

of the applied field and that of the ferroelectric dipole. It has already been ascertained, by these measurements, that the polarization state shown in Fig. 8, disregarding the arrows from the atom centers, corresponds to a field and spontaneous polarization in the *negative b* direction. When the atoms move as indicated by the arrows, the polarization direction is along the *positive b* axis.

Previous dielectric and thermal studies⁴ suggested that the transition is of order-disorder type. Preliminary x-ray examination of the paraelectric phase confirms this. The temperature dependence of the spontaneous polarization, and the second-order char-

acter of the transition, suggest that at the temperature of our x-ray observations, about 20°C, a certain degree of disorder must persist in the structure. This disorder has not as yet been taken into account in the structure analysis. Detailed x-ray and neutron studies of the structures on either side of the Curie point are in progress. A very important approach to this order-disorder problem is *via* study of the x-ray diffuse scattering. Such a study, both theoretical and experimental, is in progress. A theoretical treatment of various physical properties, based upon the structure reported here, is presented elsewhere.⁴⁶

⁴⁶ Mitsui, Shibuya, and Pepinsky (to be published).

Surface States in Metals*

G. BONFIGLIOLI, *Istituto Elettrotecnico Nazionale, Turin, Italy*

AND

R. MALVANO, *Istituto di Fisica dell'Università, Turin, Italy*

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This paper deals with measurements of conductivity modulation in metals by an electric field. The measurements have been performed using a new technique, which permits reaching an accuracy sensibly higher than that obtained in experiments already published.

Measurements on Au, Sb, and Bi films have been carried out at different temperatures between about -20 and +80°C. The existence of localized and conducting "surface states" at the metal/dielectric interface seems to be experimentally confirmed.

(1) INTRODUCTION

EXPERIMENTS on the modulation of conductivity by electrical charges induced at the surface of a flat metal specimen by a transverse electric field, strictly analogous—in principle—to those performed on semiconductors,¹ were reported in a paper already published by the present authors.²

The specimens used were in form of thin films; this was necessary in order to obtain measurable effects in spite of the enormous density of the charge carriers in a metal. The specimens were connected across an arm of a high-sensitivity Wheatstone bridge. At the same time they were used as one of two metal plates of a flat mica condenser, charged by a high-voltage power supply that produced a transverse electric field inducing a large surface charge on the specimen. The specimens (in the form of thin films of the order of magnitude 100 or 1000 Å thick, according to the metal considered) were evaporated on a convenient mica support. Unusual

results were found for Au, Bi, and Sb, that is, for metals of widely different electronic structure.

In the present paper, we report a new series of measurements which have been performed using a different detection technique which has inherent advantages and higher accuracy. Furthermore, a point of utmost importance has been investigated, namely, the dependence of the effect on temperature. It has been possible to explore the range between -20° and +80°C, where interesting effects have been found. For this purpose, an ultrathermostat has been used, with an over-all stability of better than 10⁻²°C.

The results obtained seem to lead to the hypothesis that "surface" electronic states of both localized and conducting type are present at the metal (specimen)/dielectric (mica support) interface.

(2) EXPERIMENTAL TECHNIQUE

(a) Specimens

In the preparation of the specimens, two points have been cared for in a more refined manner than in our previous experiments,² to which the reader is referred for all the technical details which are not given here. First, the evaporations have been carried out in a better

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¹ W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 29 ff.

² Bonfiglioli, Coen, and Malvano, *Phys. Rev.* **101**, 1281 (1956).

vacuum (10^{-5} mm Hg)³ to get purer, better defined, metals. Second, it seemed interesting, initially, to deal with specimens condensed, respectively, on cold or hot holders, to reach different degrees of lattice perfection. Consequently, the mica sheets on which the metals had to be condensed were held at room temperature or at about 300°C during the evaporation. Air was readmitted to the vacuum bell only when temperature had gone down 50°C. However, preliminary measurements showed no detectable difference between the two kinds of specimens, and therefore all the results to be reported concern the specimens condensed at room temperature.

(b) Detection Method

The most difficult problem we had to solve in the development of this research was to perform a rather accurate measurement of a very small "resistance modulation." The circuit used in the present experiment can be considered as a particular kind of the well-known "synchronous demodulation" circuit—in which a zero beat frequency is obtained and detected by a dc instrument. The resistance to be examined is supplied with ac, while it is subjected to a sinusoidal modulating action of the same frequency ($\omega/2\pi$), produced in the present case by the electric charge induced on the metal film.

In order to exploit fully the sensitivity of the dc ammeter, we had to provide a very effective filtering action to avoid the passage of too big an ac component in the galvanometer. This was achieved through a nonresonant bridge, supplied with ac and having in its diagonal arm a high-sensitivity dc galvanometer (Fig. 1). The behavior of this circuit (fully described in a paper by the present writers⁴) is the following. If I_0 is the amplitude of the current $I_0 \cos \omega t$ flowing across the specimen of resistance R , modulated in time according to the law

$$R = R_0(1 + k \cos[\omega t + \alpha]),$$

we can easily deduce that

$$\langle i_g(\alpha) \rangle = I_0 R_0 k \cos \alpha / 2(R_g + 2R_0), \quad (1)$$

$\langle i_g \rangle$ being the dc current flowing in the galvanometer and R_g its internal resistance. The supply current is obtained through a phase transformer, that rotates slowly with a period sensibly longer than the period of the mirror galvanometer. Therefore the light spot oscillates back and forth: its motion is registered on a rotating drum with sensitive paper.

The field effect to be measured is proportional to the ratio of the amplitude ΔG of the (periodic) variation of the specimen conductance to the amplitude $e\Delta N$ of the charge collected on its surface, e being the elemen-

³ Because of a typographical error, this figure already appeared in reference 2, Sec. 2. On the contrary the right value to be read at that place was 10^{-3} mm Hg.

⁴ G. Bonfiglioli and R. Malvano, Rev. Sci. Instr. 29, 788 (1958).

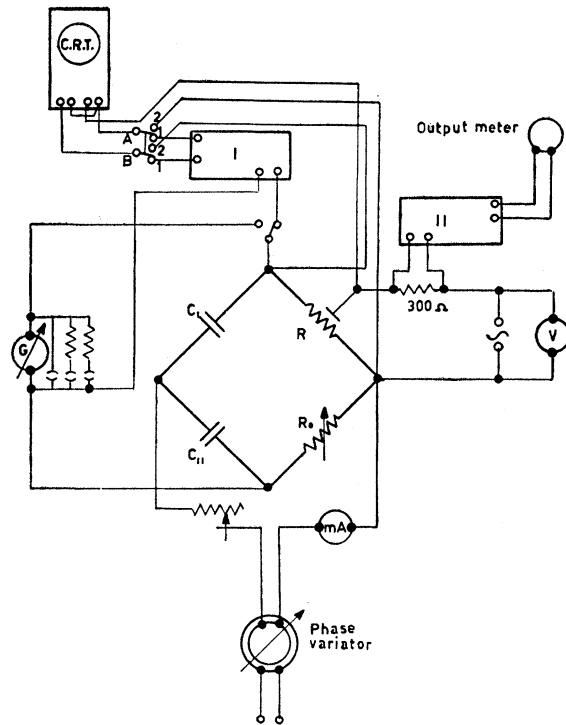


FIG. 1. Circuit used for the ac measurement of the "field effect."

tary charge and ΔN the total number of electrons induced on the surface by the applied electric field. Taking into account Eq. (1), it can easily be shown that

$$\Delta G / e\Delta N = 2 \langle \langle i_g(0) \rangle \rangle (2 + R_g/R_0) \omega / R_0 I_0 I_c, \quad (2)$$

where I_c is the amplitude of the (displacement) current through the dielectric on which the metal film is evaporated.

For reasons which will become clear in the discussion, we define as the "effective surface mobility" μ^* the left-hand side of the Eq. (2), multiplied by the square of the specimen length l ; that is,

$$\mu^* = l^2 \Delta G / e\Delta N \quad (\text{cm}^2/\text{v sec}). \quad (3)$$

Come back again to the actual experimental setup, shown schematically in Fig. 1, and note the following points:

(a) The amplifier II, followed by an output meter, is used to control the amplitude I_c of the (displacement) current. In this way one not only gets a measurement of the surface charge density induced by the modulating electric field, but also has a check that nothing has happened to the contacts or to the insulation, etc.

(b) It is a simple matter to control the sign of the effect. Since our ac measurement fails to indicate this sign directly, a cathode ray oscilloscope is used to look at the phase of the effect in the following way: by turning the switches A and B in positions (2) and (2), respectively, there appears on the screen of the cathode ray tube a pattern which indicates the difference of

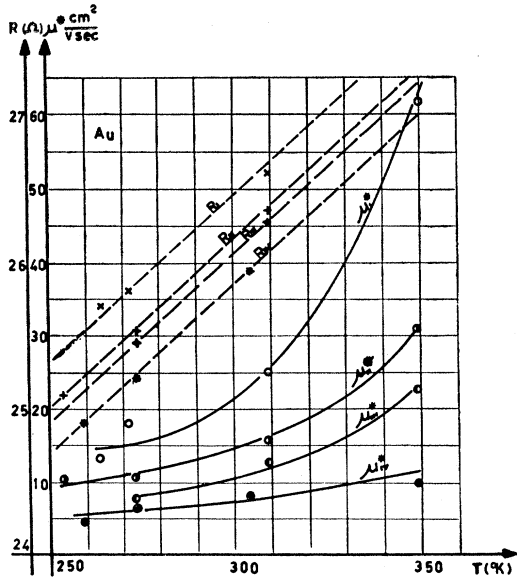


FIG. 2. μ^* vs T for a Au specimen (4 runs made after successive single days of room-temperature aging).

phase between the current which flows across the arm of the bridge where the specimen lies and the modulating electric field.

One can then stop the rotating induction phase variator to get a straight line. This means a difference of phase of 0° or 180° , according as the slope of the straight line is positive or negative. It then suffices to determine whether the galvanometer spot at that moment is at the right or at the left of its zero position, to deduce the sign of the effect. In fact (at least for 50-cycle measurements) there is no sensible phase difference between the effect and the modulating electric field.

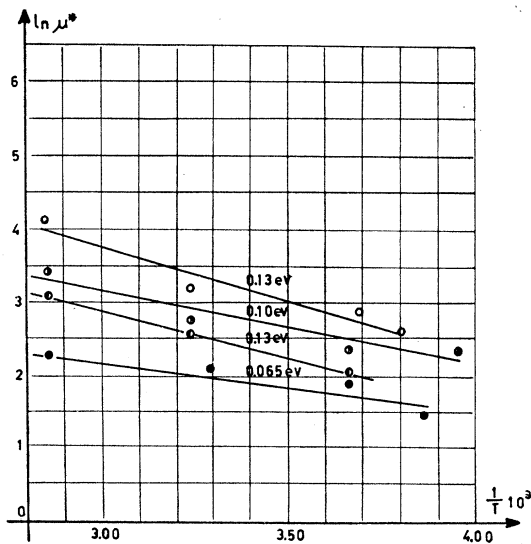


FIG. 3. $\ln \mu^*$ vs $1/T$ for the cases of Fig. 2.

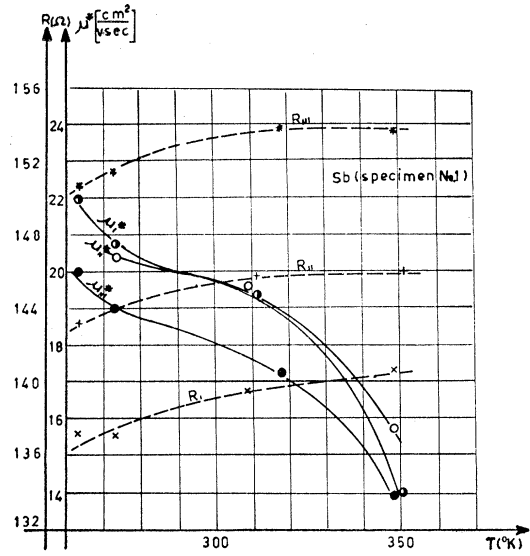


FIG. 4. μ^* vs T for Sb specimen No. 1 (three runs made after successive single days of room-temperature aging).

(3) EXPERIMENTAL RESULTS

A first point worth mentioning concerns the absence of dependence of μ^* upon the value of I_0 , which has been varied by a factor 1:3 without causing the slightest significant difference in the results.

Figures 2-7 give the experimental results obtained by plotting μ^* vs T (or, sometimes, $\ln \mu^*$ vs $1/T$) for Au, Bi, and Sb specimens prepared according to the procedure already described. Figure 8 reproduces directly a typical record. Figure 9 gives the results of some measurements performed on Bi which showed

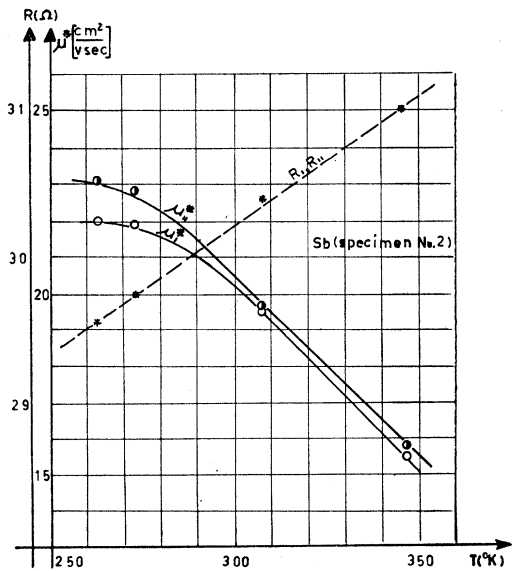


FIG. 5. μ^* vs T for Sb specimen No. 2 (two runs separated by 1-day room-temperature aging).

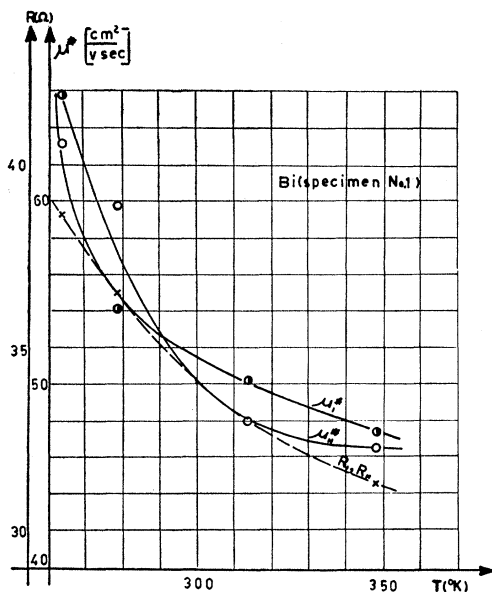


FIG. 6. μ^* vs T for Bi specimen No. 1 (two runs separated by 1-day room-temperature aging).

that, when the temperature of the specimen is changed, there is a very important delay in the establishment of the new value of μ^* belonging to the new temperature (while the value of the resistance of the specimen, on the other hand, recovers immediately as thermal equilibrium is reached).

First of all we point out that, due to the "aftereffect" just mentioned, which is more pronounced in semi-metals, all the curves $\mu^*(T)$ have been taken following the establishment of steady-state conditions. The origin of the relaxation phenomenon is presently obscure; anyway it can be observed that a behavior in

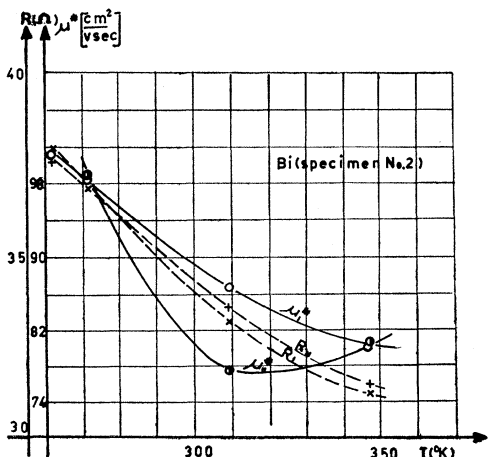


FIG. 7. μ^* vs T for Bi specimen No. 2 (two runs separated by 1-day room-temperature aging).

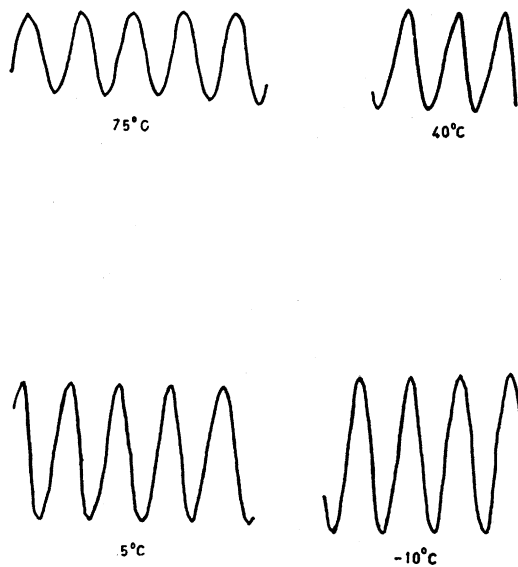


FIG. 8. The appearance of a recording of a typical run vs temperature.

some respects analogous is present also in certain semiconductors.⁵

Actually, as will be shown shortly, even our thickest (> 1000 Å) evaporated layers suffer extremely complicated "aging" effects, maybe not very strong, but still noticeable. Even though interesting in their own right, these are beyond the scope of this work, namely the study of the conductivity of a well-defined metallic surface. We think that such difficulties would be avoided if it were possible to work on thicker specimens, prepared through conventional metallurgical procedures.

Let us now list our remarks as follows:

(a) Case of Au.— μ^* is positive and increases with T . Figures 2 and 3 show the results of four successive runs (1 day apart) performed on a Au specimen, about 100 Å thick. The most striking feature of Fig. 3 is that

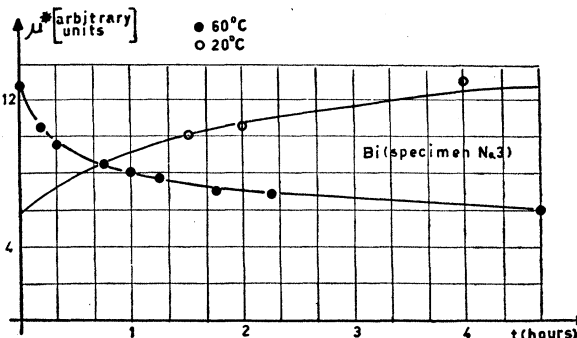


FIG. 9. The "after effect" for a Bi specimen. The black points refer to the variation of μ^* versus time after the sudden increase of temperature from 20° to 60°C. The open circles refer to the case when temperature has been lowered from 60° to 20°.

⁵ See the article by L. R. Godefroy, in *Progress in Semiconductors* (Heywood and Company, London, 1956), Vol. 1, p. 213.

$\ln\mu^*$ vs $1/T$ is a straight line; the evidence for the existence of an activation energy, which turns out to be around 0.1 eV, is clear. We remark that the spread in the values of this energy (from 0.065 to 0.13 eV) could be due either to experimental uncertainties or to a real change in the specimen surface. At present we cannot make a choice and can only conclude that the energy gap is of the mentioned order of magnitude. Actually, an aging process is noticeable through the progressive variation of the $\mu^*(T)$ curve from one run to another; besides, the $R(T)$ curves (resistance vs temperature) behave similarly.

(b) *Case of Sb.*— μ^* is negative, that is the added electrons decrease the conductivity, and its absolute value is a *decreasing* function of T . Figures 4 and 5 show the results of several runs of measurements performed on two specimens. The behavior of $\mu^*(T)$ in Sb is quite different than in Au, and weak aging phenomena are noticeable. Incidentally we observe that the sign of μ^* agrees with the sign of the Hall coefficient.

(c) *Case of Bi.*—Figures 6 and 7 show the results for Bi. μ^* is still negative. In principle, the same remarks as those made for Sb apply to this case. It is to be noted, however, that our Bi was impure, as indicated by the anomalous positive sign of the measured Hall coefficient, as well as by the negative value of the temperature coefficient of resistivity. It is very likely that traces of Pb⁶ are responsible for this behavior: actually, our Sb was of “chemical purity grade” and our Bi of “technical purity grade,” which is certainly worse than the former.

The conspicuous phenomena of aging noticeable on the pictures can perhaps be attributed to an impurity effect; in any case the general behavior of the curves agrees with those of Sb.

(4) DISCUSSION

A satisfactory interpretation of the above experimental results appears to be very difficult. A solution of the “surface problem” for a charged metal, or, what is worse, for a charged semimetal is presently lacking, even if one is interested only in the energy levels of the extra charges. When surface transport phenomena are considered, and mobilities or relaxation times are wanted, there is practically nothing available, since the approximations usually made when dealing with field effect and surface states in semiconductors are not easily applicable to the case of metals.

Consequently, for the time being, one is forced to limit himself to guessing in a reasonable way the main lines of the phenomenon. Electrostatics tells us that the extra charges must gather on an infinitely thin region near the surface—no matter whether they are electrons added to the specimen, or excess ions resulting from electron subtraction. The uncertainty principle modifies in some way the above statement, but the result holds

⁶ See, e.g., A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1953), p. 228.

that when a metal is charged (plus or minus), the density of electrons is sensibly altered only in a layer a few angstroms thick near the surface, while the interior remains practically unaffected.

It seems therefore reasonable to assume that the conductance of a metal sheet can always be considered roughly as the sum of two (or three) conductances in parallel, belonging, respectively, to the interior and to the “surface.” When the effect of the electric field is taken into account, in first approximation only the surface conductivity is altered, while the internal one is not. We write

$$G = G_0 + G_\Sigma; \quad (4)$$

$$\Delta G = G_\Sigma(\Delta N) - G_\Sigma(0). \quad (5)$$

Let us now put into G_Σ a “surface conductivity”

$$\sigma_\Sigma = en_\Sigma\mu_\Sigma, \quad (6)$$

which could be acceptable for a monovalent metal like Au, where n_Σ stands for the density of the “surface conduction electrons” (modulated by the electric field) and μ_Σ for their mobility. Considering that the experiment tells that the field effect depends on temperature as $e^{-W/kT}$, we assume that only the fraction $\Delta N e^{-W/kT}$ of the ΔN charges induced on the surface do actually conduct. This feature could be due to the existence of surface “traps” of various character, that is of “surface states” of localized type. From the above it can be shown in a straightforward way that

$$\mu^* = \mu_\Sigma e^{-W/kT}; \quad (7)$$

that is, the limiting value of our surface effective mobility for high temperature would give directly the true mobility of the surface carriers.

In considering the magnitude of μ^* , we observe that its value is greater than the value of the mobility of electrons in the Au film and even in bulk Au: 25 cm²/V sec. Such a fact could mean perhaps that surface conduction electrons belong to a group of surface states of conducting type, i.e., two-dimensional, characterized by a mobility sensibly higher than the normal conducting states of the bulk metal.

For Sb, the sign of μ^* and its temperature dependence still agree with a picture of trapped electrons which, either freed by an increment of temperature or added by the electric field, tend in both cases to reduce the surface conductivity. Anyway it must be emphasized that in Sb the electrical surface conduction, like the body conduction, should be multiband.

(5) CONCLUSIONS

The tentative picture of the phenomena which arises from the results of the above experiments is the following: surface states of localized type, that is, surface electron traps,⁷ do exist at the metal/dielectric interface. The trap depth concerned is of the order of 0.1 eV,

⁷ See J. Bardeen, *Phys. Rev.* **71**, 717 (1947).

and the density of traps is probably near to the density of metallic ions on the surface. It is very likely that absorbed monolayers of foreign impurities are responsible of this situation.

In any case the electrons freed from their traps contribute to the conduction through the existence of conductive surface states, perhaps of the type proposed by Tamm⁸ and treated in a more general way in a paper by Shockley.⁹ These can be described by Bloch functions in two dimensions, exponentially cut off along the coordinate normal to the specimen boundary. Our experimental results seem to show that the mobilities of the electrons moving in these surface states are very high.

As far as the writers know, no experimental evidence of these surface states in metals has been available.

ACKNOWLEDGMENT

The writers are glad to acknowledge the helpful discussions done on this subject with their colleague P. Brovotto.

APPENDIX. ASYMMETRY EFFECTS

In the text it has been tacitly assumed that ΔG is a linear function of ΔN . More generally, however, we ought to assume that

$$G = G_0 + \left[\left(\frac{\partial G}{\partial N} \right)_0 \Delta N + \frac{1}{2} \left(\frac{\partial^2 G}{\partial N^2} \right)_0 \Delta N^2 \right], \quad (a)$$

leaving out higher order terms that are certainly negligible if ΔN is sufficiently small. Taking into account the actual form of ΔN versus t used in our measuring set-up, $\Delta N = (CV/e) \sin \omega t$, and that the term in brackets of (a) is many orders of magnitude smaller than G_0 , we obtain in a straightforward way a relation identical to Eq. (1) of this paper, except that $\Delta G/\Delta N$ takes its limiting value $(\partial G/\partial N)_0$ calculated for the condition of a neutral metal.

In any case this type of measurement would not give any evaluation of the even coefficient of the expansion (a). Using, on the contrary, a different form of ΔN , namely

$$\Delta N = (C/e)(V_1 + V_2 \sin \omega t),$$

obtained by superimposing a dc voltage V_1 on the

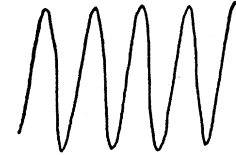
⁸ J. Tamm, Physik. Z. Sowjetunion. **1**, 733 (1932).

⁹ W. Shockley, Phys. Rev. **56**, 317 (1939).



+150 Vcc + 100 Vca

FIG. 10. The results of a measurement of $\Delta G/\Delta N$ under the combined action of a dc and an ac field. For the Bi specimen concerned, the asymmetry of the effect is clear.



-150 Vcc + 100 Vca

ordinary ac voltage V_2 , we obtain

$$(2 + R_g/R_0) \frac{\omega e}{I_0 I_c R_0} \langle i_g^+ \rangle = \left(\frac{\partial G}{\partial N} \right)_0,$$

$$(2 + R_g/R_0) \frac{\omega e^2}{I_0 I_c R_0 C V_1} \langle i_g^- \rangle = \left(\frac{\partial^2 G}{\partial N^2} \right)_0,$$

where $\langle i_g^+ \rangle$ and $\langle i_g^- \rangle$ mean the galvanometer currents corresponding to $+V_1$ and $-V_1$, respectively. This second type of measurement thus allows not only a measurement of the linear term, but also the quadratic one of Eq. (a), that is an evaluation of the *asymmetry* of the field effect *versus* the sign of the charge accumulated on the specimen surface. The experimental results are the following: in the case of a monovalent metal, as Au, the asymmetry is hardly appreciable, while in the case of Bi, the asymmetry term is very important. It is shown in Fig. 10, obtained by applying to the specimen a voltage V_1 of $+$ and -150 volts, respectively.

Two causes can be reasonably suggested as responsible for the nonlinear behavior of ΔG vs ΔN : one intrinsic to the phenomenon, the other of spurious character. The latter is probably related to a possible electrostriction effect in the dielectric support, which is quadratic in ΔN , and could well explain the small asymmetry met with in Au. The other reason belongs, probably, only to semimetals. In this case the density of the added charges is by no means much smaller than the actual density of charge carriers, which is the condition that allows termination of the expansion (a) at the linear term.