Microwave Behavior of Debye-Hückel Clouds in AgBr

GLEN EVERETT,* A. W. LAWSON,† AND GEORGE E. SMITH‡
Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois
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The real and imaginary parts of the complex dielectric constant, $\epsilon'-i\epsilon''$, have been measured at 24 kMc/sec as a function of temperature between 30° and 400°C. A maximum in ϵ' is observed near 350°C; ϵ'' increases rapidly, asymptotically approaching the value observed at lower frequencies in the intrinsic range near the melting point. These results are not explicable in terms of the currently accepted form of the Debye-Falkenhagen dispersion theory. A crude model is discussed which suggests that an alternative solution of the differential equation occurring in this theory affords an appropriate description of the observed behavior.

I. INTRODUCTION

THE electrical conductivity σ of AgBr between 175° and 350°C is determined by the Frenkel disorder.[1] Above 350°, the conductivity increases more rapidly than would be expected by an extrapolation of the behavior at lower temperatures. Attempts to explain this anomalous increase on the basis of mixed Frenkel-Schottky disorder have been abortive. Lidiard[2] has suggested an alternative explanation based on an increase in dielectric constants associated with the rapid increase of compressibility near the melting point. The dielectric measurements reported in this paper were undertaken in an effort to establish the validity of this theory.

The determination of the real part ϵ' and the imaginary part ϵ'' of the complex dielectric constant was made in the microwave frequency range for two reasons. First, it was desired to avoid complex electrode polarization effects such as those studied by Friauf.[3] Second, the relaxation time of the medium is so short at high temperatures that very high frequencies must be used in order to obtain a reasonable precision in the determination of ϵ'.

In the next section the experimental techniques are described. In the following section the values of ϵ' and ϵ'' for pure and Cd-doped AgBr are presented. In the final section a crude but suggestive model based on a theory of Reiss[4] is described which qualitatively accounts for the observed results and suggests an alternate interpretation of the Debye-Falkenhagen dispersion theory.

II. EXPERIMENTAL PROCEDURE

The single-crystal AgBr samples, either pure or doped, were placed in juxtaposition with a metallic termination of a 1.25-cm waveguide of standard dimensions as shown in Fig. 1. The sample was machined to be a slip fit into the waveguide at room temperature and subsequently annealed *in situ*. A standing wave detector was used to determine the phase and amplitude of a reflected wave with and without the sample present. These measurements suffice to determine both the real and imaginary parts of the complex dielectric constant $\epsilon'-i\epsilon''$. Let r denote the voltage standing wave ratio when the AgBr is present and Δ the shift in position of a minimum in voltage when a sample of thickness d is inserted into a shorted guide. Then,[5]

$$\tanh\gamma d/\gamma d=-i\frac{\lambda g}{2\pi d}\frac{1+ir\tan[2\pi(\Delta+d)/\lambda_g]}{r+i\tan[2\pi(\Delta+d)/\lambda_g)}, \quad (1)$$

where

$$\gamma=i(\omega/c)[\epsilon'-i\epsilon''-(\lambda/\lambda_c)]^{\frac{1}{2}}. \quad (2)$$

Here, λ_g is the guide wavelength at angular frequency ω, λ_c is the cut-off wavelength, and c is the velocity of light. From the observations of r and Δ, ϵ' and ϵ'' may be calculated with the help of published charts.[5]

In practice the silver-plated waveguide containing the sample is surrounded by a cylindrical furnace. The

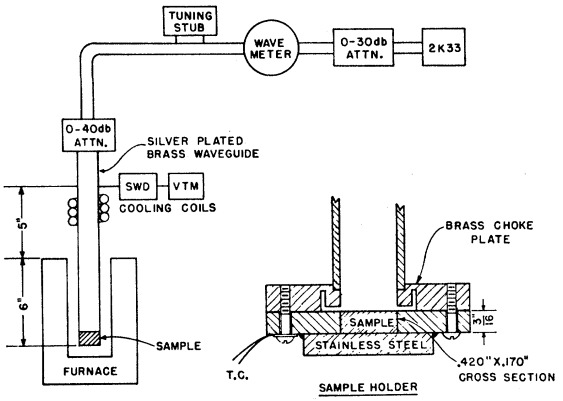

FIG. 1. Schematic diagram of microwave line used for determination of the complex dielectric constant of AgBr at 24 kMc/sec. Insert shows manner in which sample is mounted at end of shorted line.

* National Science Foundation Pre-Doctoral Fellow, 1958–1961.
† Present address: University of California, Riverside, California.
‡ Bell Telephone Pre-Doctoral Fellow, 1958–1959. Present address: Bell Telephone Laboratories, Murray Hill, New Jersey.
[1] For a review of pertinent previous work see A. B. Lidiard, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246.
[2] A. B. Lidiard, Phys. Rev. **112**, 54 (1958).
[3] R. J. Friauf, J. Chem. Phys. **22**, 1939 (1954).
[4] H. Reiss, J. Chem. Phys. **25**, 408 (1956).
[5] A. von Hippel, *Dielectric Materials and Applications* (John Wiley & Sons, Inc., New York, 1954).

phase and standing wave ratio are determined as a function of temperature in the absence of a sample; similar data are then obtained with a slab of AgBr (approximately 2 mm in length) inserted in the waveguide. This procedure permits an evaluation of Δ which is automatically corrected for thermal expansion of the waveguide. The temperature is determined by a calibrated chromel-alumel thermocouple in good thermal contact with the guide. Relative temperatures on a given run are known to within ± 1°C. Absolute temperatures are more uncertain because of the impossibility of immersing the thermocouple in the sample and the relatively large gradients caused by conduction along the waveguide. A correction is applied for the known thermal expansion of AgBr.

The frequency is determined by a transmission cavity-type wavemeter buffered from both the 2*K*33 klystron and the sample by flap attenuators. A schematic diagram of the transmission line is shown in Fig. 1. The standing wave detector was capable of measuring Δ with a reproducibility of ± 0.003 cm.

In order to stay within the range of the tables used to solve Eqs. (1) and (2) for the values of ϵ' and ϵ'' encountered in the temperature range studied, the thickness of the sample must be less than 0.075 in. With such thin samples the errors in ϵ' and ϵ'' are appreciable, becoming larger as the temperature and hence ϵ' and ϵ'', increase. Thus, at 350°C, the uncertainty in ϵ'' is 11% and the uncertainty in ϵ' is 3%. At 390°C, these uncertainties have grown to 15 and 5%, respectively.

Several resonance experiments were attempted in which the sample was mounted as a cylindrical post along the axis of a rectangular cavity. However ϵ'' is too large at high temperatures to permit measurements by this technique.

The samples were prepared from AgBr precipitated in a dilute solution of $AgNO_3$ by HBr. The precipitate was melted in a porcelain crucible and crystals were grown by retraction of a seed from the melt. Because the crystal growth was carried out in air, the AgBr contains several parts per million of oxygen as an impurity. The AgBr crystals containing $\frac{1}{2}$% $CdBr_2$ were grown by the same procedure. The crystals were annealed for at least an hour at 300°C prior to measurement.

When the sample is heated to 400°C in the waveguide, its thermal expansion exceeds that of the waveguide sufficiently so that plastic deformation occurs and the AgBr subsequently adheres to the walls of the waveguide. At high temperatures the sample anneals itself, but on cooling, progressive cold work may be introduced by thermoelastic strains which give rise to a nonequilibrium density of defects. These excess imperfections can lead to hysteresis in both ϵ' and ϵ''. Accordingly suitable care must be exercised in the thermal cycling to minimize such extraneous effects. In general our procedure was to cool the sample over a period of hours with a long rest in the neighborhood of 275°C. This procedure resulted in no detectable hysteresis.

III. RESULTS

Over the course of a year, a large number of samples were studied under a variety of different experimental conditions. The length of the sample was varied until an optimum precision was obtained and the cycling was varied to minimize the hysteresis. The boundary conditions at the surface of the AgBr were varied by changing the material in contact with the sample. In particular, experiments were conducted in which the AgBr was (a) in direct physical contact with a silver-plated waveguide, (b) in direct physical contact with a stainless-steel waveguide, and (c) insulated from the stainless steel by mica spacers.

In all these experiments, the results were substantially the same and in the interests of brevity we present here in graphical form only data on two samples, one pure AgBr and the other AgBr doped with $\frac{1}{2}$% $CdBr_2$. The values of ϵ' and ϵ'' as a function of temperature are shown in Fig. 2 and Fig. 3, respectively.

The most remarkable feature of these data is the maximum in the value of ϵ' which occurs in both the pure and doped AgBr at about 375°C. The behavior of ϵ'' is more normal, reflecting in a general way the course of the conductivity observed in the kilocycle frequency range.

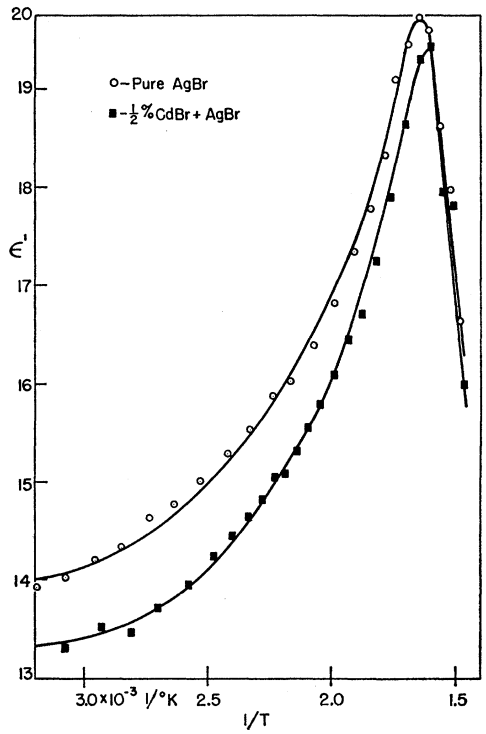

FIG. 2. The real part ϵ' of the complex dielectric constant of pure and doped AgBr.

The value of ϵ' for pure AgBr at low temperatures agrees with a previous determination[6] to within experimental error. The values of ϵ'' at low temperatures are structure sensitive and probably reflect the presence of both impurities and strain. In the intermediate-temperature range, where the value of ϵ'' for the doped sample is appreciably larger than that for the pure sample, the former should be controlled by the excess vacancies introduced by the Cd^{++} impurities. The slope of the $\ln\epsilon''$ versus $1/T$ plot in this range is 6.9 kcal/mole in reasonable agreement with the value of 8.3 kcal/mole reported by Teltow.[7]

In the high-temperature range, where the values of ϵ'' for the pure and doped samples coalesce, we expect the loss to be controlled by the intrinsic conductivity

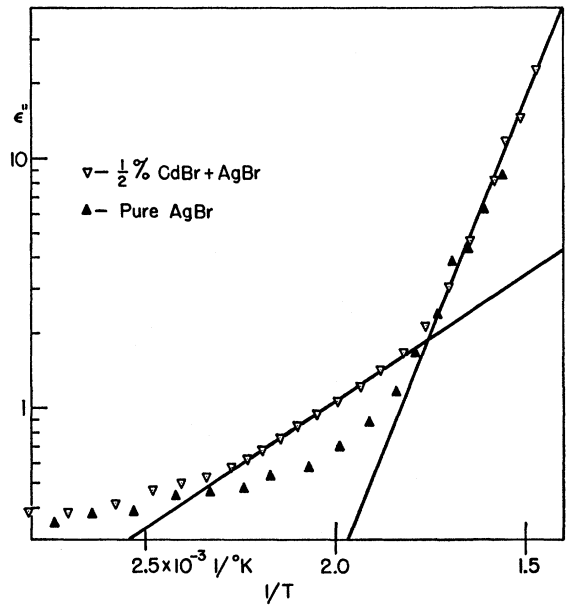

FIG. 3. The imaginary part ϵ'' of the complex dielectric constant of pure and doped AgBr.

of AgBr. The microwave conductivity σ may be calculated from ϵ'' by the relation

$$\sigma = \epsilon''\omega/4\pi. \tag{3}$$

The values of σ so calculated are exhibited in Fig. 4 where they are compared with the low-frequency conductivity data of Teltow.[7] The high-frequency data merge asymptotically with the low-frequency data extrapolated to high temperatures. The actual data at low frequencies appear to be somewhat higher than this extrapolated value. Whether this discrepancy is real or arises from a systematic error is uncertain. It may be that the process, which gives rise to the anomalous breakaway from a strictly exponential dependence of σ

[6] A. Eucken and A. Buchner, Z. physik. Chem. **B27**, 321 (1934).
[7] J. Teltow, Ann. Phys. **5**, 63 (1949).

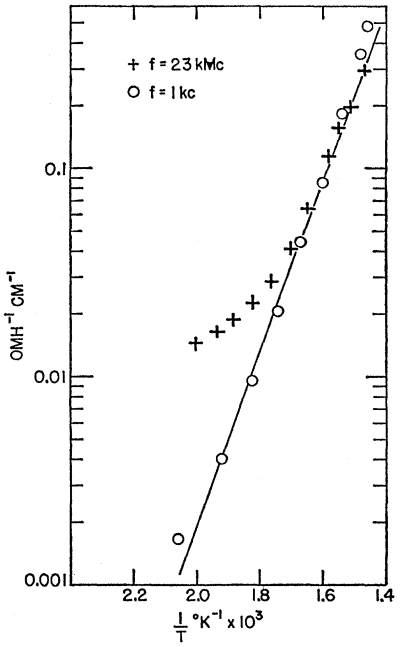

FIG. 4. The conductance of AgBr at 24 kMc/sec and 1 kc/sec.

on $1/T$ at low frequencies, is frozen out at high frequencies.

At low temperatures the microwave conductivity is substantially higher than the low-frequency conductivity. A large part of this discrepancy must be ascribed to a nonequilibrium distribution of defects introduced by the unavoidable thermoelastic strains associated with our technique. As suggested in the next section however, part of the discrepancy may have some theoretical foundation.

IV. DISCUSSION

The title of this paper implies that the authors believe that the phenomena described in the preceding sections are associated with the statistical behavior of swarms of charged imperfections. Unfortunately we have been unable to muster sufficient sophistication to give an adequate theoretical treatment of this complicated and delicate problem. In this section we shall present the reasons for eliminating various other possible explanations and discuss the data in terms of simple models and modifications of existing theories.

The principal feature to be understood is the peak in the real part of the dielectric constant ϵ'. This maximum is more reminiscent of a resonant behavior than a relaxation mechanism and led the authors to consider a variety of processes of the former type. The first possibility which springs to mind is a plasma resonance. Such a resonance is not possible for the ionic charge carriers because each diffusive jump involves a motion of only one lattice spacing and consequently, it is impossible to describe their motion by the usual equation of motion involving an acceleration term such

as for electrons or holes which have a definable mean free path. Nor can the maximum in ϵ' be ascribed to these light carriers. It is easy to show from the known temperature dependence of the electronic mobility[8] in conjunction with the effect of Br_2 vapor pressure[9] on the conductivity that these carriers are not present in sufficient quantity to give a resonant frequency in the microwave region at any temperature below the melting point. This contention is further supported by a direct calculation of the density from the known optical band gap[10] on the assumption of an effective mass approximately equal to that of a free electron.

Another possibility is that the reststrahling frequency is shifted into the microwave region by the anomalously large increase in the compressibility[11] of AgBr with increasing temperature. Generous estimates of this effect, however, indicate that the lattice dispersion would always correspond to a wavelength of less than 1 mm, i.e., approximately a factor of ten higher in frequency than that employed in these experiments.

We turn now to a consideration of Debye-Hückel[12] effects on the conductivity. The reactance and conductance of electrolytic solutions as a function of frequency have been calculated by Debye and Falkenhagen.[13] According to this theory the conductivity is *decreased* by an amount $\Delta\sigma(\omega)$ below its value σ_∞ at infinite frequency given by

$$\Delta\sigma(\omega)=-\frac{e^2\kappa}{3\epsilon_L kT}x_1(\omega\tau), \tag{4}$$

where κ is the reciprocal of a Debye length, ϵ_L is the lattice dielectric constant of the medium in absence of imperfections, τ is the relaxation time, k the Boltzmann constant, T the absolute temperature, and x_1 is an intrinsically positive function given by

$$x_1=\mathrm{Re}\left(\frac{q}{1+[q(1+i\omega\tau)]^{\frac{1}{2}}}\right). \tag{5}$$

Here q is a number between 0 and $+1$ determined by the mobilities of the positive and negative ions. For equal mobilities (approximately true for AgBr at high temperatures), $q=\frac{1}{2}$. For $\omega\tau\to\infty$, $\Delta\sigma(\omega)\to 0$; for $\omega\tau\to 0$, $\Delta\sigma$ approaches the dc value originally calculated by Onsager.[14]

Corresponding to the decrease in conductivity, there is an *increase* $\Delta\epsilon'$ in the dielectric constant given by

$$\Delta\epsilon'=\frac{4\pi\sigma_\infty}{\omega}\frac{e^2\kappa}{3\epsilon_L kT}x_2, \tag{6}$$

where x_2 is the imaginary part of the function in square brackets in Eq. (5). Because $\omega\tau\to 0$ at high temperatures, we should expect an increase in ϵ' rather than the observed decrease. Physically, this increase in ϵ' arises from warping of the Debye-Hückel clouds leading to their polarization along the direction of the applied field.

The apparent failure of the Debye-Falkenhagen dispersion theory led us to consider the following crude model.

Our starting point is a calculation by Reiss[4] which shows that for the case of divergenceless current flow the mobility μ of the charge carriers vanishes at the center of a Debye-Hückel cloud and reaches normal values at a radial distance from the center r_0 given by

$$r_0=e^2/(\epsilon_L kT). \tag{7}$$

Reiss accordingly suggests that a simple model might be constructed by assuming $\mu=0$ for $r<\frac{1}{2}r_0$ and μ normal for $r>\frac{1}{2}r_0$. We therefore are invited to suppose that, when n pairs of Frenkel defects are present in AgBr, it behaves like a mixture of inherent conductivity $\sigma_2=\sigma_2'+i\sigma_2''$ in which $2n$ spheres of radius $r_0/2$ and conductivity $\sigma_1=i\sigma_2''$ are imbedded.

If x is the volume fraction of the mixture occupied by the nonconducting spheres, then we may find the effective conductivity $\sigma_E=\sigma_E'+i\sigma_E''$ of the mixture by use of the formula[15]

$$x\left(\frac{\sigma_E-\sigma_1}{\sigma_1+2\sigma_E}\right)+(1-x)\left(\frac{\sigma_E-\sigma_2}{\sigma_2+2\sigma_E}\right)=0, \tag{8}$$

where $x=\pi nr_0^3/3$.

If we set $y=\sigma_E/\sigma_2$ and $a=\sigma_1/\sigma_2$, then the roots of the quadratic equation

$$2y^2+y(a-2+3x-3ax)-a=0, \tag{9}$$

where in our case

$$a=i\sigma_2''/(\sigma_2'+i\sigma_2'')=i\omega\tau/(1+i\omega\tau) \tag{10}$$

determine the value of σ_E in terms of σ_2 and the relaxation time τ of medium in absence of Debye-Hückel effects. The roots of Eq. (9) are

$$y=\{(2-3x+i\omega\tau)\pm[(2-3x+i\omega\tau)^2+8i\omega\tau(1+i\omega\tau)]^{\frac{1}{2}}\}\times[4(1+i\omega\tau)]^{-1}. \tag{11}$$

In the limit of $\omega\tau=0$, we have

$$\sigma_E=\sigma_2(1-\tfrac{3}{2}x), \tag{12}$$

while when $\omega\tau=\infty$, or when $x=0$,

$$\sigma_E=\sigma_2. \tag{13}$$

[8] C. Allemand and J. Rossel, Helv. Phys. Acta **27**, 212 and 529 (1954).
[9] L. M. Shamovskii, A. A. Dunina, and M. A. Gosteve, Soviet Phys. JETP **3**, 511 (1956–7); Luckey and West, J. Chem. Phys. **24**, 879 (1956).
[10] F. Moser and F. Urbach, Phys. Rev. **102**, 1519 (1956); R. Matejec, Z. Physik **147**, 593 (1957).
[11] D. S. Tannhauser, L. J. Bruner, and A. W. Lawson, Phys. Rev. **102**, 1276 (1956).
[12] P. Debye and E. Hückel, Physik. Z. **24**, 185, 305 (1923).
[13] P. Debye and H. Falkenhagen, Physik. Z. **29**, 401 (1928).
[14] L. Onsager, Physik. Z. **28**, 277 (1927).
[15] R. Landauer, J. Appl. Phys. **23**, 779 (1952).

A semiquantitative picture of the behavior of the dielectric constant and conductance as a function of temperature may be constructed from Eqs. (12) and (13) without a laborious point-by-point solution of Eq. (11).

The conductance measured in the kc frequency range is governed by Eq. (12) over the entire temperature range since $\omega\tau$ is always much less than unity. The high-frequency conductance is governed by Eq. (12) at high temperautures where $\omega\tau \ll 1$ and by Eq. (13) at low temperatures where $\omega\tau \gg 1$. Thus, the low-frequency conductance should be everywhere less than the high-frequency conductance except at very high temperatures where they should become equal. This is the observed behavior shown in Fig. 4. The difference between the two curves is much too large to be accounted for by reasonable values of x and must be primarily due to a nonequilibrium density of defects as remarked earlier.

The dielectric constant (ϵ') must be expected to rise in a perfectly normal way at low temperatures but when $\omega\tau \sim 1$, it must start to decrease so that at high temperatures Eq. (12) will be satisfied. The amount of the decrease to be expected may be estimated by calculating x from $x=\pi r_0^3 n/3$. Putting $T=700°\text{K}$, we find $x \sim k/3$ where k is the percentage concentration of defect pairs. In silver bromide at its melting point, $k \sim 1\%$, so $x \sim \frac{1}{3}$ and the observed effective dielectric constant is only about $\frac{1}{2}$ the intrinsic lattice value. Thus ϵ_L, the inherent lattice dielectric constant, would be about 30 near the melting point, which is in reasonable agreement with the value obtained by extrapolating the low-temperature behavior of ϵ'. The turnover should begin before $\omega\tau \sim 1$. From our measurements of ϵ' and ϵ'', $\tan\delta = 1$ at $1/T = 1.2\times 10^{-3}$ °K^{-1} and the maximum in ϵ' is at $1/T = 1.65\times 10^{-3}$ °K^{-1}.

Physically, the model leads to a decrease in ϵ' at high temperatures because the current flow must avoid the nonconducting cores of the Debye-Hückel clouds leading to a pile-up of charge at the interface which is equivalent to a dipole opposing the applied field. At lower temperatures, where the frequency is much greater than τ^{-1}, the charge pile-up does not have a chance to take place and the depolarization effect becomes negligible.

Despite the qualitative success of this crude model, it fails notably in one respect, namely, the prediction of a linear dependence in the decrease in conductivity on concentration rather than the well-established square-root dependence observed in electrolytic solutions. This deficiency led us to re-examine the Debye-Falkenhagen theory.

The results of the theory embodied in Eqs. (4) and (6) are obtained by solving the differential equation

$$\nabla^2(\nabla^2\psi - K^2\psi) = -\frac{e^2}{\epsilon_L kT} q\kappa^2 \frac{\partial}{\partial r}\frac{e^{-\kappa r}}{r} E e^{i\omega t}\cos\theta, \quad (14)$$

for the additional potential ψ at a central ion arising from the deformation of a cloud by the applied field E. The quantity K is given by

$$K^2 = q\kappa^2(1+i\omega\tau). \quad (15)$$

Debye and Falkenhagen assume a solution of the form

$$\psi = \left[\frac{-qEe^2}{\epsilon_L kT(\kappa^2-K^2)}\frac{\mathrm{d}}{dr}\left(\frac{e^{-\kappa r}}{r}\right) + A'\frac{d}{dr}\left(\frac{e^{-Kr}}{r}\right) + \frac{B'}{r^2}\right] e^{i\omega t}\cos\theta, \quad (16)$$

in which terms of the type $r^2\cos\theta$ and $(d/dr)(e^{+Kr}/r)$ have been rejected to avoid infinities at large values of r and the positive root of Eq. (15) is used. The requirement of a finite value for ψ at $r=0$ is met by expanding the exponentials and requiring the coefficients of $1/r^2$, etc., to vanish. This leads to

$$\psi = \frac{e^2 q\kappa^2}{3(\kappa+K)}\frac{Ee^{i\omega t} r\cos\theta}{\epsilon_L kT}. \quad (17)$$

It should be pointed out, however, that an equally good solution may be obtained by retaining terms of the type $(d/dr)(e^{+Kr}/r)$ and using the negative root of Eq. (15). Equation (17) is again obtained, but with the understanding that the negative root for K must be employed.

One now obtains

$$\Delta\sigma(\omega) = -\frac{\sigma_\infty e^2\kappa}{3\epsilon_L kT}\,\mathrm{Re}(y), \quad (18)$$

and

$$\Delta\epsilon = \frac{4\pi\sigma_\infty}{\omega}\frac{e^2\kappa}{3\epsilon_L kT}\,\mathrm{Im}(y), \quad (19)$$

where

$$y = q/\{1-[q(1+i\omega\tau)]^{\frac{1}{2}}\}, \quad (20)$$

for $\omega\tau \to \infty$, $\Delta\sigma(\omega\tau) \to 0$, and $\Delta\epsilon(\omega\tau) \to 0$. For $\omega\tau \to 0$, we have (for $q=\frac{1}{2}$)

$$\Delta\sigma(0) = -\frac{\sigma_\infty e^2\kappa}{3\epsilon_L kT}\frac{2+\sqrt{2}}{2} \quad (21)$$

and

$$\Delta\epsilon(0) = -\frac{\sqrt{2}}{12}\frac{\kappa e^2}{kT}. \quad (22)$$

It is clear that *both* the conductance and the dielectric constant are decreased in this case. If we use the same numbers as above to estimate the deficiency in ϵ' at 400°C, we find $\Delta\epsilon' = -7$. Adding this number to the experimentally determined value of 16 yields a value of $\epsilon_L = 23$ which is approximately the value to which the curve of ϵ' versus T would extrapolate.

It is our belief that the solution to Eq. (18) with y given by Eq. (20) is the appropriate solution to Eq. (14),

corresponding physically to a longer relaxation time within the Debye-Hückel cloud than in the medium.

In conclusion, it should be remarked that no effort has been made to take account of interactions between neighboring clouds, undoubtedly an appreciable factor at high temperatures where the density of imperfections is large.

In retrospect, the suggestion of Lidiard[2] that Debye-Hückel effects must also play an important role in affecting the activation energies (particularly at high temperatures where the dielectric constant of the medium is increasing so rapidly) seems eminently reasonable.

Clearly, although the models discussed earlier seem plausible, more experiments, particularly as a function of frequency, are needed to establish their validity.

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Electronic Processes and Excess Currents in Gold-Doped Narrow Silicon Junctions

C. T. SAH
Research and Development Department, Fairchild Semiconductor Corporation, Palo Alto, California
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Large amounts of excess current in gold-doped silicon tunnel junctions are observed and interpreted as due to transition processes with the two gold energy levels in the forbidden gap of silicon as intermediate states. Eight of the ten possible processes are two-step processes. These two steps may be both of the Hall-Shockley-Read type or of the type involving electron tunneling between a trap state and a band state within the space charge region of the junction. The two steps may also consist of a Hall-Shockley-Read process as one step, and the tunneling from or to the trap state as the other step. One of the remaining two possible processes is a three-step process involving two Hall-Shockley-Read steps and one tunneling step between two trap states within the space-charge region. The last process is the usual carrier injection process. Eight of the ten processes in the gold-doped tunnel diodes have appreciable transition rates. Five of the eight processes have onset structures which appear at voltages in reasonable agreement with the predicted values. Approximate theoretical current-voltage expressions are compared with experimental data of the gold-induced excess current at 4.2°K, giving an average value of $W^2m_\perp/m=1.2\times10^{-23}$ volt^2-cm^3, where W is Price's matrix element of the trap potential energy in excess of the crystal potential taken between the unnormalized trap-state wave function and the band edge Bloch wave function, normalized to unit volume, and $m_\perp/m$ is the transverse electron mass normalized to the free electron mass. It is also experimentally determined that the rate of tunneling from or to trap state is smaller than the rate of filling or emptying the trap in the Hall-Shockley-Read process.

I. INTRODUCTION

SINCE the discovery of the tunneling phenomenon in very narrow germanium p-n junctions by Esaki,[1] there have been many fundamental experiments designed to explore the detailed characteristics of the Esaki, or tunnel current. The negative resistance observed at the low forward bias voltage region (forward bias voltage means positive on the p-type side) between approximately 0.1 to 0.4 v, have been established by Esaki as due to the decrease of the density of states common to the two bands on the opposite side of the p-n junction.[1] In this model, the constant energy electronic transition would cease when the applied forward voltage is high enough so that the conduction and the valence band edges are uncrossed if sharp band edges can be defined. The turn-off voltage, of the order of 0.4 v, is generally so low that the diffusion current would not be important. Consequently, one would expect a region of nearly zero current flow under the forward bias condition between about 0.4 v to a voltage approximately equal to the energy gap of the material. However, the region of nearly zero current has not been observed experimentally for all known tunnel diode materials. In some semiconductors, such as silicon, the excess current is rather high with a magnitude of the order of 1/4 times the peak current, while in other materials such as germanium and gallium arsenide, the excess current may be as low as 1/10 to 1/100 times the peak current. The excess current and some associated structures have been noted by Esaki[2–4] who attributed the observations to band-to-band transition via deep impurity states in the energy gap. The first direct evidence of the excess current induced by deep impurity states was observed by Longo,[5] who created a sufficient amount of deep traps by subjecting germanium tunnel

[1] L. Esaki, Phys. Rev. **109**, 603 (1958).

[2] T. Yajima and L. Esaki, J. Phys. Soc. Japan **13**, 1281 (1958).
[3] L. Esaki, *Solid-State Physics in Electronics and Telecommunications* (Academic Press, Inc., New York, 1960), Vol. 1, pp. 514–523.
[4] L. Esaki and Y. Miyahara, Solid State Electronics **1**, 13 (1960).
[5] T. A. Longo, Bull. Am. Phys. Soc. **5**, 160 (1960).