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DIELECTRIC SPECTROSCOPY OF SEMICONDUCTORS

Final Report to July 1990
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STRACT

This Report d cribes the principal results of study under the US Army contract on Dielectric Spectroscopy of Semiconductors (DSS). Over the last three years, the following areas of study were pursued:

a) time-domain study of the decay of open-circuit photovoltage in p-n junctions;
b) frequency-domain characterisation of a variety of p–n junctions on high-resistivity silicon, including forward-biased junctions;
c) frequency-domain photoconductive measurements on such p–n junctions;
d) a theoretical study of the significance of the time- and frequency-dependence of the response of semiconductors.

The results obtained during this contract consolidate our understanding of the nature of the trapping and recombination processes which consistently show fractional power-law dependenced on time instead of the generally expected exponential dependence. The fact that the observed time dependence is fully consistent with that of delayed luminescence adds further incentive to the development of a general theoretical model for these processes and one such model is proposed.

INTRODUCTION

The central theme of our study of the Dielectric Spectroscopy of Semiconductors (DSS) under two consecutive US Army Grants is the applicability of the "universal" fractional power law of relaxation to the rate processes governing the trapping and detrapping of electrons in localised levels in semiconductors and phosphors. The experimental techniques include the frequency-domain measurements of the responses in wide ranges of frequency ($10^{-4} - 10^{5}$ Hz) and the corresponding time-domain measurement of the relaxation processes. These studies are usi ng specially developed equipment which is unique in its capability and which makes it possible to reveal features of the responses which are not accessible to typical measurement procedure

The result of these studies is a much deeper understanding of the various rate processes than has been available previously. In particular, we have shown conclusively that the "classical" concept of exponential time dependence of transitions resulting from external excitation of a system of trapping and localised states is not obeyed in a wide range of situations, in many cases to the extent of being completely unrecognisable. Instead, the prevailing form of response

is the "universal" fractional power law in time, whereby the decay of excited density following a δ–function excitation, follows the fractional power law

$$\Delta n \propto t^{-s}$$

or the corresponding frequency dependence of the effective complex susceptibility

$$\tilde{\chi}(\omega) \propto (i\omega)^{s-1}$$

Here the exponent s falls in the range $\{0,1\}$. Various detailed aspects of these studies have been reported in successive Progress Reports and have also been the subject of publications listed at the end of this Report.

SUMMARY OF FUNDAMENTAL RESULTS

The sustained period of funding by the US Army through two consecutive three-year grants has resulted in the emergence of a fundamental understanding of a wide range of rate processes governing the transport of hopping charges and the trapping/detrapping processes in semiconductors. In particular, we have achieved a far-reaching characterisation of the properties of p-n junctions and of Schottky barriers [8,12,14] as well as of the hopping conduction in amorphous semiconductors which conduct by localised carriers.

Our experimental studies have highlighted a range of different properties of semiconductors and of associated materials like phosphors and photoconductors and have provided their tentative theoretical interpretations. Among these we will mention the following:

An appreciation of the significance of the DSS technique for the characterisation of semiconductor materials, owing to its great sensitivity to the details of the rate processes, which in their turn reflect the structural perfection of the material and its purity [14].

An understanding of the hopping conductivity in amorphous and disordered semiconductors.

An in-depth study of the properties of a wide range of p-n junctions, from very lightly to very heavily doped ones, with the interpretation of their various spectral shapes ranging from almost Debye-like to nearly "flat", frequency-independent losses in Zener diodes [7,8].

The corresponding study of Schottky barriers, with their highly characteristic Low-Frequency Dispersive behaviour showing the presence of insatabilities at the interface [7,8].

The development of a frequency-domain photoconductive method of measuring the trapping rates by a process much more sensitive than the traditional time-domain methods [5,6].

The adaptation of the "energy criterion" approach to the theory of the rate processes [11,12,14,15]

TIME-DEPENDENCE OF PHOTOVOLTAGE IN P-N JUNCTIONS

Most recently we have been making a unique study of the time-dependence of the *open-circuit*

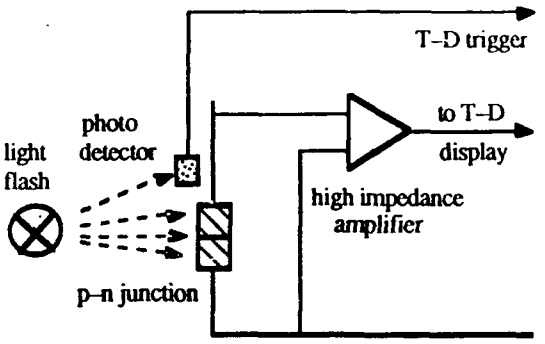

Figure 1 A schematic representation of the experimental arrangement for the measurement of the decay of the photovoltage on a p-n junction illuminated by a flash of light. The same flash triggers the Time-Domain (TD) system through a photodetector and the photovoltage is displayed on a logarithmic time base. The diode is situated in a cryostat at a controlled temperature.

photovoltage of p-n junctions after a short (1 μs duration) light pulse. Such measurements are seldom being made since they require a fast-response amplifier with a very high input impedance - in excess of $10^{13}\Omega$ and this appears not to have been generally available. It is also possible that there was insufficient motivation for this work because of a lack of appreciation of the theoretical and practical implications of the results reported by us here.

Experimental Results

The experimental arrangement is shown in Figure 1 and consists of a high-impedance voltage amplifier which feeds a Time-Domain system constructed specially for this type of work which digitises the data and displays then on a logarithmic time-base. The diode under study is mounted in a cryostat with suitable windows and care is taken to exclude unwanted light. The excitation of the diode is by means of a 1 μs flash of blue light which is absorbed near the surface of

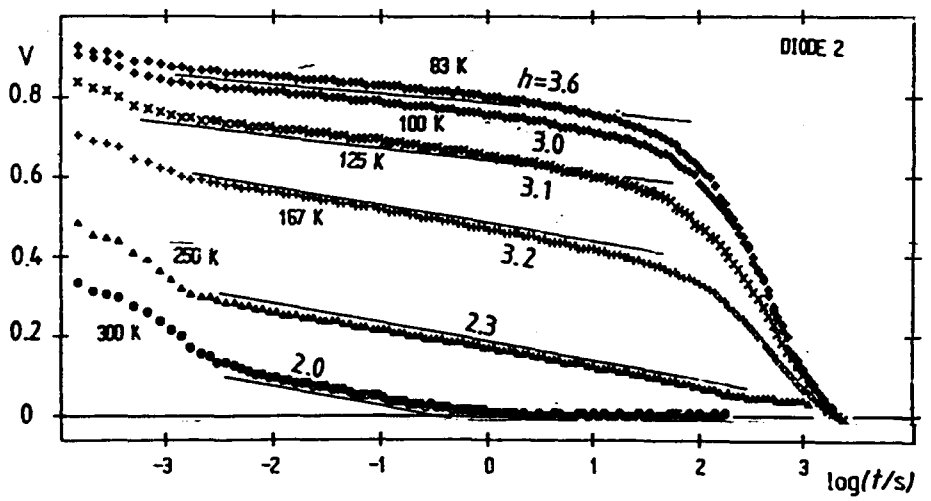

Figure 2. The decay of photovoltage in diode N° 2 for a range of temperatures plotted on a logarithmic time base. Note the extensive range - up to five decades at 250K - of linear dependence, with the slopes indicated in terms of *kT/e*. The final decay at lower tempeartures is more rapid. At higher temperatures there is a more rapid initial exponential-like decay.

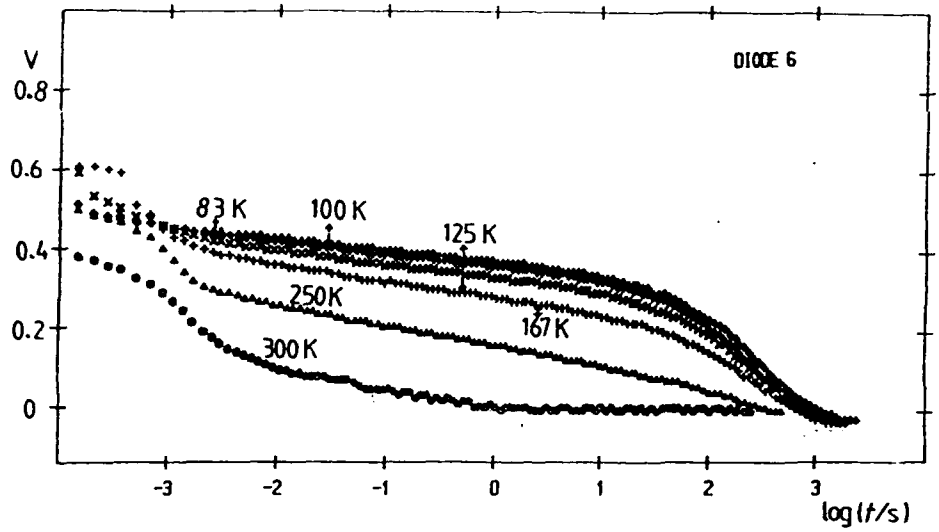

Figure 3. The decay of photovoltage in diode Nº 6 for a range of temperatures. Note the similarity with the data in Figure 2, but with a much smaller amplitude.

the semiconductor. The logarithmic time base is synchronised with the light flash - this is important if a correct interpretation is to be made of the results.

Our experimental results shown in Figures 2 and 3 reveal three regions of time dependence of V_ϕ. One which is seen more clearly in some instances than in others is a rapid, almost exponential decay which is particularly pronounced at higher temperatures and which is characterised by a "lifetime" of approximately 1 ms. The second is a clearly defined straight line relation between V_ϕ and log$t$ which extends over several decades to many seconds and which cannot be regarded as a free-carrier phenomenon. Finally there is at long times a rapid fall to zero which could be exponential in nature.

We have looked at several p-n junctions on high-resistivity silicon whose frequency-dependent dark response had been described in earlier Progress Reports. The response is shown in Figure 2 for the Harwell diode Nº 2 and in Figure 3 for diode Nº 6, whose characteristics are as follows:

Diode Nº	Implant	Annealing
1	B^+ 10 kV, $5\times10^{14}cm^{-3}$	500ºC 30 mins
2	do	600ºC 30 mins
3	BF_2^+ 40 keV, $1\times10^{15}cm^{-3}$	do

The data for diode Nº 2 at 300 and 250K consist of a relatively rapid decay which could be exponential in time although it is difficult to resolve it with any certainty, followed by a straight line portion extending at 250K over nearly five decades of time, with a slope in both cases of $1.5kT/e$ per decade. The initial fall becomes insignificant at lower temperatures and instead the decay becomes a clear straight line followed by what could be an exponential decay. The values of the slope expressed in terms of kT/e are indicated for the various temperatures.

Diode Nº 6 shows a qualitatively similar behaviour, Figure 3, while diode Nº 1 has an entirely different characteristic, Figure 4, in which a clear power law only becomes evident at 300K, below that temperature the response is rather more complex. However, Figure 5 shows the effect of a 1MΩ resistor in parallel with the diode with the decay due to trapping being eliminated and leaving mainly the near-exponential decay at short times. We interpret this in

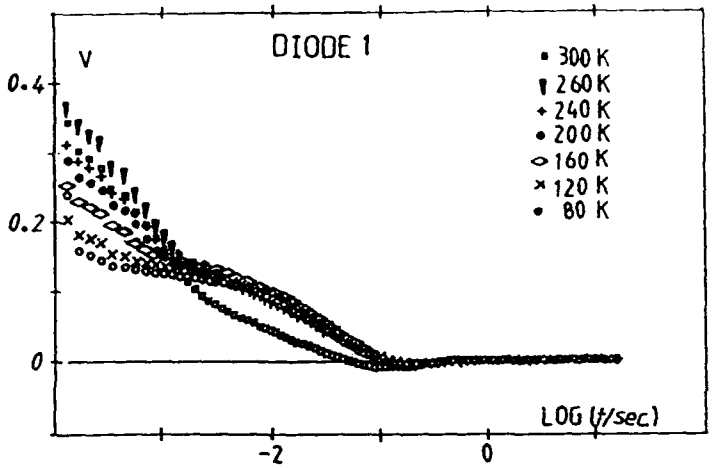

Figure 4. Similar data for diode N° 1, showing the virtual absence of long-term decay.

terms of the collapse of the QFL splitting in the presence of an external resistor, since the effect of the trapped charge is insufficient to maintain V_ϕ with a relatively high current flowing in the system.

This long-term logarithmic decay of V_ϕ is almost certainly due to trapping processes in deep levels in the space charge region and in the lightly doped base region. Its presence can be eliminated by flooding the sample with continuous light, as shown in Figure 6, where only the rapid decay remains. There exists to our knowledge no accepted theory predicting or explaining power-law decay of trapped densities, although there are excellent examples of the decay of delayed luminescence under delta-function excitation which all follow power laws with negative exponents greater than unity (Reference 1). Postulating that both processes are manifestations of charge detrapping from deep levels, and bearing in mind that luminescence measures the *rate* of carrier removal, while V_ϕ represents (logarithmically) the trapped density, luminescence decay should follow the $-s-1$ law in our notation, in qualitative agreement with experimental evidence.

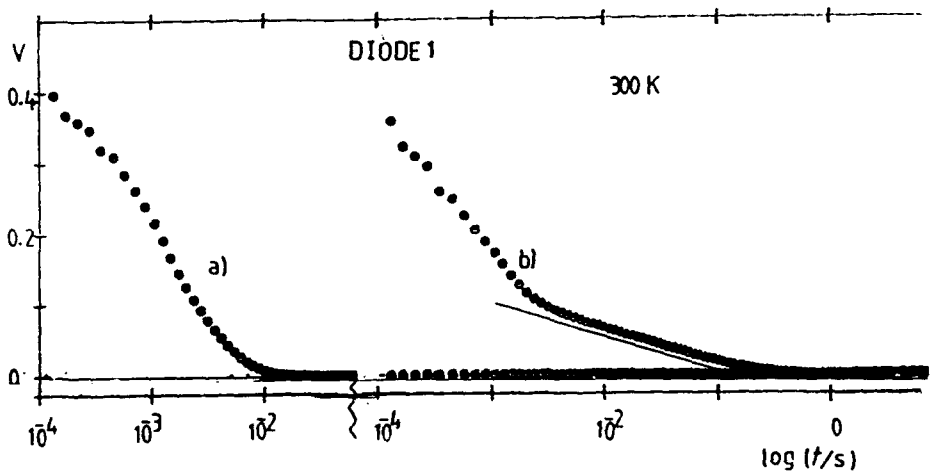

Figure 5. The response of diode n° 2 when shunted by a 1 MΩ resistor, resulting in a rapid decay of photovoltage because the release trapped carriers is insufficient to maintain V_ϕ.

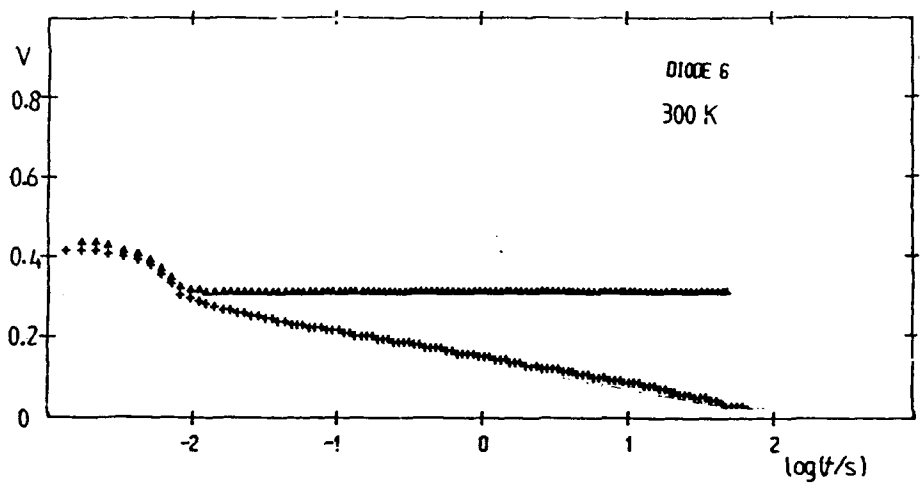

Figure 6. The effect of steady background illumination on the time-dependence of the photo-voltage on diode N° 1 at 300K. The long "tail" disappears under illumination, suggesting that it is due to the detrapping of trapped electrons.

Interpretation of the photovoltage data

The interpretation of these results is based on a model of an open-circuited p-n junction as shown in Figure 7. The generation of excess electron-hole pairs in this system brings about a rapid sweeping of these into the respective majority regions and this has to be counteracted by a forward photovoltage V_ϕ of the required magnitude induced on the junction. At the far end the ohmic contact assures a vanishing excess density so that the density profile is as shown in Figure 1, but recombination does not generate any net electric current since identical particle currents flow in the same direction. The sweeping out of the charge carriers takes place in a time of the order of the diffusion time $t_d = w^2/D$, where w is the base width and D the diffusivity of the carriers. Free excess carriers are also removed by recombination with its characteristic lifetime τ.

The photovoltage V_ϕ is expected to be related to the boundary density Δn_0 of the excess minority carriers in the p-type material at the edge of the space charge region through some relation of the form:

$$\Delta n_0 = n_p \exp(eV_\phi/\alpha kT)$$

where α is the non-ideality factor in the expression for the forward current [17]. Typical values of α are between 1 and 2. This may be re-written in the form:

$$V_\phi = (\alpha kT/e) \ln(\Delta n_0/n_p) = (\alpha kT/e) \log(\Delta n_0/n_p) / \log e$$

It follows that if a plot of V_ϕ against log time represents a straight line of slope $-hkT/e$, then the decay of charge follows a power law in time:

$$\Delta n_0 \propto t^{-s}$$

where the following relation applies between the slope h and the exponent s :

$$h = \alpha s \ln 10$$

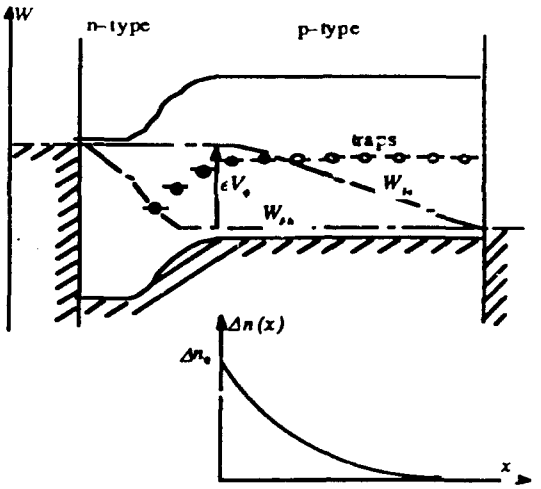

Figure 7. The band diagram of an illuminated p–n junction with some deep trapping levels on the lightly doped p–side, showing the splitting of the quasi-Fermi levels W_{Fe} and W_{Fh} by the amount eV_ϕ. At the far contact the excess densities go down to zero. The trapping levels below W_{Fe} are filled with electrons. The distribution of the excess density $\Delta n(x)$ is shown by the lower diagram. The excess density free carrier density decays after the removal of excitation by transport to the back contact or by recombination, while the trapped density takes a much longer time to decay to its equilibrium distribution.

If the slope h is approximately independent of T then the exponent s is also independent of T.

With the observed slope for diode N°2 equal to $h \approx 3.6$ - 2.0, depending on temperature, the quantity αs becomes 1.5 - 1.1, with an almost constant value of around 1.3 between 100 and 167K. This is consistent with the "universal" law of polarisation decay which should follow a t^{-s} dependence, with $s < 1$, bearing in mind that the factor α is most likely between 1 and 2 and may be temperature dependent.

The effect of trapping on V_ϕ may be seen with reference to Figure 7 in which the excited base region has its electron and hole quasi-Fermi levels (QFL) W_{Fe} and W_{Fh} split by eV_ϕ due to the excess densities of free electrons. Any deep trapping levels also become correspondingly filled with electrons and these remain long after the removal of the free carriers by recombination and transport to the back contact. As soon as the free carriers have been substantially removed, the electron QFL drops to the trapping level and this brings about a reduction of V_ϕ corresponding to the rapid initial decay.

Our conclusion is, therefore, that the decay of the photovoltage V_ϕ after the short flash illumination is dominated initially by the relatively reapid processes of recombination and sweeping out of excess free carriers, followed by a much slower process of detrapping from deep levels. The latter obeys the "universal" fractional power law in time, which is similar to that observed in the an alogous situation of the decay of liminescence in phosphors.

THE ENERGY CRITERION APPROACH

The discovery of the applicability of this universal fractional power law to detrapping of carriers from deep levels in semiconductors poses the very fundamental question of the interpretation of this type of decay. There is no generally accepted theory leading to this type of result and the

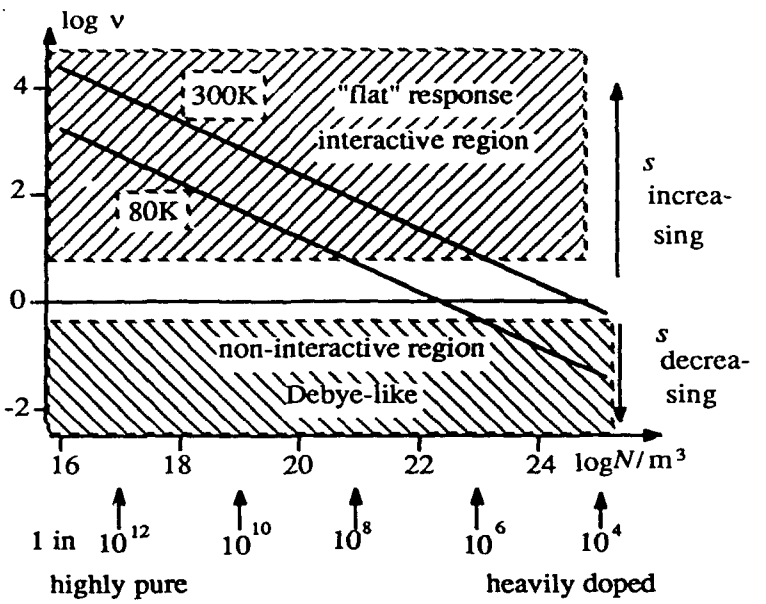

Figure 8 Screening relations in a free electron gas showing the number ν of particles within a sphere of Debye radius λ_D for a wide range of electron densities and two temperatures of 80 and 300K. Assumed relative permittivity $\varepsilon_r = 10$. The non-interactive region is characterised by $\nu < 1$, interactive region by $\nu > 1$. The arrows at the lower edge indicate the corresponding densities in relation to the number of atoms in the lattice. The effect on the exponent s is indicated on the right.

one attempt to provide an explanation of the corresponding luminescence decay is that of Dissado [16].

An alternative approach based on Jonscher's "energy criterion" has been presented in reference [12]. The essential feature of this approach is the concept of the ratio of energy lost per reversal of polarisation to the energy stored in the polarised system. When this ratio is independent of the frequency of reversals, the inevitable consequence is the "universal" fractional power law. The basic reason for the constance of loss in the case of electronic systems of interest to the present situation is the "screening" of localised charges by other charges in the system. This screening gives rise to a lowering of the potential energy of the localised charge in comparison with the energy of the unoccupied state and this lowering constitutes an irreducible energy loss on each reversal of polarisation. The question which has to be answered is the *magnitude* of this lowering which must depend on the strength of the interaction between neighbouring charges.

In addition to the magnitude of the energy loss there is also the question of the *interaction* between various centres. If the system may be considered to be *non–interactive* then the constitutent charges act independently and the resulting relaxation response is exponential in time or Debye-like in frequency. If, on the other hand, the interaction is strong, we have the typical many-body situation in which "nothing can move without everything else moving as well". This is then the case of a stongly interactive system with low losses and nearly frequency-independent dielectric response.

In our approach, we have proposed that a measure of the interaction may be provided by the Coulombic interactions between mutually screening charges with a density N. The concept of Debye screening distance $\lambda_D = (\varepsilon kT/e^2N)^{1/2}$ may be extended to cover the present situation, with

due allowance for the difference between free and localised charge carriers. In plasma physics a measure of interaction is provided by the number ν of charges within a Debye sphere, $\nu = 4\pi\lambda_D^3 N/3$. This number is plotted against N in Figure 8 which shows the non-interacting region in which $\nu < 1$, *i.e.* where there is less than one charge within the interaction sphere, ae interacting region for which $\nu > 1$. Somewhat paradoxically, the strongly interactive region corresponds to *rarified* plasmas, the non-interactive region to *dense* plasmas. This explains why relatively "pure" systems with very few hopping charges are strongly non-Debye in character with low and nearly "flat" frequency-independent losses, while relatively more dense charges are more nearly Debye-like and rather lossy. A more detailed discussion of this will be given elsewhere, with particular reference to other types of mechanisms.

It is not possible at this early stage to give a definitive verdict on the relative merits of these various approaches.

CONCLUDING COMMENTS

The DSS technique sponsored by the US Army has contributed significantly to a better understanding of the relaxation processes in semiconductors and semi-insulators, and has provided a basis for the development of new thinking regarding the various rate processes in these materials.

Bt providing a firm basis of experimental facts, DSS has shown that the accepted theoretical ideas are largely inapplicable in that they are unable to account or the observed responses. To that extent, it should provide a firm basis for the development of new theories.

DSS is also capable of discriminating between different materials on the basis of their different "spectra" which are very sensitive to the presence of structural imperfections and of impurities.

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