a domain, let A be the cross section of a Barkhausen region, and l its length. The region then has equal and opposite charges of amount PA on its end faces, so that on reversing the voltage, a charge $2PA$ travels the distance l. If Q is the charge measured by the external circuit, and L the distance between electrodes, we have, on the assumption of uniform field within the crystal:

$$Q=2PA(l/L)=2Pv/L,$$

where v is the volume of the Barkhausen region. Using[7] $P=16\times10^{-6}$ coul./cm², and the measured $L=0.15$ cm, we get

$$v=5\times10^{-9}\text{ cm}^3.$$

This seems to be a reasonable order of magnitude for the largest v involved.

In order to measure the total charge transferred by all the pulses following a change of field, the size distribution of the pulses was determined roughly by counter methods. The average pulse was estimated to be about one-fifth of the largest, or

$$\text{average } v=10^{-9}\text{ cm}^3.$$

At 300 volts, or a field of $300/0.15=2000$ volts/cm, the total number of pulses, averaged over about fifteen observations, was 2200. Hence,

$$\text{total volume change}=2200\times10^{-9}=2.2\times10^{-6}\text{ cm}^3.$$

The total volume of the crystal is 5.6×10^{-4} cm³, so that the fraction of the total volume which changed polarization discontinuously is

$$2.2\times10^{-6}/5.4\times10^{-4}=0.4\text{ percent.}$$

The variation of total number of pulses counted as a function of voltage is shown in Fig. 1. The number seems to be a linear function of voltage over the range studied, although the function does not pass through the origin. If we make the large extrapolation to 4500 volts by this linear relation, and assume that the average pulse size is constant, we get a total volume change of 6 percent. This should be compared with the figure of 7.5 percent deduced by Mason,[8] for the same field strength, from electrostriction studies.

For measuring the duration of the individual pulses, a video amplifier was used which gave a time resolution of less than 0.05 μsec., and a gain of 90 db. A free running calibrated sweep was used, giving time scales from 0.3 to 5 μsec. per inch. The input characteristics of the amplifier were such that the pulses were again integrated, and the recovery from a pulse had a time constant of 100 μsec. Thus the pulses gave in the oscilloscope what was essentially a step-

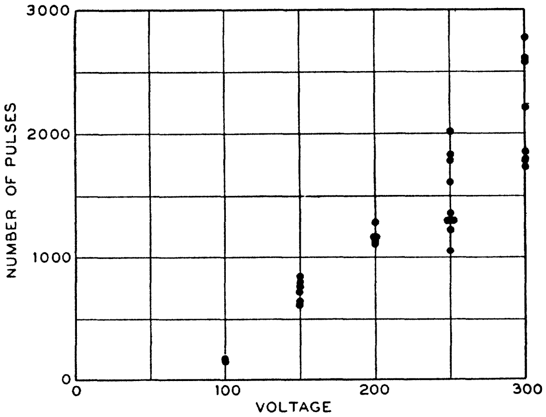

FIG. 1. Number of pulses obtained on reversal of voltage as a function of voltage.

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[7] J. K. Hulm, Nature **160**, 127 (1947).

[8] W. P. Mason, Phys. Rev. **72**, 869 (1947).

function whose rise time equals the duration of the pulse. These rise times were estimated visually, without adopting a precise definition of rise time.

With the high sweep speeds used, only a few pulses occurred while the oscilloscope beam was on the screen, so that at most, one, and frequently zero pulses, could be observed upon each voltage change. About forty pulses were observed visually with duration generally about 1 μsec., but ranging from 0.2 μsec. to greater than 6 μsec. The distribution of pulse height and duration are given in Fig. 2. The data suggest, but are far from demonstrating, a rough correlation between size and duration. For the data which were actually recorded, the pulses which gave an upward deflection had a noticeably longer average duration than those which gave a downward deflection. It is quite possible, however, that this was caused by the unavoidable subjective elements involved in selecting the pulses which were recorded.

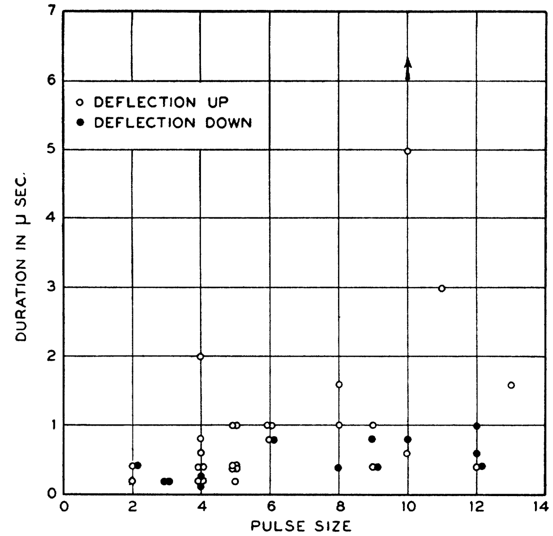

FIG. 2. Duration of pulses against pulse size on an arbitrary scale.

If the volume involved is about 10^{-9} cm^3, the distance which the polarizing disturbance has to travel is about 10^{-3} cm. If the time required is about 1 μsec., we have

$$\text{velocity of propagation} \approx 10^3 \text{ cm/sec.}$$

This is a relatively low velocity, and its value may be significant.

Most of the pulses appeared smooth, but a few (perhaps 1 percent to 10 percent) showed structure. Two were observed which rose steeply at first, and then broke sharply into a portion of much slower rise. Several were observed to have three ripples, which seemed to be quite smooth and regular.

Finally, the search for a Curie point was undertaken. In order to heat the crystal in vacuum, a small heater filament was placed on one side of it, and a thermometer on the other side. The thermometer tells only whether the crystal is warming or cooling, but does not tell its temperature. The resistance of the crystal was also measured in these experiments. The temperature was adjusted by varying the current through the filament.

When large filament currents were used, considerable noise appeared on the oscilloscope, and the apparent resistance of the crystal fell to a quite low value (about 20 megohms). We attributed these effects to gas released from the filament. In order to avoid them, we tried using filament currents just large enough to hold the thermometer reading steady. Under these conditions the circuit was quiet, and the indicated resistance of the crystal stayed above 500 megohms. At a thermometer reading of about 70°C, no conductivity pulses were observed. With the thermometer reading 5° lower, many pulses were observed. This critical point was passed through several times in both directions, always with the same results. Finally, the temperature was lowered slowly to room temperature, and the response observed frequently. The response (measured by visual observation of oscilloscope activity) passed through a maximum at a temperature roughly halfway between the Curie point and room temperature. The existence of this maximum, at which the activity was considerably larger than at room temperature or just below the Curie point, was confirmed by passing through it several times in either direction. The observations are not good enough to say whether it is spread over a narrow or a wide temperature range.

The thermometer reading (70°C) at the Curie point does not agree at all with the known Curie point at 120°C. Because of the geometry, however, we expect the thermometer reading to be much lower than the crystal temperature, and we do not believe that the discrepancy is serious.

In concluding, it should be pointed out that the experiments were essentially qualitative, designed to test the hypothesis that we were observing the Barkhausen effect, and were not intended as careful studies. In making careful studies, somewhat different techniques would be desirable. We believe that the experiments prove the existence of the ferro-electric Barkhausen effect fairly conclusively, and that they further suggest useful applications of the effect in studying ferro-electricity, particularly in barium titanate. We believe also that the three important measurements for one crystal: size of Barkhausen region 10^{-9} cm^3, total volume which changes orientation discontinuously ≈ 0.4 percent of crystal (at 2000 volts/cm), and velocity of propagation $\approx 10^3$ cm/sec., are correct as to order of magnitude.

We do not believe that the photographs in Fig. 1 of de Bretteville's letter[6] support the conclusion that he was observing Barkhausen jumps. They seem to us more consistent with the hypothesis that his crystal contained regions of different coercive forces. Further, our data do not support his remark that ferro-electric domains are larger than ferro-magnetic ones. In the crystal which we used for most of our tests, the volume of a domain was certainly less than 10^{-3} cm^3, while ferromagnetic domains are frequently as large as 10^{-3} cm^3 or more.

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A Calculation of the Changes in the Conductivity of Metals Produced by Cold-Work*

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The increase in the electrical resistance of severely cold-worked metals has been calculated by assuming that the important change which occurs during cold-work is the introduction of large numbers of Taylor dislocations. The results obtained are as follows: The calculated increase in the electrical resistance of polycrystalline copper is in good agreement with the measured value. In case single crystals are considered, the calculations show that there is a decided dependence of the dislocation resistance on the orientation of the electric field relative to the crystallographic axes. In copper the ratio of the largest dislocation resistance to the smallest is 8. This ratio is large for materials having a small Poisson's ratio. It is found that if the dislocations are not too closely clustered no interference effects will occur. The detailed calculations for copper assume that clustering is unimportant. Measurements on single crystals are in progress.

I. INTRODUCTION

It is found experimentally that if a metal is severely cold-worked its electrical resistance increases by several percent. The available data are summarized in Table I.[1] In the table $\Delta\rho$ is the change in the electrical resistance produced by cold-work, and ρ is the electrical resistance of the annealed metal at room temperature. It should be noted that except for the data on tungsten the specimens used were polycrystals of undetermined purity.

It is the aim of this paper to calculate theoretically the magnitude of this effect and to calculate the dependence of $\Delta\rho$ upon the orientation of the electric field with respect to the various crystallographic axes in a single crystal. The calculation will be made by assuming that the important change which occurs during cold-work is the introduction of a large number of dislocations[2] of the type shown in Fig. 1. It will

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* This research was supported by Contract N6ori-47 with the Office of Naval Research. Some of the work was done while the author was a Westinghouse Research Fellow in 1941.

[1] E. Schmid and W. Boas, *Kristallplastizität* (Verlag Julius Springer, Berlin, 1935), p. 214.

[2] F. Seitz, *The Physics of Metals* (McGraw-Hill Book Company, Inc., 1943), p. 88, references to original work are given.