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Effect of Shallow Trapping and the Thermal-Equilibrium Recombination Center Occupancy on Double-Injection Currents in Insulators

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Further understanding of the double-injection (DI) mechanism of current flow in insulators has been obtained from a theoretical treatment, largely based on a theory by Lampert, which allows an arbitrary thermal-equilibrium occupancy of the recombination centers and also shallow trapping of both carriers. The major new results are: (1) The existence of a negative-resistance region in the DI current-voltage characteristic is a consequence of difficulty in neutralizing the space charge due to one carrier type by transport of the other, i.e., of unequal lifetimes in the absence of trapping. (2) The threshold voltage for DI current flow with space-charge neutrality is infinite if the centers are not completely filled in the absence of injected carriers. The low-level regions of the characteristics for initially completely filled or initially partly filled centers are very different. (3) The relative "effectiveness" of hole and electron traps in storing carriers is an important factor because of the space charge which can be stored in them and which has to be neutralized by carriers of the other type.

1. INTRODUCTION

BECAUSE of the very low thermally generated carrier densities in insulating solids, the mechanism of current flow by the simultaneous injection of both holes and electrons is important in such materials. Injection of the two carriers into the crystal bulk allows a relatively high density of carriers to be attained for conduction purposes.

Parmenter and Ruppel,[1] Lampert,[2] and Lampert and Rose[3] have carried out theoretical studies of drift-controlled double-injection currents in the case in which holes and electrons have the same lifetime. Lampert[4] has considered the case of an insulator with recombination centers, so that the hole and electron lifetimes may be different. This treatment neglected the existence of any space charge and made the assumption that the centers are completely filled in the absence of injected carriers, i.e., at thermal equilibrium. It was concluded that, (a) there was a finite nonzero threshold voltage for double-injection (DI) current flow, (b) if the capture cross section of the centers for holes was very much greater than their cross section for electrons, there was a negative-resistance region in the DI current-voltage characteristic and, (c) at higher currents the characteristic becomes similar to that in an n-type semiconductor, considered by Lampert and Rose.[3]

A previous article[5] reported an analysis based on the theory of Lampert,[4] which considered the more general case of centers partly filled at thermal equilibrium. This treatment showed that when the density of holes in the recombination centers at thermal equilibrium is nonzero, the voltage threshold for DI current flow with space-charge neutrality becomes infinite. It was also reported that this analysis demonstrated that the existence of the negative-resistance region depends on unequal carrier lifetimes rather than on unequal carrier capture cross sections of the centers.

It is proposed to report in this article the analysis for the more general case of centers partly filled in the absence of injected carriers. The effect of shallow hole and electron traps will also be considered.

2. THE BASIC PHYSICS OF DOUBLE-INJECTION IN INSULATORS WITHOUT TRAPPING

The low thermal-equilibrium carrier densities in insulators result in conductivities which are very low without carrier injection. Because of the long dielectric relaxation time associated with the low conductivity, local space charge may exist in the insulator bulk. Thus majority carriers may be injected into the solid to increase the free majority carrier density and thereby increase the conductivity. However, there is a limit to the net space charge injected at a given voltage. This is given roughly by the expression $Q=CV$, where C is the capacitance and V the voltage, so that the current is limited. If, however, both electrons and holes can be injected and transported easily across the crystal, then both free-carrier densities can be increased markedly despite the limit on Q. Thus, assuming no limitation on carrier injection from the electrodes, any limitation on the DI current is due to difficulty in transporting one or more of the carriers across the crystal, due to recombination. For example, if the hole lifetime is very much shorter than the electron lifetime, then the limitation arises because very few holes can be transported across the recombination "barrier" in the bulk to maintain quasineutrality at the electron-injecting contact.

However, once a hole current begins to flow, the hole density in the centers increases because of the shorter lifetime. Thus, the hole lifetime increases. This allows an increased flow of holes and a further increase in life-

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[2] M. A. Lampert, RCA Rev. **20**, 682 (1959).

[3] M. A. Lampert and A. Rose, Phys. Rev. **121**, 26 (1961).

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time, and so on, which gives rise to the negative resistance region reported by Lampert.[4] The negative-resistance region continues until the two carrier lifetimes become equal when further increase in the hole lifetime becomes impossible. At currents above this, the limitation on the DI current is due to the presence of the same recombination "barrier" to both carriers and, since the lifetimes are equal, the characteristic is similar to the characteristic obtained by Lampert and Rose[3] with the assumption of equal lifetimes. It is to be noted that analogous behavior is to be expected if the low-level electron lifetime is very much shorter than the low-level hole lifetime.

3. THEORY

The model on which this work is based is a somewhat generalized form of that used by Lampert.[4] It is assumed that only one set of recombination centers exists in the insulator and that its occupancy under DI conditions is determined entirely by recombination kinetics. The Fermi occupation probability for the centers at thermal equilibrium, F_R, has the range $0 \leqslant F_R \leqslant 1$; the case $F_R = 1$ has already been considered.[4] Recombination by interband transitions is assumed to be negligible. The model includes shallow electron and hole traps which are always more than a few kT away from the quasi-Fermi levels. The other assumptions made in Sec. II of the article by Lampert[4] are also made here: (1) charge neutrality everywhere, (2) volume-controlled current flow, (3) negligible diffusion currents, (4) field-independent mobility, (5) negligible thermal free-carrier densities. The comments on these assumptions made by Lampert[4] will not be enlarged upon here although the effect of assumption (1) on the characteristics will be discussed below.

The recombination kinetics for the present model are identical with those for the model used by Lampert:

$$r = p\langle v\sigma_p\rangle n_R = n\langle v\sigma_n\rangle p_R\,,$$
$$n_R + p_R = N_R\,. \tag{1}$$

Here, r is the recombination rate density, $\langle v\sigma_n\rangle$ and $\langle v\sigma_p\rangle$, are the suitably averaged products of thermal velocity and capture cross section of the centers for electrons and holes, respectively; n_R and p_R are the electron and hole densities in the centers, N_R is the density of centers and n, p are the densities of injected free carriers.

From (1)

$$p_R = N_R/(\beta u + 1)\,,$$

where

$$u = n/p \quad \text{and} \quad \beta = \langle v\sigma_n\rangle / \langle v\sigma_p\rangle\,. \tag{2}$$

It is now necessary to write down a suitable neutrality equation. The density of injected electrons trapped in the shallow states close to, and in equilibrium with, the conduction band may be written as $n\cdot\eta_n$ where

$$\eta_n = \sum_i \frac{N_{ti}}{N_c} \exp(E_i/kT)$$

and N_{ti} and E_i are the density and ionization energy of the ith set of such traps and N_c is the density of states in the conduction band. The summation is over all sets of such traps. Similarly, the density of injected holes trapped in states close to, and in equilibrium with, the valence band may be written as $p\cdot\eta_p$, where

$$\eta_p = \sum_i \frac{N_{tj}}{N_v} \exp\left(\frac{E_j}{kT}\right)$$

and N_{t_j} and E_j are the density and hole ionization energy of the jth set of such traps and N_v is the density of states in the valence band. Thus, our neutrality is written as:

$$n(1+\eta_n) - p(1+\eta_p) + p_{R0} - p_R = 0\,, \tag{3}$$

where p_{R0} is the hole density in the centers in the absence of injected carriers (i.e., at thermal equilibrium). This is to be compared with Lampert's neutrality equation:

$$n - p - p_R = 0\,,$$

where the centers are completely filled at thermal equilibrium (i.e., $p_{R0} = 0$) and there are no traps ($\eta_n = \eta_p = 0$). Substituting (2) in (3)

$$p = \frac{N_R - p_{R0}(\beta u + 1)}{(u-\eta)(\beta u + 1)(1+\eta_n)}\,; \quad \eta = \frac{1+\eta_p}{1+\eta_n}$$
$$= \frac{\beta N_R(1-F_R)}{(1+\eta_n)} \cdot \frac{\gamma - u}{(u-\eta)(\beta u + 1)}\,, \tag{4}$$

if $\gamma = (N_R - p_{R0})/\beta p_{R0} = \tau_{n0}/\tau_{p0}$, where τ_{n0}, τ_{p0} are the low-injection-level values of the carrier lifetimes, defined as $1/\tau_n = \langle v\sigma_n\rangle p_R$ and $1/\tau_p = \langle v\sigma_p\rangle n_R$. F_R is, of course, given by $n_{R0}/N_R = 1 - (p_{R0}/N_R)$. From (4)

$$n = up = \frac{\beta N_R(1-F_R)}{(1+\eta_n)} \cdot \frac{u(\gamma - u)}{(u-\eta)(\beta u + 1)}\,. \tag{5}$$

Now the physical conditions of the problem require that the range of u be $0 \leqslant u \leqslant +\infty$. In this range there are two domains:

(I) $\tau_{n0}/\tau_{p0} > \eta$, i.e., $\gamma > \eta$. This is the domain in which the limitation on the DI current at low currents is due to difficulty in transporting enough holes across the crystal (against recombination) to neutralize electrons. We have $\eta \leqslant u \leqslant \tau_{n0}/\tau_{p0}$ so that p, given by (4), remains positive.

(II) $\tau_{n0}/\tau_{p0} < \eta$, i.e., $\gamma < \eta$. This is the domain in which the DI limitation is due to an electron lifetime which is too short, the opposite case to (I). We have $\gamma \leqslant u \leqslant \eta$ to maintain p, and n, positive.

We continue the analysis working closely with the formal theory of Appendix A of Lampert[4] to facilitate comparison.

Now $J=e\mathcal{E}(n\mu_n+p\mu_p)$ if J is the current density, $\mathcal{E}$ is the electric field strength and μ_n, μ_p are the carrier mobilities.

Thus, using (4) and (5),

$$\mathcal{E}=(J/e\mu_n\alpha N_R)h(u)$$

where

$$h(u)=\frac{\alpha(1+\eta_n)}{\beta(1-F_R)}\cdot\frac{(u-\eta)(\beta u+1)}{(u+\alpha)(\gamma-u)}. \tag{6}$$

α is the mobility ratio μ_p/μ_n.

From the particle conservation equations,

$$\mu_p(d/dx)(p\mathcal{E})=r=-\mu_n(d/dx)(n\mathcal{E}),$$

we have $(d/dx)[(p-n)\mathcal{E}]=(1+\alpha)r/\mu_p$, where x is the spatial variable along the direction normal to the electrodes, with $x=0$ at the cathode and $x=L$ at the anode.

Hence, substituting for p, n, r, p_R from Eqs. (1), (2), (4), and (5).

$$J(du/dx)=-[\alpha e N_R^2\langle v\sigma_n\rangle/f(u)],$$

$$f(u)=\frac{\alpha^2(1+\eta_n)}{\beta(1-F_R)}\cdot\frac{(u-\eta)(\beta u+1)^2}{u(u+\alpha)^2(\gamma-u)}. \tag{7}$$

We now examine the boundary conditions appropriate to the present problem. As was pointed out by Lampert,[4] we expect the field to be a minimum at the contact which injects the "difficult" carrier. Thus, for case (I), we impose the boundary condition $\mathcal{E}=0$ at $x=L$, the anode, in agreement with Lampert. However, for case (II), we must take the opposite condition, $\mathcal{E}=0$ at $x=0$, the cathode. The condition $\mathcal{E}=0$ corresponds to $u=\eta$, from Eq. (6). Using these boundary conditions, we have, from (7),

$$\mathcal{J}_1=J_1/J'=\frac{1}{F_1(u_0)},\quad F_1(u_0)=\int_\eta^{u_0}f(u)du, \tag{8a}$$

$$(\eta\leqslant u_0\leqslant\tau_{n0}/\tau_{p0})$$

$$\mathcal{J}_2=J_2/J'=\frac{1}{F_2(u_L)},\quad F_2(u_L)=\int_{u_L}^{\eta}f(u)du, \tag{8b}$$

$$(\tau_{n0}/\tau_{p0}\leqslant u_L\leqslant\eta).$$

Here, the subscripts 1, 2 refer to cases (I), (II) above, respectively, $J'=\alpha e N_R^2\langle v\sigma_n\rangle L$ and the $\mathcal{J}$'s are dimensionless currents. u_0 and u_L are the values of u at $x=0$, $x=L$, respectively.

From (6) and (7),

$$\mathcal{V}_1=V_1/V'=\mathcal{J}_1^2G_1(u_0),\quad G(u_0)=\int_\eta^{u_0}f(u)h(u)du, \tag{9a}$$

$$\mathcal{V}_2=V_2/V'=\mathcal{J}_2^2G_2(u_L),\quad G(u_L)=\int_{u_L}^{\eta}f(u)h(u)du. \tag{9b}$$

Here, V_1, V_2 are the relevant potential differences across the crystal, $V'=L^2N_R\langle v\sigma_n\rangle/\mu_n$ and the $\mathcal{V}$'s are dimensionless voltages.

4. LOW CURRENT BEHAVIOR OF THE CURRENT-VOLTAGE CHARACTERISTIC

We now examine the behavior of $\mathcal{V}$ as $\mathcal{J}$ tends to zero. The condition $\mathcal{J}=0$ corresponds to poles in $F_1(u_0)$ and $F_2(u_L)$ at u_0, $u_L=\tau_{n0}/\tau_{p0}$. Thus, $\mathcal{J}$ tends to zero as u' tends to $\gamma=\tau_{n0}/\tau_{p0}$, where u' is either u_0 or u_L. Expanding $f(u)$ and $f(u)h(u)$ as partial fractions, we have

$$f(u)=\frac{A_1}{u}+\frac{B_1}{u+\alpha}+\frac{C_1}{(u+\alpha)^2}+\frac{D_1}{(\gamma-u)},$$

$$f(u)h(u)=\frac{A_2}{u}+\frac{B_2}{u+\alpha}+\frac{C_2}{(u+\alpha)^2}+\frac{D_2}{(u+\alpha)^3}+\frac{E_2}{(\gamma-u)}+\frac{H_2}{(\gamma-u)^2}.$$

Now, as $u'\rightarrow\gamma$, the largest term in $F(u')$ is the one in $\ln(\gamma-u')$ whilst the largest term in $G(u')$ is the one in $(\gamma-u')^{-1}$. Now $\mathcal{V}=\mathcal{J}^2G(u')=G(u')/F(u')^2$. Thus, as u' tends to γ, $\mathcal{J}$ tends to zero and $\mathcal{V}$ tends to

$$1/(\gamma-u')[\ln(\gamma-u')]^2.$$

and this tends to infinity as u' tends to γ. Thus, when $0<F_R<1$, the threshold voltage for DI current flow with space-charge neutrality is infinite whereas, when $F_R=1$, this threshold is finite.[4] Mathematically, this difference arises because, when $p_{R0}=0$ ($F_R=1$), the singularity at $\mathcal{J}=0$ is of higher order.

Physically, the difference is best discussed in terms of the differences in recombination-center occupancy between the two cases. In Lampert's case, as J tends to zero the electron occupancy of the centers increases at a decreasing rate because $p_{R0}=0$ and thus the hole lifetime decreases at a decreasing rate, tending to become constant at $1/\langle v\sigma_p\rangle N_R$. The electron lifetime is tending to infinity as $\mathcal{J}$ tends to zero and p_R tends to zero. Thus the recombination "barrier" to the holes is becoming constant and that for the electrons is vanishing so that a finite threshold voltage results. In the present case, because $p_{R0}>0$, the hole lifetime decreases at a greater rate than in Lampert's case as $\mathcal{J}\rightarrow 0$ and the electron lifetime is not becoming infinite but tending to a value $1/\langle v\sigma_n\rangle p_{R0}$. Thus the hole-recombination

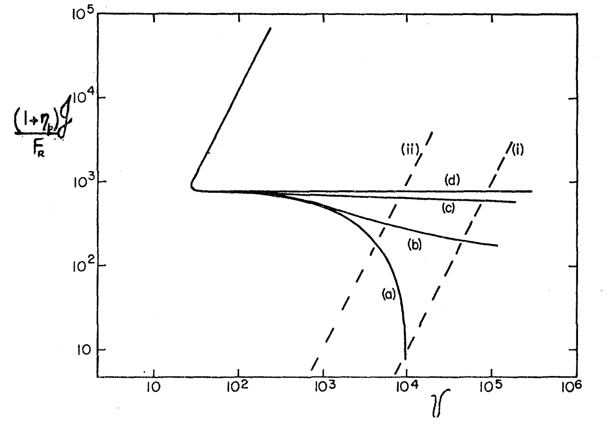

FIG. 1. The effect of changes in F_R on the current-voltage characteristics. Solid line: Double injection characteristics: (a) $F_R=1$, (b) $F_R\approx0.99$, (c) $F_R\approx0.91$, (d) $F_R\approx0.09$. Dashed line: SCL characteristics: (i) $N_RF_R(1-F_R)=10^{14}$ cm^{-3}, (ii) 10^{12} cm^{-3}.

"barrier" continues to increase and the electron-recombination "barrier" does not vanish as $\mathcal{J}\to 0$. As a result, in the present case, the recombination "barrier" for electrons as $\mathcal{J}\to 0$ prevents the neutralizing existence of electrons near the anode. This prevention occurs because the electrons cannot traverse the cathode end of the crystal without setting up a space charge, which is excluded by assumption (1) of the theory. Hence, the voltage increases to infinity as the current tends to zero, i.e., the negative resistance region continues to infinite voltages.

Of course, if the existence of space charge is allowed, the voltage threshold as such will not exist since current flow at low currents will be close to the one-carrier space-charge-limited (SCL) mechanism considered elsewhere.[6,7] Thus, as suggested previously,[5] there is a need for a unified theory of injected carrier currents which includes space-charge and two-carrier flow and recombination. This could be carried out by replacing the zero on the right-hand side of (3) by $-(\epsilon/e)(d\mathcal{E}/dx)$ (where ϵ is the permittivity of the solid) and carrying out the analysis from there. Unfortunately, this presents considerable difficulties. Lampert[4] has attempted to approximate to this unified theory by considering the current flow at low currents to be the one-carrier SCL mechanism and by investigating where this characteristic intersects the DI characteristic. We also carry out this procedure here in the belief that it may be useful.

The SCL characteristic, below the trap-filled limit, with electrons as the injected carrier, is given by[7]:

$$J=[9\epsilon\mu_n/8(1+\eta_n)L^3]V^2,$$

so that after change of variables,

$$\mathcal{J}=[9\epsilon\langle v\sigma_n\rangle/8e\mu_p(1+\eta_n)]\mathcal{V}^2.$$

This is rearranged, for reasons which will be apparent in the next section, so that

$$\frac{1+\eta_p}{F_R}\mathcal{J}=\frac{9\epsilon\eta\mathcal{V}^2}{8e\mu_pN_RF_R(1-F_R)\tau_{n0}}. \tag{10}$$

5. HIGH-CURRENT BEHAVIOR

The high-current region of the DI characteristic corresponds to small values of $F(u')$ and thus to u' close to η as Eqs. (8) show. If we write $u=\eta+\Delta$ and assume $|\Delta|\ll\eta$ and $|\Delta|\ll|\gamma-\eta|$, then Eq. (7) approximates to

$$f(u)\simeq M\Delta,\quad M=\frac{\alpha^2(1+\eta_n)(\beta\eta+1)^2}{\beta(1-F_R)\eta(\eta+\alpha)^2(\gamma-\eta)},$$

and

$$f(u)h(u)\simeq N\Delta^2,\quad N=\frac{\alpha^3(1+\eta_n)^2(\beta\eta+1)^3}{\beta^2(1-F_R)^2\eta(\eta+\alpha)^3(\gamma-\eta)^2}.$$

Hence,

$$F(u')=|M|\tfrac{1}{2}\Delta'^2,\quad G(u')=N\tfrac{1}{3}\Delta'^3,$$

where

$$\Delta'=|u'-\eta|,$$

and thus

$$\mathcal{J}=9|M|^3\mathcal{V}^2/8N^2$$

or

$$\mathcal{J}=\frac{9\beta(1-F_R)|\gamma-\eta|}{8(1+\eta_p)}\mathcal{V}^2. \tag{11}$$

This is the $\mathcal{J}\sim\mathcal{V}^2$ region of the DI characteristic discussed by Lampert in conclusion (c) of his article.[4] Its similarity to the result for a semiconductor[3] arises because in this region, the ratio of the two-carrier lifetimes has become constant. Even though recombination is, in this case, via centers, this constancy causes the DI current to be controlled in the same way as in a semiconductor. If $\gamma\gg\eta$, and thus for cases well into the domain of case (I), Eq. (11) becomes

$$\mathcal{J}=[9F_R/8(1+\eta_p)]\mathcal{V}^2. \tag{12}$$

If $\gamma\ll\eta$, i.e., for case (II), we have

$$\mathcal{J}\simeq\frac{9\beta(1-F_R)}{8(1+\eta_n)}\mathcal{V}^2=\frac{9F_R}{8(1+\eta_p)}\cdot\frac{\eta}{\gamma}\mathcal{V}^2. \tag{13}$$

Comparison of (10) and (12) shows that, for $\gamma\gg\eta$, the existence of a negative-resistance region will require:

$$\frac{\epsilon}{e\mu_pN_R\tau_{n0}F_R(1-F_R)}\ll1/\eta.$$

Taking values of the parameters which should be typical (e.g., $N_R=10^{17}$ cm^{-3}, and $\mu_p=3000$ cm^2 V^{-1} sec^{-1} with $\tau_{n0}=20$ μsec or $\mu_p=15$ cm^2 V^{-1} sec^{-1} with $\tau_{n0}=4$ msec), this inequality becomes

$$F_R(1-F_R)\gg10^{-9}\eta.$$

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[6] A. Rose, Phys. Rev. **97**, 1538 (1955).

[7] M. A. Lampert, Phys. Rev. **103**, 1648 (1956).

Thus, for example, if there are no traps (i.e., $\eta=1$), if the centers are less than about 0.5 eV from the Fermi level at room-temperature equilibrium, and if $\tau_{n0}\gg\tau_{p0}$, this implies that a negative-resistance region will exist at this temperature for the parameter values chosen.

For case (II), the low-current mechanism of current flow will again be SCL. However, in this case, the injected space charge will be positive and the majority carriers will be holes. An analogous inequality condition for the existence of a negative-resistance region can be obtained for this case.

6. NUMERICAL CALCULATIONS

In order to obtain a better picture of the DI current-voltage characteristics between the high- and low-current limits, numerical calculations have been carried out. The procedure followed was perfectly straightforward. The quantities $f(u)$ and $h(u)$ were computed from Eqs. (6) and (7) and integration was carried out by Simpsons rule to obtain $F(u')$ and $G(u')$. The interval for integration was chosen so that the error in $\mathcal{V}$ was always less than a few percent, this being considered satisfactory in view of the logarithmic display of the results. Because the work reported in this article was prompted by the results of experimental work on CdS,[8] the parameters were chosen, in many cases, with CdS in mind. In addition, most of the results obtained correspond to case (I), relevant to CdS. Computations of the DI characteristic were also carried out for $F_R=1$, using the analysis of Appendix A of Lampert,[4] for comparison purposes. In all the following calculations, the mobility ratio α was taken as 0.05.

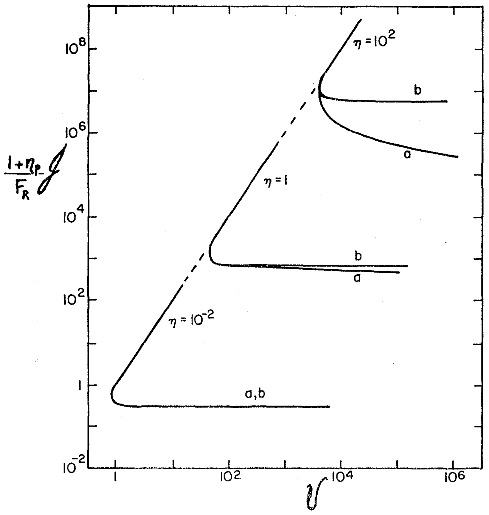

FIG. 2. The effect of shallow trapping on the characteristics. Case (I). (a) $F_R\approx0.91$, (b) $F_R\approx0.09$.

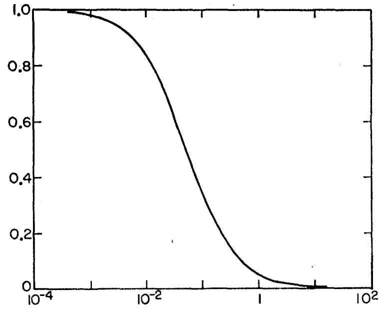

FIG. 3. The effect of the relative effectiveness of hole and electron trapping on the injection ratio at one of the contacts.

6.1 Effect of Changes in F_R on the Characteristics

Two DI characteristics obtained by computation have already been published[5] to demonstrate the effect of changes in F_R. The characteristics of Fig. 1 show this in greater detail. Curve (a) is the characteristic obtained for $F_R=1$ from Lampert's theory.[4] Curves (b), (c), and (d) were computed from the present theory for $F_R=100/101$, $F_R=10/11$, $F_R=1/11$, respectively. All four curves correspond to $\beta=10^{-3}$, i.e., $\mathcal{V}_{\text{th}}=10^4$, and $\eta=1$. The current is plotted as $[(1+\eta_p)/F_R]\mathcal{J}$ so that the curves coincide in the square-law region.

The characteristic for $F_R=1$ shows the threshold reported by Lampert.[4] Although it follows this curve at the high-current end of the negative-resistance region, the characteristic for $F_R\simeq0.99$ shows very different behavior at low currents. It will be noted that the characteristic for $F_R\simeq0.91$ behaves more like the $F_R\simeq0.09$ characteristic than like the $F_R\simeq0.99$ curve. Also shown in Fig. 1 are the SCL characteristics calculated from (10) for $\epsilon=10^{-10}$ mks units, $\mu_p=15$ cm^2/V/sec, $\tau_{n0}=4$ msec, typical of CdS; η is unity again. If we assume that the voltage maximum would occur in the neighborhood of the intersection of the DI and SCL characteristics, then it is plain that, if $F_R<1$, the "threshold" can occur at much greater voltages than Lampert's $\mathcal{V}_{\text{th}}$.[4] Thus, as was reported previously,[5] the use of Lampert's result in interpreting experimental "thresholds" can lead to values of hole lifetime which are much too small. This appears to have been the case in some earlier work.[8,9]

6.2 Effect of Shallow Trapping on Double-Injection Currents

The effect of trapping is important because it reduces the current flow by reducing the free-carrier densities. Moreover, the ratio of the carrier densities is in part determined by the relative effectiveness of the two kinds of trap as well as in part by recombination

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[8] P. N. Keating, Phys. Chem. Solids **24**, 1101 (1963).

[9] G. A. Marlor and J. Woods, Proc. Phys. Soc. (London) **81**, 1013 (1963).

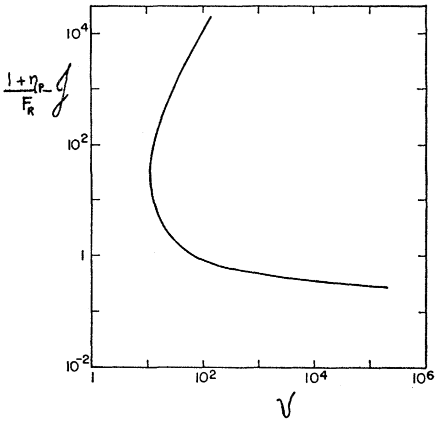

FIG. 4. Double-injection characteristic for $\langle v\sigma_n\rangle = \langle v\sigma_p\rangle$.

kinetics. The physical arguments of Sec. 2 are modified as follows when trapping is present.

The control of the DI current flow by trapping arises from the fact that, if one type of trap contains a large number of trapped carriers, these carriers give rise to space charge for neutralization of the other carriers without directly changing the recombination rate. For example, consider a system in which the two low-level life-times are equal. If the electron traps are very much more effective than the holes ($\eta \ll 1$), the hole transport will be the bottleneck to double-injection current flow because more free holes than free electrons are required to neutralize the trapped negative space charge. Thus, the case (I) domain, for example, is characterized by $\tau_{n0}/\tau_{p0} > \eta$, rather than $\tau_{n0}/\tau_{p0} > 1$. Similarly, the case (II) domain corresponds to $\tau_{n0}/\tau_{p0} < \eta$.

The negative-resistance region is again characterized by an increasing lifetime for the "difficult" carrier. However, the lifetime ratio now tends to η rather than unity. This is because, if no further changes in the lifetime ratio are to take place, there must be no further changes in the occupancy of the centers. Thus all further increases in the carrier densities must be distributed between the bands and the traps. Equations (12) and (13) indicate that in this high-level region of the characteristic, the current depends primarily on the trapping of the "difficult" carrier rather than on the trapping of the other carrier, if the transport of one is appreciably more difficult than that of the other. This arises because, even at these high injection levels, the DI current is still primarily controlled by the transport of the difficult carrier. It can be seen, for example, in Fig. 2, which corresponds to the case (I) domain where the current is independent of the electron traps. For each of three values of η, the variation of $[(1+\eta_p)/F_R]\mathcal{J}$ with $\mathcal{V}$ is shown in Fig. 2 for $F_R \simeq 0.91$ and $F_R \simeq 0.09$. In each case $\gamma = 10^4$. Below this high-level region, it will be noted that the dependence of the characteristic on trapping is more complex and includes the effect of the electron traps.

The effect of the ratio of the effectiveness of the hole and electron traps on the ratio of the carrier densities manifests itself again by influencing the injection ratios necessary at the two electrodes. The injection ratio at the electrode from which the "difficult" carriers are injected is, in fact, directly related to η since $n/p = \eta$ at this electrode. This electrode is the most important one in ensuring that current flow is volume controlled since the electric field is a minimum here. The injection ratio at this electrode, γ_i, is thus given by $(1+\eta/\alpha)^{-1}$ and is shown as a function of η for $\alpha = 0.05$ in Fig. 3. One interesting facet of this result is that, although for a case (I) solid one would expect a high-injection ratio to be required at the anode (i.e., hole injecting) contact, this is not necessarily so. Thus if η is greater than about 0.5, a small injection ratio is required. For large η, more free electrons are required to neutralize the space change due to the trapped holes since the hole traps are more effective. Similarly, for a case (II) solid, the injection ratio can be large at the cathode if η is small, i.e., if the electron traps are very effective.

6.3 Other Results

It was stated previously[5] that in the absence of trapping, the requirement for the existence of a negative resistance region was not that the capture cross sections of the centers for the two carriers must be very different but that the low-level lifetimes are very different. The negative-resistance region is a consequence of the increases in the shorter lifetime which take place as the lifetimes equalize. The curve shown in Fig. 4 demonstrates that the capture cross-section ratio is not itself important from this point of view. This characteristic was calculated for $\beta = \langle v\sigma_n\rangle / \langle v\sigma_p\rangle = 1$, $\tau_{n0}/\tau_{p0} = 10^2$ and for negligible trapping ($\eta = 1$). It is interesting to note also that current flow only occurs at voltages which are *greater* than $\mathcal{V}_{\text{th}}$,[4] which is 10 in this case; this shows again that $\mathcal{V}_{\text{th}}$ is an unimportant parameter for $F_R < 1$.

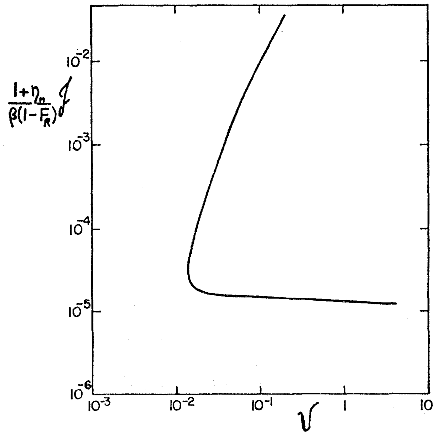

FIG. 5. Double-injection characteristic corresponding to case II.

For the sake of completeness, a computation was also carried out for values of parameters corresponding to a class (II) solid, i.e., for a solid in which the low-level hole lifetime is appreciably longer than the corresponding electron value, in the absence of trapping. The resulting characteristic, for which $\eta=1$, $V=10^{-3}$, is shown in Fig. 5. Although the values of $\mathcal{V}$ involved are rather smaller than those involved in the previous results, the form of the characteristics is extremely similar, as one expects from consideration of the symmetry present in the problem.

Note added in proof. K. L. Ashley and A. G. Milnes have recently reported [J. Appl. Phys. **37**, 369 (1964)] an analysis of the region of the characteristic below, and up to, the threshold. This also demonstrates that the "threshold voltage" is different if the centers are not completely filled at thermal equilibrium.

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Anelastic and Dielectric Relaxation due to Impurity-Vacancy Complexes in NaCl Crystals*

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Appreciable pairing of divalent metallic impurities with Na^+ vacancies occurs in NaCl below 300°C. The reorientation of such pairs or complexes had previously been observed under an applied electric field. In the present work stress-induced reorientation of pairs in NaCl doped with $CaCl_2$ and $MnCl_2$ has been studied by means of internal friction measurements. An internal friction peak attributed to pair reorientation under stress was observed near 100°C for a vibration frequency of ~10 kc/sec. Data obtained for longitudinal stress along both the ⟨100⟩ and ⟨111⟩ crystal directions yields information about the rates of relaxation corresponding to various mechanical relaxational modes. The data can be interpreted consistently in terms of an extension of the theory previously applied to dielectric relaxation, according to which the paired vacancy occupies only nearest-neighbor (n.n.) and next-nearest-neighbor (n.n.n.) sites to the impurity. Relations obtained between the relaxation rates and the various possible jump rates for a Na^+ ion into the vacancy enable each of the specific vacancy jump rates to be determined. It is concluded that the most rapid means for the reorientation of an impurity-vacancy pair between two n.n. sites is for the vacancy to move via a n.n.n. site. The rate of jump of the impurity ion into the vacancy is found to be a relatively slow process.

I. INTRODUCTION

The addition of divalent metallic ions to alkali halide crystals introduces an equal number of positive ion vacancies, in order to maintain charge neutrality.[1] Below a temperature of ~300°C, each of these vacancies is bound to a divalent impurity ion by electrostatic attraction. This impurity-vacancy complex can be viewed as an electric dipole, since the impurity ion has an excess positive charge while the vacancy is the center of an excess negative charge. Such a dipole can reorient by means of suitable vacancy jumps. Several workers[1–3] have observed dielectric relaxation in doped alkali halide crystals due to the reorientation of these dipoles in the presence of an electric field. Most experiments measure the dielectric loss arising from the fact that a component of the polarization is 90° out of phase with an ac electric field.[1,2] If this process is a simple one, involving only a single relaxation time, this loss as a function of frequency ω takes the form of the well-known Debye peak:

$$\tan\delta=\Delta(\omega/\zeta+\zeta/\omega)^{-1}, \qquad (1)$$

where δ is the "loss angle" by which the polarization lags behind an alternating field. Here the constant Δ is the relaxation strength, while ζ is the relaxation rate (or reciprocal relaxation time). The second type of experiment observes the relaxation as an exponentially decaying polarization current j following the application of a dc field E. For the case involving a single relaxation time this takes the form[3,4]

$$j=\Delta(\epsilon E\zeta/4\pi)\exp(-\zeta t), \qquad (2)$$

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