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## SCL CURRENT INJECTION IN A DEEP FAST TRAPPING DIELECTRIC

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The interplay between free and trapped charges greatly complicates the solution of the system of partial differential equations governing the one carrier flow in dielectric materials under injection from an ohmic contact. Many and Rakavy<sup>(1)</sup> derived approximate expressions for an insulator with slow trapping and for shorter trapping times they solved numerically the pertinent equations. A situation that also seems to be treatable is that of deep fast trapping, a case already considered by H. Wintle<sup>(2)</sup> in open circuit. By deep fast trapping we mean traps that, at each place, are completely filled as long as there is a non zero value of the density of free charges therein. Currents vs time curves are obtained including the interesting case in which the current goes to zero due to the large amount of trapping.

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## CONDUCTION OF ELECTRICITY IN LIQUID DIELECTRICS

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A theoretical model for the steady state ionic conduction of electricity in liquid dielectrics is developed neglecting diffusion effects. The electrodes are considered non injecting and no particular generation mechanism is invoked. A second order non-linear differential equation is obtained for the field distribution inside the condenser or cell. Analytical solutions for the case of equal mobilities of the carriers are shown to be strongly dependent upon the ratio of the recombination constant and the mobility. General solutions are expressed in terms of transcendental functions but reasonable physical arguments and adequate boundary conditions limit the possible solutions to simple analytical expressions. Using branches of particular solutions found one obtains expressions for the field distribution inside the dielectric medium, in the middle part of the condenser and near the electrodes. Expressions are given for the linear extension of the inhomogeneous field distribution, the potential fall near the electrodes, the potential distribution, the current density and carrier distribution as a function of applied field. The main conclusion reached is that conduction of electricity in liquid dielectrics occurs in two stages: in the first one, at low fields, space charge is the controlling factor up to the onset of the second stage when the external applied field determines conduction.

(Conduction of electricity...)

It is shown how experimental d.c. conductivity curves are analysed and relevant parameters obtained. The fit of experimental published curves to the theoretical expression is very good giving strong support to the conduction mechanism used. Extension to the case of unequal mobilities of the carriers is considered using the solutions found.

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EXPERIMENTAL VALIDATION OF A FUNDAMENTAL THEORY OF  
PHOTOCONDUCTIVITY QUANTUM YIELDS

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The applicability of Onsager's theory of geminate recombination<sup>1</sup> to free carrier generation in solids will be reviewed. Emphasis will be placed on photocarrier generation in single crystals of anthracene<sup>2-7</sup> because the critical experiments which test the theory<sup>3,4,6,7</sup> are most complete for that material. A parallel and more extensive development<sup>8</sup> of most of these same ideas has been carried out by radiation chemists who have been interested in the free ion yields produced when ionizing radiation is absorbed by organic liquids.

Photoionization of most solids produces hot electrons which, however, do not escape completely from the coulomb field of the parent positive ion (hole) before coming to thermal equilibrium with the lattice. As a result, the mutual diffusion of hole-electron pairs in the field produced by their own coulombic interaction plus any applied field determines whether the free carriers will separate to infinity or recombine (geminate recombination). For an isolated pair, Onsager's recombination theory treats the above situation exactly and results in an expression which may be used to understand the implications of the applied field and temperature dependence observed for photoconductivity carrier quantum yields<sup>3-7</sup>. We have pointed out as did Onsager that low-field values of the slope to intercept ratio  $S/I$  of carrier quantum yield vs. applied field plots



(Experimental validation of a fundamental...)

provide a sensitive test of the applicability of Onsager theory to carrier generation. The low-field limit of the slope to intercept value is:

$$S/I = \frac{e^3}{8\pi\epsilon\epsilon_0 k^2 T^2}$$

where  $\epsilon$  is the high frequency dielectric constant and  $\epsilon_0$  (F/cm) is the permittivity of free space. For anthracene, which has a mean optical dielectric constant of  $3.2 \pm 0.1$ ,<sup>9</sup> the predicted value of  $S/I$  at 298K is  $(3.4 \pm 0.1) \times 10^{-5}$  cm/V. Our most recent experimental values<sup>6,7</sup> are  $(3.21 \pm 0.12) \times 10^{-5}$  for electrons and  $(3.02 \pm 0.08) \times 10^{-5}$  cm/V for holes. Anthracene crystals are dielectrically anisotropic so that this nearly quantitative agreement with theory is perhaps the best that one can expect from a theory that assumes an isotropic dielectric constant. Furthermore, we have experimentally confirmed the predicted  $T^{-2}$  dependence of  $S/I$ .

We are thus convinced that Onsager theory allows fundamental understanding of free carrier yield experiments in single crystal anthracene. Its prediction are in spectacularly better agreement with experiment than are those of one-dimensional<sup>10</sup> or pseudo-three-dimensional<sup>11,12</sup> Poole-Frenkel theory.

In Onsager theory, the temperature dependence and high field dependence of the free carrier yield are each governed by the separation attained by the electron-hole pair at the time they come to thermal equilibrium with the lattice. This thermalization length has been measured for anthracene as a function of photon energy<sup>13</sup>. The interesting correlation of thermal-

(Experimental validation of a fundamental...)

ization length with the excitation spectrum for free carriers will be discussed.

Thermalization lengths have also been estimated for the technologically significant materials amorphous Se<sup>14</sup> and for the photoconducting polymer PVK<sup>15</sup>. Experiments by radiation chemists have also established an interesting correlation of thermalization length with electron mobility<sup>6</sup>. Thus a substantial body of recent experimental work appears to establish that the Brownian motion problem solved by Onsager in order to interpret ion collection efficiencies in gas-filled radiation detectors has immediate and widespread applicability to free carrier generation in all materials.

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(Experimental validation of a fundamental...)

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THE COSTA RIBEIRO EFFECT AND THE THERMODIELECTRIC  
ELECTRET

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During a phase change to solid phase a dielectric becomes electrified by a separation of charges. This is Costa Ribeiro Effect (CRE)<sup>(1)</sup>. The dielectric forms so an electret with the application of no field called thermodielectric electret. If in the solid there is a bulky distribution of positive charges and another of negative charges in a very thin layer at the surface at which phase transition occurred the substance is called thermodielectric positive, and negative if the contrary happens. We collected 21 positive substances and only 4 negative. The CRE has been neglected and is little known, so there is a number of reported effects that may be attributed either to the CRE or to allied effects in the thermodielectric electret. Such are: spontaneous polarization of SO<sub>2</sub> at solidification<sup>(2)</sup>, anomalous photo-voltaic effects, discrepancies in resistivity measurements, negative photoconductivity<sup>(3)</sup>, and permittivity anomalies<sup>(4)</sup>. The analysis of the electric potential and field inside the dielectric due to a constant distribution of charges in two layers, one positive and the other negative, shows the existence of two movable zero field planes inside the layers, its position being dependent of the age and of the distance of the dielectric to the electrodes. Experiments

(The Costa Ribeiro effect and...)

may be made to show this<sup>(5)</sup> and explain anomalous facts mentioned above<sup>(3)</sup>

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## ELECTRON BEAMS AS VIRTUAL ELECTRODES

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Ehrenberg and co-workers and Spear, in a series of papers published between 1948 and 1968, have investigated the currents induced in dielectrics irradiated with electron beams whose range was smaller than the thickness of the samples. The irradiated dielectrics were sandwiched between thin ( $500^{\circ}\text{A}$ ) Al electrodes. Currents were measured as a function of electrodes energy for various values of the electrode bias. It was found that significant currents started to flow before the extrapolated electron range became equal to the sample thickness; a minimum electron range was, however, found below which no currents could be observed whatever was the value of the applied field (up to  $10^6$  V/cm). The interpretation of this threshold has remained controversial. The authors have found that the theory of space-charge-limited currents can provide a satisfactory interpretation. Following Hirsch, the dielectric is divided into an irradiated region characterized by a uniform radiation-induced conductivity and a non-irradiated region whose intrinsic conductivity is zero. The irradiated region contains a plasma of positive and negative carriers. The interface between the two regions behaves as an electrode from which carriers can be spontaneously injected into the non-irradiated region or pulled into it by the electric field. The current flow in the non-irradiated region is described by the laws of space-charge-limited currents. The

(Electron beams as...)

boundary conditions at the interface are those of an injecting electrode within a wide interval of voltages. Thus the electron beam can be said to generate a virtual electrode within the dielectric. For electron ranges below the threshold value the device can be represented by the simple circuit diagram which has been found useful in recent measurements by Dow, Nablo, Sessler, West and Gross. Range straggling of the electrons and diffusion in the interface region are effects which at a later stage of the theory will have to be considered. Numerical analysis of Spear's result by the present theory has nevertheless allowed to obtain values for radiation-induced conductivity, trap-modulated electron mobility, and Schubweg which are in overall agreement with values obtained by other methods.

FUNDAMENTAL LIMITATIONS ON THE SENSITIVITY OF  
PHOTOCONDUCTIVITY-CONTROLLED IMAGING SYSTEMS

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There exists now a large variety of imaging systems which make use of a photoconductive insulator to modulate a second image-forming process. Examples are television camera tubes (Vidicons), office copiers (Xerography, Electrofax), light valves (liquid crystal, ferroelectric, electro-optic, thermoplastic) and light amplifiers (electroluminescent). A common aim in all of these systems is to reduce the optical exposure required to form an image. In general, the required optical exposure, measured in photons/cm<sup>2</sup>, is numerically carried to the electric field across the photoconductor, measured in electron charges/cm<sup>2</sup>. Hence, a reduced optical exposure requires a reduced electric field. It is then necessary that both the photoconductor and the image forming process be able to work at the reduced field. A general argument will be outlined to show that in order for the photoconductor to perform effectively at the reduced field (or any field), the total number of traps/cm<sup>2</sup> in the thickness of the photoconductive layer and lying near the Fermi level must not exceed the electric field, measured in electron charges/cm<sup>2</sup>. This is also the criterion for observing space-charge-limited currents at the field in question. In order to achieve sensitivities approximating photographic speeds, the electric field should be in order of 10<sup>3</sup> volts/cm and the trap density near the Fermi level for a 10 micron thick layer should be less than 10<sup>13</sup>/cm<sup>3</sup>.kT. This represents a challenge in the synthesis of relatively trap-free insulating solids having bandgaps in the neighborhood of two electron volts.



## RECOMBINATION CONTROLLED PHOTOCURRENTS

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In this short note we indicate some of the complications which might arise in the interpretations of experiments on recombination controlled photo-currents in low mobility materials where there may be field dependences of the mobility ( $\mu$ ) and the recombination coefficient ( $b$ ). In low mobility materials, recombination is governed by the rate of encounter between the charged particles. The field dependence of  $b$  is simply illustrated by using a derivation due to Onsager<sup>(1)</sup> for a constant density of charge ( $n_0$ ) and a point recombination center:

$$1) \quad b = \frac{1}{n_0} \int_A \vec{J} \cdot d\vec{S} = \int_A \mu \vec{E} \cdot d\vec{S}.$$

$\vec{J}$  is the current density,  $\vec{E}$  is the electric field acting on the carriers, and the integration is over an absorbing surface  $A$  around the recombination center. Diffusion does not contribute to  $\vec{J}$  because the density is assumed constant. (Other models eg Silver and Jarnagin<sup>(2)</sup> include diffusion but the result is the same.) Without applied field,  $E = e/4\pi\epsilon r^2$  and  $b_0 = \mu e/\epsilon$ , the Langevin value. An applied field  $\vec{E}_a$  will have no contribution to  $b$  if  $\int_A \mu \vec{E} \cdot d\vec{S} \approx \langle \mu \rangle \int_A \vec{E} \cdot d\vec{S}$  (or  $\mu = \text{constant}$ ) since  $\int_A \vec{E}_a \cdot d\vec{S} = 0$ . However, if  $\mu$  is field dependent, then  $\mu$  cannot be taken out of the integral and  $b$  will be field dependent. To illustrate some of the consequences of the field dependence of  $b$ , we study the steady state current ( $i_{ss}$ ) when a high square wave uniform excitation is applied and the photocurrent is recombination

(Recombination controlled...)

limited. The rise of the carrier density is in this case  $dn/dt = g - bn^2$ , where  $g$  is the generation rate. The steady state value of  $n$  with the excitation on is  $n_0 \equiv (g/b)^{1/2}$ . The steady state current is therefore

$$2) \quad i_{ss} = \mu E n_0 = \left| \frac{\epsilon g(E) \mu(E)}{e \alpha(E)} \right|^{1/2} E.$$

Studying the rise of the photocurrent gives

$$3) \quad \frac{1}{t_b} \equiv \frac{1}{i_{ss}} \frac{di}{dt} \Big|_{t=0^+} = \frac{1}{n_0} \frac{dn}{dt} \Big|_{t=0^+} = |g(E) \mu(E) \alpha e / \epsilon|^{1/2}.$$

Equations (2) and (3) together gives

$$4) \quad \alpha(E) = \frac{CV}{i_{ss} t_b}$$

and can be determined experimentally.

The decay of the photocurrent after the excitation is removed, is more complicated because space charge neutrality is not maintained everywhere. Consequently the current decay depends upon the build-up of the space charge layers as well as the decay of the density of carriers due to recombination. When the bulk field is reduced to zero (due to the space charge layers at each electrode) the current is no longer determined by the density of carriers in the bulk but by motion in the space charge layers. As an example, take the case where one of the carriers is immobile. In this case,

$$5) \quad \frac{1}{i} \frac{di}{dt} \Big|_{0^+} = \frac{1}{n_0} \frac{dn}{dt} \Big|_{0^+} + \frac{1}{E} \frac{dE}{dt} \Big|_{0^+}$$

where  $0^+$  is a small time after the excitation is removed.

Equation 5 can be rewritten as

$$\frac{1}{i} \frac{di}{dt} \Big|_{0^+} = b_0 n_0 [\alpha(E) + \frac{1}{L} \int_0^{0^+} \mu E dt]$$

and the decay of the photocurrent is faster than the rise and the photocurrent will be asymmetric (with step function excitation) when  $\alpha \ll 1$  because the space charge build up may be as rapid as the decay of carriers.

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HIGH FIELD ELECTRON AND HOLE TRANSPORT IN AMORPHOUS  
GLASSES AND POLYMERS\*

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High mobility electrons in liquid dielectrics have been studied for a number of years, but it is only recently that we have shown that high mobility electrons can exist in a disordered glass, pure  $\text{SiO}_2$ . Electron-hole pairs are generated in thin specimens of amorphous  $\text{SiO}_2$  by a 3 nsec pulse of high energy X-rays and the transit times of electrons across the specimen are measured, at fields up to  $7.5 \times 10^5$  V/cm. It is found that the mobility of the electrons is controlled by scattering from LO phonons, which, in the disordered material, have the characteristics of the local Si-O bending and stretching modes. The magnitude and the temperature dependence of the electron mobility ( $\sim 20 \text{ cm}^2/\text{V}\text{-sec}$  at  $300^\circ\text{K}$ ) are in good agreement with theory, except at low temperatures where the mobility appears to be controlled by the disorder. At very high fields the theory predicts that the mobility will drop with increasing field (the drift velocity will saturate) due to LO phonon emission. The optic lattice modes to which the electron is strongly coupled are very high energy ( $\sim .1 \text{ eV}$ ) and thus very high drift velocities are predicted, and for the first time, excess electron drift velocities over  $10^7$  cm/sec are observed in a dielectric medium. Studies of thin oxide films ( $< 1\mu$ ) up to fields of  $4 \times 10^6$  V/cm show no impact ionization, which indicates that phonon emission is still controlling the kinetic energy of the electrons below the band-gap energy (9 eV). Similar studies of electron transport in Mylar films up to  $3 \times 10^6$  V/cm show that no high mobility electrons exist on the

(High field electron and hole ...)

nanosecond time scale, but that a significant field dependence of the electron mobility appears at the highest fields.

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## A HIGH PRECISION PERMITTIVITY MEASURING DEVICE

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Instruments<sup>(1)</sup> for measuring dielectric constant  $\epsilon$  consist essentially of a plane capacitor; one plate is a central circular electrode with guard ring, the other connected to a micrometer for determining the distance between them. The accumulate errors limit the precision in  $\epsilon$  to 1%. A capacitance bridge<sup>(1)</sup> may have a precision of 0,01%; we developed a device for getting this precision<sup>(2)</sup>. The central electrode has a 8mm diameter with a 38mm guard ring both having 5mm thickness; between them is a 0,01mm gap with a resistance greater than 2.000 M $\Omega$ . The other is a 68mm plate, both are geometrical planes within a few wavelengths. The central electrode is under the other in horizontal position. Three micrometer screws placed at the vertices of an equilateral triangle whose sides have 45mm may be displaced vertically 0,5mm, for each complete revolution produced by 30mm diameter plates fixed at the screws. The contact between the screws and the upper electrode is obtained by observing the displacement of the pointer of the bridge with its precision, and warrants to obtain the same thickness of the dielectric when it is removed; by the geometry involved if one screw turns one degree, the upper electrode raises or lowers about  $0,5 \times 10^{-3}$  mm in the central region. After getting the capacitance  $C$  of the capacitor with the dielectric, the superior plate is removed, the dielectric withdrawn, then the plate is again replaced on the screws. The capacitance  $C_0$  is measured and  $\epsilon$  determined. The technique to get the maximum precision available is easily acquired after some practice,

(A high precision permittivity...)

there are two other methods for getting with this jig.

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England.
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## INDUCED PIEZOELECTRICITY IN AMORPHOUS MATERIALS

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Although materials with high symmetry do not show true piezoelectricity, the application of a fixed electric field  $E$  causes the appearance of a strain-dependent polarization  $P$  indistinguishable from that caused by true piezoelectricity. We have shown that the complex induced piezoelectricity strain coefficient

$$e \equiv \frac{dP}{dS} = E \left( \epsilon + \frac{d\epsilon}{dS} \right) + \frac{(J+dP/dt)}{j\omega} \left( \rho + \frac{d\rho}{dS} \right)$$

for a strain  $S$  applied at a frequency  $\omega$  to a material with resistivity  $\rho$  and dielectric constant  $\epsilon$ . The constant electric field is  $E$ .  $J=E/\rho$  is the current density, and  $dP/dt$  is any polarization or depolarization current in the sample. Using a differential electrometer we have measured induced piezoelectricity for synthetic polymers ( $\omega\rho\epsilon > 1$ ) and for some natural polymers ( $\omega\rho\epsilon < 1$ ). Electric field induced piezoelectricity and current induced piezoelectricity respectively are observed in our data, and in the latter samples, a relaxation of the depolarization current is observed. The measurements yield values of some components of  $d\epsilon/ds$ ,  $d\rho/dS$  and  $dP/dt$  for comparison with those obtained by other methods.



ELECTROSTATIC COLLECTION OF  $(n,\lambda)$  RECOIL PRODUCTS IN  
AN AZEOTROPIC DIELECTRIC SYSTEM

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The possibility of electrostatically collecting nuclear recoil products in liquid dielectric targets has been previously described<sup>1</sup>. However, this effect has so far been restricted to those compounds of the target nucleus which can be prepared as a dielectric liquid, eg., methyl iodide. Obviously, this condition presents a serious restriction in as much that relatively few elements have liquid-dielectric compounds. In the work to be presented here an attempt has been made to load an azeotropic/dielectric system with a given target nucleus for instance, indium trichloride dissolved in isopropanol dissolved in carbon tetrachloride. Experimentally, the choice of indium as a target nucleus has several advantages, such as, the solubility of indium trichloride in isopropanol, the high thermal neutron cross-section for indium - 116mb, reasonable half-life ( $t_{1/2} = 54\text{min}$ ), and ease of detection. The above characteristics allow the use of a 100 mCi Am/Be neutron source having a total neutron emission of  $2.5 \times 10^5$  n/sec. The experimental arrangement consists of a round bottomed Pyrex glass container of a little over one liter capacity. The metal top of the container supports the neutron source tube, the conductivity measuring electrodes, pH electrode, stirrer and thermometer. A pair of electrodes, consisting of a cylinder and center wire, are used for the collection of  $(n,\lambda)$  recoil products. Nuclear recoil product collection efficiency is measured as a function of target nuclide concentration, conductivity, and collection voltage in the range 1 to 25 kV. The nuclear recoil process of substitution is examined and some applications of the phenomena suggested.

STUDY OF THE TRANSITIONS IN  $K_4Fe(CN)_6 \cdot 3H_2O$ 

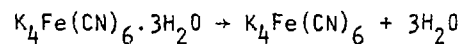
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By measuring Dielectric Constant ( $\epsilon$ ) vs. temperature and by performing Derivatography it was possible to classify this crystal as

- 1) Ferroelectric order-disorder crystal in the temperature range  $-80^\circ C$  to  $-25^\circ C$ ;
- 2) A non-ferroelectric order-disorder crystal from  $-25^\circ C$  to  $105^\circ C$ .

At  $105^\circ C$  the following reaction occurs



The  $\epsilon$  vs T curve for anhydrous salt does not show any anomaly in the temperature range  $-80^\circ C$  to  $300^\circ C$ .

## CHARGE DISSIPATION AND TRANSPORT MECHANISMS IN INSULATORS

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Charge dissipation and transport mechanisms in insulators are discussed in general, with particular emphasis on new ideas that have recently appeared in the literature. Topics treated briefly are the roles played by dielectric loss due to dipole polarization and/or carrier hopping, space charge effects, trapping, tunneling, Maxwell-Wagner effects, diffusion, thermal generation of carriers, and most of all, carrier injection in the dark. It is felt that injection is a process that has been largely overlooked in the past, and that it plays a major role in determining, for example, absorption currents, decay of charged surfaces, etc. We assume a sample with a high concentration of surface traps, and a weaker concentration in the bulk. These traps might arise from handling, oxidation, damage during charging, etc. We envision a competition at the surface between trapping and field or time-dependent charge injection into the bulk. The surface potential decay curves for polyethylene, corona charged to high and low initial potentials, cross each other. We have found that this phenomenon also occurs in Mylar, Teflon, and polystyrene, and we believe it to be a general one. Heretofore, it has remained unexplained. Neither field dependent mobilities, nor finite depth of initial charge penetration, nor any of the above mentioned non-injection processes, can explain the cross-over phenomenon. We show theoretically that field or time dependent injection predicts cross-over, and include a weak field dependence of the drift mobility. Comparisons are made between theory and experimental results on polyethylene.

PIEZOELECTRICITY AND PYROELECTRICITY IN POLY(VINYLCHLORIDE  
AND A POLY(VINYLDIFLUORIDE-TETRAFLUOROETHYLENE) COPOLYMER

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The piezoelectric and pyroelectric response in polymer electrets is explained using a model of frozen-in molecular dipoles aligned during the poling procedure. Allowing for the mutual interaction of aligned dipoles and the surrounding medium as in the Onsager cavity approach, the total polarization  $P$  is found to be  $\frac{\epsilon_{\infty} + 2}{3} \frac{N\mu_0}{V} \langle \cos \theta \rangle$ . In this expression,  $\epsilon_{\infty}$  is the dielectric constant for immobilized dipoles,  $\frac{N\mu_0}{V}$  is the number of dipoles with permanent moment  $\mu_0$  per unit volume and  $\langle \cos \theta \rangle$  is the average component of the dipole along the original poling direction. The piezoelectric and pyroelectric coefficients for an elastically isotropic medium are related to the pressure derivative of  $P$  respectively. The piezoelectric coefficient  $d_p$  for a change in hydrostatic pressure is equal to  $\beta P / \epsilon_{\infty}$  where  $\beta$  is the isothermal volume compressibility. Similarly, the pyroelectric coefficient  $p$  is approximately equal to  $P[\alpha \epsilon_{\infty} / 3 + (\Delta\phi)^2 / 2T]$  where  $\alpha$  is the volume thermal expansion coefficient,  $T$  is absolute temperature, and  $\Delta\phi$  is the RMS angular fluctuation of dipoles about a mean position. These expressions are compared with experimental results for a glassy polymer, polyvinylchloride, in which  $P$  is a linear function of the polarizing electric field and found to account well for the data.

(Piezoelectricity and pyroelectricity in...)

The above expressions are also compared with data obtained for poled samples of a copolymer of vinylidene fluoride containing 27 percent tetrafluoroethylene. Such a copolymer crystallizes in the nearly all-trans chain conformation without requiring mechanical alignment of the molecular chains. When it is assumed that the oriented dipoles lie within the crystalline regions of the polymer, the results obtained so far can be accounted for by invoking less than the predicted maximum polarization.

THERMAL STABILITY OF THE PIEZOELECTRIC EFFECT  
IN POLAR POLYMERS

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Heterocharged electret foils of the polar polymer  $PVF_2$  exhibit marked piezoelectric properties when unidirectionally stretched before poling. Other polar polymers, such as PVF, also show this effect, though to a lesser extent. Since these polymers have a low glass-rubber transition temperature, it seems doubtful whether their piezo-effect is sufficiently stable. We have therefore investigated the stability of the effect at various temperatures, an additional reason being that piezo-electric  $PVF_2$  is now commercially applied in head-phones. In this study, which was mainly aimed at  $PVF_2$ , the piezo-electric strain constant ( $d_{31}$ ) was measured along the draw axis as a function of temperature, by heating the electret at a constant rate in a thermostated tensile stress meter. The measurements were done under nearly static conditions by means of a procedure described by Broadhurst. In agreement with the results obtained by Fukada at medium frequencies, it was found that the  $d_{31}$  of  $PVF_2$  does not decay to zero at higher temperatures, but rises temporarily above its original value at room temperature. In fact, the  $d_{31}$  vs T curves were seen to exhibit two peaks. The thermal stability of piezo-electric  $PVF_2$  was also studied by isothermal measurements at high temperatures. Results on the sensitivity of a  $PVF_2$  microphone as a function of temperature will also be presented. The thermal stability of  $d_{31}$  will further be related to the stretching and poling conditions of the polymer. Obviously, such a relation cannot readily be given, because the number of process parameters involved is too large. We have therefore tried to characterize the state

(Thermal stability of the ...)

of the  $PVF_2$  film, as provoked by the stretching and poling, by means of a few relevant state parameters. The charge created by the poling process could be specified by a TSD current thermogram. The effect of the stretching process was characterized by measurement of the IR absorption bands at  $510$  and  $530\text{ cm}^{-1}$ , which give the volume ratio of the two main crystal forms of  $PVF_2$ . We also measured the optical birefringence, which quantifies the molecular orientation caused by the stretching. It will finally be shown how the state parameters can be used for choosing the most favourable conditions for formation of strongly piezo-electric foils. These parameters may also help to elucidate the molecular origin of the piezo-effect.

A 16 1

STUDIES OF CHANGES IN VALENCE ELECTRONIC STRUCTURE  
 DURING REACTIONS FORMING SOLID ORGANIC CHARGE  
 TRANSFER COMPLEXES

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The molecule tetracyanoquinodimethane (TCNQ) is a strong electron acceptor which when reacted with suitable donor species forms ionic salts that can be insulating, semiconducting, or metallic organic solids. For example, the complexes between alkali metal atoms and TCNQ are all semiconducting, while several recently made complexes of TCNQ with molecular donors, such as N-methylphenazinium (NMP) and tetrathiofulvalinium (TTF) form the first known organic metals. In all cases the reaction which forms the salt involves electron transfer from the donor to TCNQ, and the partially occupied orbitals of the TCNQ anion contribute to the electrical properties of the resulting complexed solid. Ultraviolet photoelectron spectroscopy in the range from the photoemission threshold to 12 eV has been used to investigate the occupied electronic orbitals of the insulating molecular solid composed of neutral TCNQ and to observe how these orbitals are altered when TCNQ accepts an electron to form  $TCNQ^-$ . This was accomplished by recording the emitted electron kinetic energy distributions for a solid film of TCNQ prepared in situ in ultra high vacuum, and subsequently monitoring these electron distributions while the TCNQ film was allowed to chemically react with cesium vapor to form the semiconducting solid  $C_{s2} (TCNQ)_3$ . The results indicate that the excess charge on TCNQ in solids is localized to a molecular scale and that, even for low concentrations of excess electrons, the anionic charge is not shared among neighboring sites.



A 16 :

2

(Studies of changes in valence...)

In addition large adjustments (as much as 1 eV or more) in the TCNQ occupied orbital energies take place when the molecule accepts an electron. The insights obtained from these studies will be used to explain the electronic structure of the highly conducting organic solid TTF-TCN; and to discuss the energetics of charge transfer in these systems.

PROPERTIES OF POLYSULFURNITRIDE - THE FIRST SUPER-  
CONDUCTING POLYMER

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Recently it has been possible using slow solid state polymerization to produce high quality large single crystals of the inorganic polymer of sulfur nitride,  $(\text{SN})_x$ . Unlike the cyclic sulfur nitride structures  $\text{S}_4\text{N}_4$  and  $\text{S}_2\text{N}_2$ , which form insulating molecular crystals,  $(\text{SN})_x$  is a metal at all temperatures below  $300^\circ\text{K}$ . As such it represents the first quasi-non-dimensional system which does not undergo a distortion to an insulating state upon cooling. Recently, it has been found that  $(\text{SN})_x$  becomes superconducting at  $0.3^\circ\text{K}$ , which is the first occurrence of this phenomenon in a polymer or in any material composed of only elements from the "insulating" region of the periodic table. Results will be reported on the electrical conductivity, heat capacity and optical properties of  $(\text{SN})_x$ , including studies of the anisotropy of this solid. The superconducting transition has been characterized by four-probe conductivity recorded in the Montgomery configuration, by measurement of the critical magnetic fields parallel and perpendicular to the polymer chain, and by studies of the influence of hydrostatic pressure on the transition temperature and width. The unusual properties of this polymer metal will be discussed and interpreted using the results of electronic structure calculations based on both an OPW band model and on cluster models of the molecular chains.

XEROGRAPHIC DISCHARGE OF ORTHORHOMBIC SULFUR  
SINGLE CRYSTALS\*

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The xerographic discharge of orthorhombic sulfur single crystals has been studied in the 4200-5800 Å optical range. Sulfur single crystals were grown by slow evaporation of CS<sub>2</sub> solution. Platelets of about one millimeter thickness and one square centimeter of area were prepared by ground and chemical attack in a diluted solution of CS<sub>2</sub>. On one of the broad surfaces, a black HgS contact was made by chemical reaction and on the other surface positive charge was deposited by a corona discharge in air. The samples prepared as described above were discharged by a beam of monochromatic light coming from a 1000 watts Xe-lamp through a prism monochromator and 100 Å band pass interference filters. The light was focused on the charged surface of the sample. The charge on the surface was measured in the dark and during illumination by means of a vibrating electrode using a modified Kelvin null method<sup>1</sup>. During the illumination time  $t$  the charge decayed as  $e^{-t/\tau_D}$ . The decay time  $\tau_D$  as a function of the wavelength  $\lambda$  was fitted to the theoretical relation

$$\tau_D^{-1} = \frac{|q| F \mu_h \tau_h n_h(\lambda) \alpha(\lambda)}{\epsilon (e^{\alpha(\lambda)L} - 1)}$$

(Xerographic discharge of...)

derived on the assumption that  $\tau_D^{-1}$  is proportional to the resistance and capacitance of the sample. Here  $F$  is the photon flux,  $\eta_h$  the quantum efficiency for hole generation<sup>2</sup>,  $\mu_h$  is the hole drift mobility and  $\tau_h$  is the hole lifetime.  $L$  is the sample thickness,  $\alpha$  is the absorption coefficient<sup>3</sup> and  $q$  is the electron charge. The fitting produced the value  $\mu_h \tau_h = 10^{-6} \text{ cm}^2/\text{V}$ . The electron contribution to the conductivity is neglected since  $\mu_e \tau_e \eta_e(\lambda) \ll \mu_h \tau_h \eta_h(\lambda)$  in the studied range of wavelengths<sup>3</sup>.

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DISSOCIATION OF MgO FILMS UNDER HEAT AND ELECTRON  
BOMBARDMENT AND ITS EFFECTS ON SECONDARY EMISSION

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The dissociation of MgO films produced by heat and 1000 eV electrons was studied with a quadrupole mass spectrometer. The films were prepared by oxidation of 1000 Å thick Mg films at 400°C using the isotope  $O^{18}$ . The measurements were made at a background pressure of  $10^{-9}$  torr and refer to the reproducible properties of films cleaned by a combination of Ar sputter-etching and heating in high vacuum. In the temperature range 230 to 500°C, the thermal dissociation of MgO is non-congruent, the evaporation rate of O being much greater than that of Mg. However, electron bombardment strongly enhances the evaporation of Mg, while leaving the evaporation of O unchanged. The bombardment-induced evaporation of Mg increases as the square of the current density, until it ultimately saturates at a value close to that for oxygen. Oxygen evaporates mostly as the monomer, with the ratio  $O^{36}/O^{18} = 0.1$ . In all cases, the Mg and O atoms are detected as neutrals. We have correlated changes in secondary emission under electron bombardment or under heating alone with changes in surface stoichiometry.

RADIATION INDUCED CHARGE STORAGE IN METAL-OXIDE-  
SEMICONDUCTOR DEVICES

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Oxides used as the insulating element of Metal-Oxide-Semiconducting Structures will store positive charge when exposed to ionizing radiation. This charge interacts with the free carriers in the semiconductor and alters the operating characteristics of the MOS device. In order to circumvent this problem techniques such as implantation with  $Al^+$  ions are employed. Oxides treated in this manner are found to exhibit smaller shifts in their operating characteristics when operated at room temperature under positive gate bias conditions but still to be radiation sensitive at liquid nitrogen temperatures. The techniques of thermally stimulated current, photoinjection and photodepopulation have been used to determine the electronic trap structure of both implanted and unimplanted  $SiO_2$ . Thermal annealing experiments have been performed to study the stability of these traps and the effect of their removal on the radiation sensitivity of an MOS device. A simple model has been developed to explain the equilibrium charge storage observed at both room temperature and liquid nitrogen temperature under both positive and negative gate bias.

## SPECTRAL ANALYSIS OF POLYMER ELECTRETS

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Results obtained by a spectroscopic study of polyvinylidene fluoride thermoelectrets will be described and discussed. Raman and infra-red spectroscopy study has been carried out on  $PVF_2$  and copolymer  $PVF_2$ -teflon thermoelectrets. The two crystalline forms ( and ) of  $PVF_2$  are considered as well as the effect of stretching. Polarizing fields used vary between 200 and 1600 Kv/cm formation temperature of thermoelectrets is  $80^\circ C$ .

STUDIES OF BAND STRUCTURE, EXCITONIC PROCESSES AND TRAP  
DISTRIBUTIONS IN MOLECULAR CRYSTALS\*

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Two experimental methods of determining the band structure of molecular crystals are reviewed. One involves photoemission from metal contacts into the sample under study. The other consists of first filling up bulk traps by carrier injection through an ohmic contact and then measuring the spectral yield of the photocurrent resulting from optical excitation out of the traps into conducting states of the crystal. Both methods can serve, at least in principle, as a spectrometer for monitoring the density-of-states variation in the conduction or valence band. In molecular crystals, however, the second method proved more feasible and so far useful information has been derived by its use on the band structure of anthracene. In this paper we report on recent results obtained for pyrene. The bottom of the conduction band is found to consist of a series of narrow ( $\leq 0.1$  eV) conducting sub-bands. The energy separation between adjacent sub-bands is 0.1 - 0.2 eV, as expected for splittings of a narrow, tight-binding band by molecular vibrations. This is followed by a broad, free-electron band, starting about 0.45 eV above the lowest sub-band. The derivation of these characteristics was made possible by the fact that only one discrete set of traps contributes to the spectral yield of the photocurrent in the range of interest (near threshold). At higher photon energies, other sets of traps become also involved. Here, de-trapping is mainly due to the interaction of the trapped electrons with photo-generated triplet excitons. The rate constants for this process, as well as the cross



(Studies of band structure,...)

section for direct optical excitation, were determined. The observation of electroluminescence in pyrene as obtained by double injection is also reported. The recombination radiation is characterized by a very low quantum yield ( $4 \times 10^{-3}$  photons per injected hole-electron pair). The electroluminescence spectrum differs substantially from the fluorescence spectrum (excimer emission). Possible reasons for this rather unexpected observation are discussed.

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LIGHT INDUCED IONIC POLARIZATION IN  
Pb DOPED ALKALI HALIDES

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The reorientation of ionic dipoles in their ground electronic state (g.e.s.), for instance Impurity-Vacancy dipoles in alkali halides, was extensively studied by means of various dielectric techniques. Recently reorientation was found, even at very low temperatures, when the I.V. dipoles have absorbed light, i.e., when they are in the excited electronic state (e.e.s.)<sup>(1)</sup>. This phenomenon is well known for a few anisotropic color centers, possessing an identifiable symmetry axis, such as  $F_A$ ,  $M$  and  $V_k$  centers, which change their lattice orientation after illumination with polarized light. According to Dreyfus<sup>(2)</sup>, the light induced reorientation of  $F_A$  center is due to the lowering of the reorientation energy wall in the e.e.s. (diffusion model). This scheme holds also for permanent dipoles, like I.V. dipoles which absorb light; ITC is a suitable technique to detect either a photostimulated disorientation (a) or orientation (b). At such low temperatures, when the relaxation time in the g.e.s.  $\tau = \tau_0 \exp \frac{E}{kT}$  is practically infinite in the e.e.s., it is possible either to randomize a fraction of previously frozen in polarization (a) or to induce polarization in a sample not previously polarized. In this work we have studied the heterogeneous phase present in supersaturated solutions of Pb

(light induced ionic...)

in KCl, a "Suzuki-like" phase, with stoichiometry  $6\text{KCl}\cdot\text{PbCl}_2$  and containing a large fraction of cation vacancies<sup>(3)</sup>. We were able to observe down to 78 K both orientation and disorientation phenomena induced by light absorption in the u.v. region. The ionic polarization in the g.e.s. relaxes only at relatively high temperature (278 K) and shows an orientation activation energy of 0.7 eV. The photostimulated orientation and disorientation turned out 1) to be a function of the absorbed light dose; 2) to be thermally activated, as expected if a diffusion model holds 3) to be induced with the highest yield in the spectrum range of A absorption band of Pb in KCl.

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IONIC THERMOCONDUCTIVITY IN  $\text{CdF}_2$  DOPED WITH  
TRIVALENT EUROPIUM

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The capability shown by trivalent rare-earth (R.E.) doped  $\text{CdF}_2$  to be converted from an insulator to n-type semiconductor<sup>(1)</sup> has made the study of the electrical properties of this compound attractive. From the point of view of the structure and of the lattice disorder, it is very similar to  $\text{CaF}_2$ . However, when investigations were carried out to ascertain if also  $\text{CdF}_2$  exhibits the typical dipolar defects induced by the trivalent R.E. in  $\text{CaF}_2$ , i.e. Rare-Earth-Fluorine Interstitial dipoles (RE-FI), the results showed surprisingly that this property is restricted to a given R.E., such as  $\text{Eu}^{3+}$  (2), and does not hold for other trivalent ions, such as  $\text{Gd}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{In}^{3+}$  (3) and  $\text{Y}^{3+}$  (4). In the previous work<sup>(2)</sup> our attention was focused on the identification of R.E.-F.I. dipole relaxation by means of ITC technique and on the determination of its reorientation parameters in  $\text{CdF}_2:\text{eu}$ . In the present work we have studied the whole set of ITC peaks which occur in the low temperature range (140-220K) very close to the R.E.-F.I. peak at 152.5 K. The complexity of the peak resembles more closely that of  $\text{SrF}_2:\text{Eu}^{3+}$  (5) than the simpler situation of  $\text{CaF}_2$ , and depends both on the origin of the sample and on its history. The role of the nature of contact (blocking electrodes or not) on the intensity of observed peaks is not so important as in the case of  $\text{Gd}^{3+}$  doped samples, where the use of blocking electrodes involves the suppression of ITC peaks. The relationship between peak height and polarizing electric field  $E_p$  is linear for all peaks: for the peak at 188 K linearity was checked over four

(Ionic thermoconductivity in...)

orders of magnitude of  $E_p$  up to  $\sim 3.8 \times 10^4$  V/cm. Furthermore the relative weight of various components of the complex ITC spectrum has been studied both in samples with different concentrations of  $\text{Eu}^{3+}$  and in samples submitted to different thermal treatments in order to check if solution and precipitation of impurity affect the ITC spectrum and to clarify the nature of the components.

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OFF-CENTER  $\text{Cu}^+$  IONS IN  $\text{RbCl}$  AND  $\text{RbBr}$   
STUDIED WITH IONIC THERMOCURRENTS

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It had been concluded, through several techniques, that substitutional  $\text{Cu}^+$  ions occupy off-center positions in potassium halides<sup>(1,2,3,4)</sup>, so they present electric dipole properties. We have used the ITC (Ionic Thermocurrents) technique to detect the electric dipole and to study the temperature dependence of their relaxation in rubidium halides. A modified liquid helium cryostat from Janis was used to reach lower temperature than LNT. From the integrated ITC bands we found the activation energy for reorientation of the  $\text{Cu}^+$  dipole to be 230 meV and 310 meV with maximum peak of the ITC band at 67°K and 91°K in  $\text{RbCl}$  and  $\text{RbBr}$  respectively. We also found that the relaxation time for dipole reorientation follows the classical Arrhenius rate theory. With these results we are attempting to analyse the behavior of the potential barrier as a function of the lattice parameter and in this way, to obtain a critical lattice parameter between the off-center position and the on-center position.

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EFFECT OF GAMMA RADIATION ON THE THERMOELECTRET  
STATE OF BeO\*

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The thermoelectret state of Beryllium Oxide (Brush Thermalox 995) crystals exposed to gamma radiation have been studied by the thermal depolarization current technique. The gamma exposures have been performed either before polarizing the samples or after the formation of the thermoelectret state. It was found no qualitative change in the thermal depolarization spectra of irradiated or unirradiated samples, but there is an enhancement of the induced polarization of pre-irradiated specimens relatively to the unirradiated ones. Moreover a proportionality is found between gamma radiation exposures and released charge densities. The possibilities of using BeO as thermoelectret gamma radiation dosimeter will be considered.

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DIPOLAR POINT-DEFECTS IN IONIC CRYSTALS STUDIED BY  
MEANS OF IONIC THERMOCONDUCTIVITY

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Vacancies, interstitials and aliovalent impurity ions, having an effective electric charge, interact in ionic crystals mainly through the long range Coulomb force. As a result one has complex defects, such as vacancy pairs and impurity-vacancy pairs which act as electric dipoles. The dipolar polarization due to this kind of imperfection was studied in the last few years by means of the ionic thermoconductivity method (ITC). The method consists in the measurement of the displacement current which flows when heating the crystal, previously polarized by cooling from a suitable temperature with an applied field. The current arises from the thermally activated reorientation of a set of partially aligned dipoles, to reach the random distribution. The crystal behaves as a weak thermoelectret. The analysis of the ITC diagram allows a straightforward determination of the kinetic parameters of the dipolar orientation and of the dipole concentration. For the more complex case of dipoles of different nature, the analysis has been discussed by Gross. The results obtained so far in many laboratories can be divided in two groups: 1) study of different dipoles in various ionic matrices, with the aim of determining the nature of the dipole, the activation energies for reorientation and the frequency factor; in recent years much attention has been devoted to ionic crystals where the nature of the dipolar imperfections is not as well known as in the traditional alkali halides. 2) Study of the change in dipole concentration, when the crystal undergoes significant physical treatment, such as radiation damage,



(Dipolar point-defects in ionic...)

optical excitation, thermal ageing and quenching. Thanks to its high sensitivity the ITC method allows the measurement of small changes of concentration, down to very low concentrations; through the study of the effect of thermal treatments, a substantial contribution was brought to the understanding of solution and precipitation phenomena also, in the initial stage of the process.

THE ITC SPECTRUM AND OTHER TECHNIQUES IN THE STUDY  
OF DEFECT IN IONIC SOLIDS

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The Ionic Thermal Current technique has been used to study several kinds of defects in alkali halides such as impurity vacancy dipoles due to divalent ions as  $\text{Ca}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Mn}^{++}$  etc., and off center ions such as  $\text{Cu}^{++}$ . The use of other techniques than the ITC has also been used to study the same class of defects. These techniques have been applied in order to know the surroundings of the i.v. dipole. Between these techniques are the dielectric loss, I.R. and u.v. spectroscopy, ultrasonic attenuation, etc. The information obtained from the ITC spectra and other techniques allows the understanding of several phenomena in ionic solids. The possibility of the use of ITC technique to understand phase transformations and other techniques as modulated ITC currents will be discussed.

DIELECTRIC RELAXATION OF POLAR LIQUIDS

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The dielectric response of polar liquids is discussed in the low frequency limit based on Langevin's equation. The Onsager-Kirkwood-Debye theory is reviewed. By the use of sum rules high frequency limits of the transport equation the high frequency behaviour of the dielectric function is predicted. An interpolation procedure is introduced for the dielectric function and relaxation for intermediate frequencies. A collective dipolar mode is thus predicted and the damping of this oscillation is calculated.

THE ROLE OF DIELECTRIC CONSTANT AND VISCOSITY IN THE  
THEORY OF ELECTROLYTIC SOLUTIONS

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Equivalent conductance  $\Lambda$  initially decreases as concentration  $c$  of electrolyte increases from zero. The decrease is a combination of two fundamentally different physical processes: first, short range forces cause the formation of non-conducting entities (paired ions, which in some cases may rearrange to neutral molecules) whose relative concentration increases with increasing stoichiometric concentration; and second, long range electrostatic and hydrodynamic volume forces retard the drift of the unpaired ions in an external electric field. Empirically, it can be shown that three parameters are necessary and sufficient to construct a function  $\Lambda(c)$  which reproduces observations within the experimental precision of  $\pm 0.02\%$ . The macroscopic dielectric constant  $D$  and viscosity  $\eta$  may be used in the theoretical calculation of the volume forces, which requires the solution of a fourth degree differential equation, and hence requires four boundary conditions, which, however, must not involve any short range molecular parameters. The following model permits the theoretical calculation of the desired three parameter function  $\Lambda(c; \Lambda_0, K_A, R)$ : all ions are surrounded by spheres of diameter  $R$ , outside of which the macroscopic values of  $D$  and  $\eta$  describe the medium. When an anionic and a cationic sphere overlap, the two ions are counted as a non-conducting pair. For all unpaired ions, the integral of the surrounding space charge from  $r=R$  to  $r=\infty$  equals the balancing charge required by electroneutrality. The other boundary conditions are continuity of all function at  $r=R$ , vanishing of field at  $r=\infty$  and no singularities at zero concentration. This model replaces the former unrealistic primitive model (rigid charged spheres of diameter  $a$  in a continuum described by the macroscopic  $D$  and  $\eta$  for  $r \gg a$ ) and permits treatment of short range ( $a \leq r \leq R$ )

(The role of dielectric constant...)

processes by molecular rate theory. The unsolvable problem of the meaning of dielectric constant and viscosity at distances of the order of molecular diameters is thereby eliminated.

## THERMOELECTRET PROPERTIES OF BeO\*

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Thermoelectret properties of Beryllium Oxide have been studied in the temperature range 200 - 600 C. Depolarization currents detected during thermal destruction of the thermoelectret state have been measured under different polarization conditions yielding the following main results: i) the charge densities thermally released from the BeO samples are found to be comparable to the ones obtained in other inorganic thermoelectrets ( $10^{-9}$  Coul/cm<sup>2</sup>), ii) two peaks of depolarization current have been detected and their related activation energies determined (0.47 eV and 0.65 eV) and iii) the induced polarization is uniform. These results will be discussed and a model based on thermal reorientation of impurity-vacancy dipoles will be proposed to explain the observed thermal depolarization current spectra.

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\*\* Also at the Instituto de Física of the University of São Paulo.

ANOMALY IN THE PERMITIVITY DUE TO THE THERMO-  
DIELECTRIC SPACE CHARGE

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The dielectric tensor  $\epsilon_{ij}$  has been determined in anthracene<sup>(1,2)</sup> and naphthalene<sup>(3)</sup>, the component normal to the a,b plane of naphthalene mono-crystals was  $\epsilon_{c'c'} = 3,21 \pm 0,07$ , previous determination is very discrepant: 4,2. Yet the possible influence, the Costa Ribeiro Effect<sup>(5)</sup> space charge may have, was ignored, although de Queiroz<sup>(6)</sup> had shown that capacitors with dielectric of polycrystalline plates of naphthalene impurified with  $\beta$ -naphthol could show capacitance variations of 45%, and da Fonseca<sup>(7)</sup> exposing previously the crystals to light to eliminate the space charge determined  $\epsilon_{c'c'} = 3,27$ . Nevertheless no study has been made of the evolution of  $\epsilon_{c'c'}$  with time and following a technique similar to those used in references (1,2,3). We have done this using an Autobalance Precision Bridge B331 and a specially constructed device for this measurement, both having 0.01% precision. The bisublimed naphthalene crystals showing specular surfaces parallel to the a,b plane were kept inside plastic vessels with excess naphthalene and repolished when measurements were made during three months. In the first month crystals show a little increase (maximum 0,40%) in  $\epsilon_{c'c'}$ , then a decrease (maximum 0,80%) during the rest of the period. The evolution was rapid if the crystals were submitted to light.

(Anomaly in the permittivity due to...)

The permittivity value depended on the impurity content, age and defects of the structure. The maximum initial value relatively to air, at 25°C, of one crystal, was:  $3,2634 \pm 0,0009$  which in 18 days lowered to  $3,2518 \pm 0,0012$ , and the minimum, of another,  $3,2388 \pm 0,0014$  which lowered to  $3,1986 \pm 0,0015$  in 8 days, both submitted to sunlight, the latter a very long time.

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DISCHARGE OF THE SCL CURRENT CHARGE DISTRIBUTION  
WITH SHORTED AND OPEN ELECTRODES

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The problem of one carrier free space charge motion under an applied voltage has recently been solved<sup>(1)</sup> by transforming it in a system of two ordinary differential equations from whose solution the total current can easily be derived. A very interesting case to be studied is that of the discharge of the SCL current charge distribution whose results are presented. A general theorem can be established saying that the total amount of charge circulating in the external circuit is independent of the mobility of the free carriers. Results are also presented for the case when, after complete charge, the circuit is open, the voltage decaying due to the motion of the charges in presence of the existing field.

1) Yet unpublished work; see also "One Carrier Free Space Charge Motion under Applied Voltage", L.E.Carrano de Almeida, G.F. Leal Ferreira, submitted for publication to the Revista Brasileira de Física.

NEW BONE FORMATION BY ELECTRETS<sup>§</sup>

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It has been shown that electric micro-currents stimulate fracture healing when the negative pole of a circuit is put in the fracture. On the other hand, Fukada and col. were able to produce new bone formation wrapping sheets of teflon electrets around the femurs of dogs.

In the present work negatively and positively charged pieces of plastic material were implanted in the cortex of the femur of rabbits and dogs. These cylindrical pieces had longitudinal slots cut in the periphery allowing the bone to grow into those slots. Preliminary results seem to indicate that the ingrowth of bone into the slots is enhanced by the negative charge of the plastic electret cylinders. It seems reasonable to assume the possibility of stimulating bone growth by the electric fields of charged implants.

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FAPESP

## ELECTRETS IN BIOPHYSICS AND BIOENGINEERING

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The author discusses the applications of the electret in the interdisciplinary fields of biophysics, medical physics and bioengineering. Applications in medical physics and bioengineering range from the use of electretized anti-thrombogenic surfaces to the use of very sensitive dosimeters used in radiation therapy or health physics. The presence of the electret effect in several biomaterials like bones, keratin, and various tissues is also described. In the more fundamental field of biophysics the electret effect for the understanding of basic phenomena such as charge and polarization storage in biopolymers like proteins, polysaccharides and polynucleotides. Theoretical models for the interpretation of important biophysical phenomena like neural action, membrane potentials are also discussed. In particular the electret behaviour of enzymes is discussed and its possible relation with the Fröhlich Model in which a metastable ferroelectric state is induced in enzymes. However, one of the most important results in the area is the electret behaviour of bound-water in proteins and polysaccharides. The electret behaviour of this phase is used to investigate its possible structure and organization in an ice-like phase around the biopolymer. The experimental behaviour of bound-water in cases of enzymes, hemoglobin, collagen and gelatin are described.

THERMALLY-STIMULATED CURRENT STUDIES OF CARRIER  
TRAPPING AND MOBILITY

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A study of carrier trapping and carrier mobility utilizing open-circuit and short-circuit thermally-stimulated current (TSC) techniques is reported. The experimental results were obtained on 25  $\mu\text{m}$  Teflon films charged by injection of 10 to 40 keV electrons or by application of corona or breakdown methods. Among the parameters investigated are the trap-modulated mobility in the virgin material as a function of temperature for the different trapping levels, the retrapping process, the spatial charge depth, the time-dependence of the radiation-induced conductivity, and the trapping characteristics of secondary carriers generated by irradiation. Recent experimental results and their analysis will be discussed.

FOIL-ELECTRETS AND THEIR APPLICATION

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The application of foil-electrets to electroacoustic and electromechanical transducer design and performance will be emphasized. The experimental use of foil electrets in electrophotography, air filtering, radiation dosimetry, and blood compatibility studies will also be presented. Foil-electret transducers incorporating 5 to 25  $\mu\text{m}$  polyfluoroethylenepropylene (Teflon FEP) or related materials carrying a charge from 10 to 20  $\text{nC}/\text{cm}^2$  have excellent frequency response, low distortion, small vibration sensitivity and have been used over a frequency range extending from  $10^{-3}$  to  $4 \times 10^8$  Hz. Electret transducers are presently being produced as microphones with various directivity patterns for use in amateur and studio applications, tape recorders, sound measuring instruments, operator's headsets, hearing aids, acoustic graphic tablets. Such transducers are also being made as transmitters in earphones, and as electro-mechanical transducers in phonograph pick-ups. More than 10 million such electret systems are being manufactured annually by Japan, the United States and Europe. Foil electret transducers are also used for experimental and research applications in such widely different fields as gas analysis, aeronautics, atmospheric studies, telephony, ultrasonics, acoustic imaging, data transmissions, leak detection, hydrophones and intrusion monitors.

THERMOSTIMULATED CURRENTS FROM POLY (CHLORO-  
TRIFLUORETHYLENE) ELECTRETS

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Thermostimulated current profiles were obtained for electrets of poly(chloro-  
fluorethylene) poled under various conditions of field strength, temperature  
and electrode contact. The principal current peak was located at  $145^{\circ}\text{C}$  for  
electrets poled at elevated temperature ( $100^{\circ}\text{C}$  to  $178^{\circ}\text{C}$ ) and at  $125^{\circ}$  for  
electrets poled at room ambient ( $20^{\circ}\text{C}$ ). Increase in the poling field from  
3 to 300 KV/cm produced continuous variations in the discharge current profile  
consistent with a transition from heterocharge to homocharge. Both hetero-  
charge and homocharge appeared to be released simultaneously at the principal  
current peak. Similar curves were obtained for samples poled between metal  
electrodes or corona charged.

New Result  
Sept. 1st

## COMPUTER-AIDED DESIGN OF ULTRASONIC TRANSDUCERS

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This paper presents a method developed by Martin and Sigelmann<sup>(1)</sup> to analyse the characteristics of ultrasonic transducers which operate on a single-mode vibration of a piezoelectric material (ceramic and crystals). The transducer, considered as a three-port linear device (one electrical and two mechanical), is characterized by well known<sup>(2)</sup> linear equations. From these equations a computer program was developed to calculate the input impedance of any port when the two remainder ports are loaded with arbitrary impedances. Also a computer program was developed to characterize any port as a Thevenin equivalent source, when one of the remainder ports is driven (by an electrical source if an electrical port or mechanical source if a mechanical port) and the other arbitrarily loaded. These computer programs are useful in problems of transmission and reception of ultrasonic signals, matching of transducers to loads, in obtaining dielectric, mechanical and piezoelectric constitutive constants through measurements of the transducer characteristics.

- 1) R.W.Martin and R.A.Sigelmann "Force and Electrical Thevenin Equivalent Circuits and Simulations for Thickness Mode Piezoelectric Transducers" Submitted to the Journal of the Acoustic Society.
- 2) B.A.Auld "Acoustic Fields and Waves in Solids" Vol. I Wiley Interscience, p. 333

New Result

Sept. 2nd

ULTRASONIC ATTENUATION IN FERROELECTRIC OR FERRODISTORTIVE  
PHASE TRANSITIONS. APPLICATION TO SrTiO<sub>3</sub>

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The ultrasonic attenuation of  $\sigma$  is calculated above  $T_0$  assuming: a) a non-resonant interaction between ultrasonic and critical phonons; b) a lorentzian shape for the central peak; c) a quite general form for its width

$$\gamma_{\vec{k}} = a + \sum_{i=1}^d |b_i| |k_i|^{n_i} \quad \text{where } a \rightarrow 0 \text{ if } T \rightarrow T_0;$$

d) a first-order procedure to calculate  $\sigma$ . There are two distinct regimes,  $\Omega \gg a$ , and  $\Omega \ll a$  and the  $x$ - and  $\eta$ -exponents ( $\sigma \propto \Omega^x a^{-\eta}$ ) are determined in both regimes as a function of the dimensionality  $d$  and exponents  $\{n_i\}$ . Anisotropy in  $\vec{k}$ -space is shown to be irrelevant. Comparison is made with available experimental results for SrTiO<sub>3</sub>.



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