

Massachusetts, 1959), Sec. 130.

<sup>5</sup>See, e.g., E. P. Gross, *J. Math. Phys.* **4**, 195 (1963); P. S. Hohenberg and P. C. Martin, *Phys. Rev. Letters*

**12**, 69 (1964); A. L. Fetter, *Phys. Rev.* **138**, A429 (1965).

<sup>6</sup>Reference 4, Sec. 29.

## CHANGING PROPERTIES OF METALS BY FERROELECTRIC POLARIZATION CHARGING

H. L. Stadler

Scientific Laboratory, Ford Motor Company, Dearborn, Michigan

(Received 5 April 1965)

This Letter describes a new method of studying the properties of metals and other conductors by inducing large electric charges on them. The method involves depositing a thin film of the substance to be studied onto a ferroelectric crystal and measuring the film properties while the polarization of the substrate is directed toward and away from the film. The difference in film properties between the two substrate polarization states is the quantity of interest. This technique has produced changes of 2% in the resistance of 100Å-thick gold films on BaTiO<sub>3</sub>, of 0.0013°K in the superconducting transition temperature of 160Å-thick tin films on triglycine sulfate (TGS), and of as much as 0.7% in the reflectivity of 200Å-thick silver and 150Å-thick gold films.

The ferroelectric polarization effect, like the similar field effect,<sup>1-4</sup> is described by the relation

$$\sigma = \Delta D_n = \Delta(E + 4\pi P)_n \quad (1)$$

for the density  $\sigma$  of charge on a capacitor plate as a function of the discontinuity  $\Delta D_n$  in the normal component of the electric displacement.  $E$  is the electric field and  $P$  is the polarization. Previous charge changing has been effected by varying the term  $E$  in (1) (field effect); the present method varies the term  $P$  (at negligible values of  $E$ ) by reversing a ferroelectric capacitor. The first advantage of the ferroelectric method is that the charge densities are much higher since  $4\pi P$  for common ferroelectrics (e.g., BaTiO<sub>3</sub>) is  $3 \times 10^8$  V/cm compared to the breakdown strength of usual dielectrics ( $\sim 10^6$  V/cm). The reversal of polarization of BaTiO<sub>3</sub> changes the charge induced on its electrodes by  $3 \times 10^{14}$  electrons/cm<sup>2</sup>, or by  $3 \times 10^{20}$  electrons/cc if the electrode is 100 Å thick. The second advantage of the ferroelectric method is that the effects are measured, after the polarization is reversed, with no electric field

applied to the dielectric. Since the quantities measured are ordinarily very small electric voltages or currents, this can be a great advantage.

In order to test the hypothesis that the changes of film properties are due to charging, several experiments using the electrical resistivity as the property of interest were performed. Films were evaporated onto both sides of etched ferroelectric single crystals in a conventional high-vacuum plater at about  $10^{-6}$  Torr. The conductivity of the film was measured by a four-electrode method at constant current with the polarization of the ferroelectric directed toward or away from the film, using a potentiometer principle to detect the small voltage changes precisely. The amount of charge needed to reverse the polarization was always measured during reversal and was always found to equal the product of the electrode area on the crystal times twice the published polarization of the crystal ( $26 \mu\text{C}/\text{cm}^2$  for BaTiO<sub>3</sub> and  $2.8 \mu\text{C}/\text{cm}^2$  for TGS). The resistance changes were believed to occur in the films rather than in the substrates because the ferroelectric crystals used have resistivities of  $\geq 10^{12} \Omega \text{ cm}$  and because even if extra impurities are diffused into BaTiO<sub>3</sub>, the carrier mobilities in doped BaTiO<sub>3</sub> are so low ( $\sim 10^{-3} \text{ cm}^2/\text{V sec}$ )<sup>5</sup> that such an impurity layer would not show observable resistance changes on polarization reversal of the substrate.

Variations were made of film material, substrate material, temperature of measurement, and film thickness. The films used were gold and gadolinium (both  $n$ -type conductors), germanium and tellurium (both  $p$ -type). The charging hypothesis predicts that electrons will be added to a film when the ferroelectric polarization is directed toward it and that these extra electrons will lower the resistance of an  $n$ -type film and raise the resistance of a  $p$ -type film. This predicted sign of resistance change

was found on every film tested. The magnitude of change is hard to predict exactly because the charging could alter both the carrier concentration and the mobility (through changes in shielding of ion cores and, thus, of scattering) and because of trapping in the semiconducting films.

Gold films were applied to two substrate ferroelectric single crystals, *c* plates of BaTiO<sub>3</sub> and *b* plates of TGS, which both have the advantage that they do not change shape on polarization reversal. This, and the fact that all measurements were made with zero electric field across the crystal during measurements, meant that the resistance changes could not be due to strain changes in the thin films. The resistance changes should (by the charging hypothesis) be nine times as great in films on BaTiO<sub>3</sub> as in films on TGS because of the larger polarization. They were found to be of the same sign, but only five times as great. This could be due to differences in surface-state density or to differences in diffuseness of scattering between TGS-Au and BaTiO<sub>3</sub>-Au interfaces. Such interfacial differences can be eliminated by comparing the resistance changes during polarization reversal of a film on a TGS crystal at +20°C with those of the same film at -195°C. The polarization of TGS at -195°C is twice as great as that at +20°C, and the relative resistance change expected on the charging hypothesis should also be twice as great. The measured relative resistance change was found to be 1.8 times as great at -195°C as at +20°C, supporting the charging hypothesis and the idea of interface differences mentioned above.

The dependence of resistance changes on film thickness cannot be predicted very exactly by the hypothesis of charging. While thin films should show greater relative changes than thick ones, the exact shape of the curve depends on where the induced charges are in the film, what part of the resistivity arises from bulk scattering rather than surface scattering, and whether the scattering is changed by the induced charges. Figure 1 shows that the resistance changes in gold films were found to be approximately proportional to reciprocal film thickness. The dashed line is the expectation if the induced charges were distributed uniformly throughout the film and if these charges changed the carrier concentration without affecting the mobility. To sum up, the results of all the experiments on resistance changes agree with the

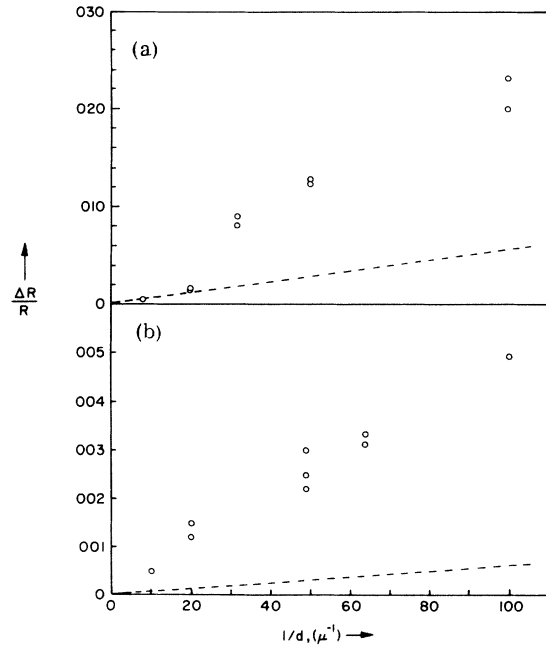


FIG. 1. Fractional change in electrical resistance of gold films (due to the polarization reversal of their ferroelectric substrates) plotted versus reciprocal thickness of the film. (a) BaTiO<sub>3</sub> substrate. (b) Triglycine sulfate substrate. The dashed line in each section indicates the values expected for uniform change in charge-carrier density at constant mobility.

charging hypothesis in sign and order of magnitude.

Another physical property, the superconducting transition temperature  $T_C$ , has previously been altered by field-effect charging.<sup>4</sup> In the present experiment  $T_C$  of tin films on TGS was measured by observing the vapor pressure of liquid He (including the hydrostatic head) needed to make the film resistance equal to one-half the normal-state resistance. The regulated vacuum pump could hold a desired pressure to 0.1 Torr for minutes, and measurements were usually made during very slow cooling. Glover's concern about piezoelectric substrates for measuring strain-sensitive thin films was avoided by measuring  $T_C$  at zero field using *b* plates of TGS, whose shape is independent of polarization direction. The tin films were applied to both sides of the TGS crystal so when its polarization was reversed  $T_C$  for one film rose 0.0013°K while the other dropped 0.0013°K. (A shape change of the TGS would have moved  $T_C$  for both films in the same direction.) The polarization was reversed at ~6 kV/cm by warming the crystal during reversal to about 40°K. This ferroelectric charg-

ing change in  $T_C$  was twenty times as large as and of the same sign as Glover's, for induced charge per atom twenty times as great as his. The changes in the reflection spectra will be reported separately.<sup>6</sup>

Suggestions helpful to these experiments were contributed by many members of this Laboratory but especial by G. A. Alers, A. D. Brailsford, R. C. Jaklevic, J. J. Lambe, A. W. Overhauser, and R. W. Terhune, as well as by R. F. Schwarz of Philco Laboratory, Blue Bell, Pennsylvania.

P. J. Zachmanidis gave skillful assistance in the measurements.

<sup>1</sup>E. Bose, *Physik. Z.* **7**, 373 (1906).

<sup>2</sup>R. W. Pohl, *Physik. Z.* **7**, 500 (1906).

<sup>3</sup>G. Bonfiglioli, E. Coen, and R. Malvano, *Phys. Rev.* **101**, 1281 (1956); *Phys. Rev.* **115**, 330 (1959).

<sup>4</sup>R. E. Glover, III, and M. D. Sherrill, *Phys. Rev. Letters* **5**, 248 (1960).

<sup>5</sup>G. C. Harman, *Phys. Rev.* **106**, 1358 (1957).

<sup>6</sup>H. L. Stadler, J. J. Lambe, W. C. Vassell, and P. J. Zachmanidis, to be published.

### PROPAGATION OF TRANSVERSE ACOUSTIC WAVES IN A SPIN-DENSITY-WAVE METAL\*

Roger C. Alig,† John J. Quinn, and Sergio Rodriguez

Department of Physics, Purdue University, Lafayette, Indiana

(Received 10 May 1965)

Overhauser<sup>1</sup> has suggested recently that the electronic ground states of sodium, potassium, rubidium, and cesium possess spin-density waves (SDW). In order to explain why the distortion of the Fermi surface in the direction of the SDW is not observed experimentally,<sup>2</sup> he has postulated that the SDW orients itself parallel to the direction of a sufficiently strong magnetic field. One obvious experimental test of Overhauser's hypothesis is the study of the propagation of acoustic waves parallel to the dc magnetic field.<sup>3</sup> The object of this note is to present the results of a calculation of the attenuation and velocity of shear acoustic waves propagating parallel to the magnetic field for a SDW model of a metal, and to compare these results with the predictions of the free-electron model.<sup>4</sup> For example, in Fig. 1 we display the attenuation coefficient  $\gamma$  as a function of the magnetic induction  $B_0$ . The calculation was carried out for a model appropriate to potassium, assuming that the SDW is characterized by an energy gap  $G = 0.62$  eV as required to explain<sup>1</sup> the optical data of Mayer and El Naby.<sup>5</sup>

The position of the absorption edge (called the Kjeldaas edge) in Fig. 1 is determined by the condition

$$\omega_c = qv_m = (\omega/s)v_m, \quad (1)$$

namely that the frequency experienced by at least some electrons moving in the self-consistent electromagnetic field associated with the acoustic wave be equal to the cyclotron resonance frequency  $\omega_c$ . In Eq. (1) we have neglect-

ed  $\omega$ , the frequency of the acoustic wave, as compared to  $\omega_c$ . The symbol  $q = \omega/s$  stands for the wave vector of the sound wave,  $s$  is the velocity of sound, and  $v_m$  the maximum velocity of an electron on the Fermi surface in the direction of  $\vec{B}_0$ . For the free-electron model  $v_m$  is equal to the Fermi velocity  $v_F$ , but for a SDW model<sup>6</sup>  $v_m$  is considerably smaller.

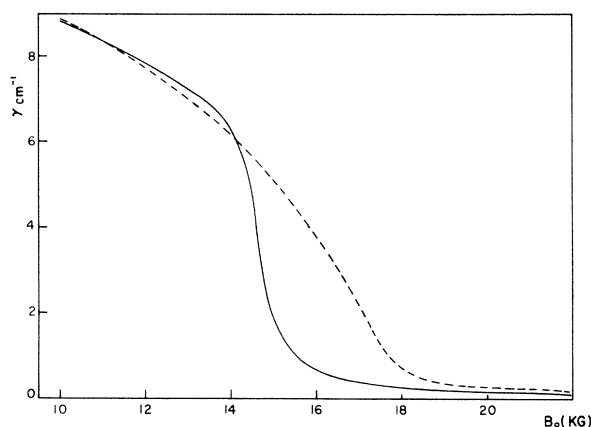


FIG. 1. The attenuation coefficient  $\gamma$  in  $\text{cm}^{-1}$  versus magnetic induction  $B_0$  in kilogauss for a left-circularly polarized sound wave. The solid curve is for the linear SDW model, and the dashed curve for the free-electron model. Both curves are appropriate to an acoustic frequency of 100 megacycles per second and an electron relaxation time of  $1.58 \times 10^{-10}$  sec, giving a value of the parameter  $ql$  of approximately 50. Detailed calculations for the velocity and attenuation of both circular polarizations and for helicons have been carried out. A more complete account of this work will be reported elsewhere.