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Large, plate-like crystals of vanadium pentoxide were grown under air atmosphere from the melt. The degree of singularity of these crystals was studied by microscopic observation between crossed Nicol prisms and by taking transmission X-ray diffraction patterns at the appropriate regions of the crystal. The results of these studies show that the part of crystal used for measurements had a high degree of single crystallinity, with at most a $\pm 4^{\circ}$ of misorientation in its layers.

These crystals were prepared into three-terminal parallel-plate capacitors. The conductance and capacitance of these capacitors were measured simultaneously in the temperature and frequency ranges of 79° to 200° K and 10^{2} to 10^{4} Hz respectively.

The evaluation of these electrical measurements indicates the presence of the Debye type of dielectric loss. Based on the Debye theory of dielectric relaxation, the relaxation times, T(T), were deduced, and the activation energy for the dipolar reorientation, H, was

determined by either the shift or the half-width method. Averaging over four crystals, the values of H and τ_{o} were 0.24 \pm 0.03 eV and 1.1 x 10⁻¹² sec respectively.

Three different possible relaxation processes were considered, and the most probable one was concluded to be the hopping of a trapped electron around a defect in a donor center. Based on the published ESR works and ESR measurements reported here for the single crystals of V_2O_5 , two models of dipolar centers, having oxide-ion vacancy or univalent interstitial impurity ion as defect, were proposed. The process and the energy of dipolar reorientation for these models were explained in terms of the small polaron theory.

ESR measurements of the crystal and calculations of the intracenter mobility and the dipolar concentration, N_0 , on the basis of the proposed models can not prove their exclusive existence. However, the possibility of simultaneous existence of both types of centers in the same crystal provides an explanation for the observed deviation from the Debye model. The values of N_0 confirm the assumption of low dipolar concentration.

For dc conduction, the activation energy, determined either from the slope of the log σ_{dc} vs T^{-1} plot or from the extrapolated curve of the linear portions of the superimposed log σ_{ac} vs T^{-1} plots for the different frequencies, is 0.27 ± 0.01 eV. The ionization energy of the charge carrier from the donor center is shown to be approximately 0.54 ± 0.02 eV. After ionization from the donor center, the electron moves through the crystal lattice via a dominant process of nonthermally activated tunneling.

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by

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DEDICATION

To my parents,

Mr. & Mrs. Frank K. Mar

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DIELECTRIC RELAXATION IN CRYSTALLINE V205

I. INTRODUCTION

In the last two decades much interest has been shown in the electronic properties of the transition metal oxides. The wide range of possible valence for these oxides suggests a great variety of energy band structures and transport processes. For instance, at room temperature eleven oxides of vanadium have been observed (2); electrically, V_2O_5 , the highest oxidation state of vanadium, is a semiconductor, and V_2O_3 , a lower oxide, is a metallic conductor.

Early researches on the mechanism of electrical conduction of the transition metal oxides, mainly in NiO, indicated that an appreciable conductivity can only be achieved by the introduction of cations with different valency at the crystallographically equivalent lattice points (55). This situation can be attained by introducing a deviation from stoichiometry or by incorporating in the lattice the appropriate foreign ions through a method of controlled valency. Subsequent work on either doped or reduced samples of NiO and other transition metal oxides showed that the drift mobility, μ_D , of the free carrier at room temperature has an exceptionally low value, which increases exponentially with temperature. These features of μ_D can not be explained by the band model of a solid, and the small polaron theory was developed by Yamashita and Kurosawa (62) and Holstein (25).

Fröhlich, Machlup, and Mitra (18) have shown that substances which exhibit Debye type of dielectric loss due to electrons in the bulk would also have very low electronic mobility. In substances such as ionic crystals, for example the oxides, containing positive ions with relatively high ionic charge, conditions are favorable for a breakdown of the band model. In these materials, the lattice imperfection which attracts electrons may lead to Debye type of dielectric loss because the electron can then be localized near any equivalent ion around the defect. The jumping probability between these states should show some deviation from those of an electron not bound to the defects because of the defect's influence on the wave function. Thus, the properties and the nature of the bound electron around a defect can be studied through dielectric relaxation measurements.

Due to the high oxidation state of vanadium, V_2O_5 seems to be a good test case to confirm the simultaneous existence of low electronic mobility and of Debye type of loss due to a localized electron around a defect. ESR spectra of V_2O_5 single crystals, which were grown from material of various degrees of purity and under either air or oxygen atmosphere have been interpreted as arising from an electron associated with either an oxygen vacancy (19) or an impurity ion (29).

McCulloch (37) estimated a value of 0.4 cm²/volt sec at room temperature as the upper bound of the Hall mobility, $\mu_{\rm H}$. According to Bosman and Van Daal (8), for a non-adiabatic, multi-phonon hopping process in the presence of strong electron-lattice coupling,

2

both μ_D and μ_H increase exponentially with temperature. However, the activation energy for μ_H is three times smaller than that of μ_D . Hence, V_2O_5 is undoubtedly a substance with low electronic mobility.

In addition, previous work in this laboratory has developed a method to grow V_2O_5 crystals with high degree of single crystallinity. Single crystal has a distinct advantage over the sintered samples in the interpretation of the dielectric relaxation data because the effect of Maxwell-Wagner type of relaxation in the single crystal is minimized.

II. CLASSICAL THEORY OF DIELECTRIC DIPOLAR RELAXATION

Macroscopic Description of the System

The measurements of permittivity and dielectric loss of a dielectric material can be made simultaneously by introducing the material into a parallel-plate capacitor which forms a part of an electrical circuit. This circuit is then connected to a signal generator, and the application of a voltage across the capacitor will generate an electric field in the dielectric material. The material responds by becoming polarized.

The displacement of charges connected with the polarization usually shows some inertia; therefore, two field quantities are required to describe the electric field inside the dielectric. These two field quantities are usually \vec{E} , the electric field strength, and \vec{D} , the electric displacement. For a continuous application of sinusoidal ac voltage, after a certain length of time \vec{E} will become sinusoidal, and it can be expressed, in complex notation, as

$$\vec{E}(\omega, t) = \vec{E}_{o} \exp(-i\omega t)$$

or as

$$E(\omega, t) = E_0 \cos \omega t$$

when only the real part is considered. The angular frequency ω is normally in rad/sec, and correspondingly the time t is in sec. Also, \vec{D} will become sinusoidal; however, it will not necessarily be in phase

(2, 1)

with \vec{E} . Therefore, \vec{D} can also be expressed as

$$\vec{D}(\omega t) = \vec{D}_{o} \exp[-i(\omega t - \delta)], \text{ or}$$

$$\vec{D}(\omega, t) = \vec{D}_{o} \cos(\omega t - \delta)$$
(2.2)

where δ is the phaseshift between \vec{E} and \vec{D} . These two field quantities are correlated through the expression

$$\vec{D}(\omega, t) = \underbrace{\boldsymbol{\varepsilon}}^{*} \vec{E}(\omega, t) , \qquad (2.3)$$

$$\vec{\mathbf{D}} = \vec{\mathbf{E}} + 4 \pi \vec{\mathbf{P}}. \qquad (2.4)$$

The Equation (2.3) is in the most general form, and simplication can be introduced through consideration of the crystal structure and experimental conditions. Therefore, for an orthorhombic crystal with the applied electric field parallel to the \vec{b} -crystallographic axis, $\vec{\epsilon}^*$ becomes a scalar quantity and is designated as $\vec{\epsilon}^*_{\vec{b}}$ or just $\vec{\epsilon}^*$ when no other crystallographic direction is considered. Expressing it in complex notation,

$$\epsilon^* = \epsilon_1 + i\epsilon_2 \tag{2.5}$$

where ϵ_1 and ϵ_2 are known respectively as the real and the imaginary dielectric constant. The asterisk here, and later, indicates a complex quantity. All field quantities parallel to the b-axis will be represented later by the symbol without the arrow. Expanding Equation (2.3), considering only the real parts and equating the resulting

expressions to the real parts of Equation (2.2), one finds

$$\epsilon_1 = \frac{D_0}{E_0} \cos \delta$$
, and (2.6)

$$\epsilon_2 = \frac{D_o}{E_o} \sin \delta$$
 (2.7)

Both D_o/E_o and δ can be functions of ω and temperature, T; hence, ϵ_1 and ϵ_2 can vary with ω and T.

For this investigation, the dielectric constants ϵ_1 and ϵ_2 are related to the experimentally measurable quantities, capacitance $C(\omega, T)$ and specific dielectric conductivity $\sigma_{diel}(\omega, T)$, through these expressions:

$$C(\omega, T) = \epsilon_{1}(\omega, T) \epsilon_{o d}$$
(2.8)

$$\mathcal{O}_{\text{diel}}(\omega, T) = \omega \epsilon_0 \epsilon_2(\omega, T)$$
(2.9)

where ϵ_0 is the permittivity of free space, A is the area of the capacitor plates, and d is the separation between the two plates with the geometric condition that the dimensions of the plate are much greater than d. It will be shown later that only ϵ_2 gives information on the relaxation process.

All materials conduct electricity, and the application of an electric field will cause current to flow. For constant ω , the total current density J(t, T) for a dielectric in a time-dependent field and at temperature T is

$$J(t, T) = J_{D}(t, T) + J_{c}(T)$$
 (2.10)

where $J_c(T)$ is a conduction current due to electronic or ionic carriers, and $J_D(t, T)$ is the displacement or dipolar current density. If the conduction current behaves according to Maxwell's equations, and if the contacts between the dielectric and electrodes are ohmic,

div
$$J_c = 0$$
, and
$$\left[\frac{\partial D(t,T)}{\partial t}\right]_{T,\omega} = J_D(t,T)$$

If the contacts between the dielectric and the electrodes are nonohmic, a part of the electronic or ionic carriers which contribute to conduction piles up at the electrodes. This build-up of space charge will in turn oppose the flow of current. Then $J_c(T)$ will decrease with time until a value $J_s(T)$, the steady-state current density, is reached, and

 $\operatorname{div} J_{e}(T) = 0$

Then Equation (2.10) becomes

$$J(t, T) = J_{D}(t, T) + J_{i}(t, T) + J_{s}(T)$$
 (2.11)

where $J_i(t, T)$ is due to conduction in the dielectric associated with the build-up of space charges at the electrodes or at the ends of some internal conduction paths which do not reach the electrodes. The quantities $J_D(t, T)$ and $J_i(t, T)$ can not be separated from each other under the experimental conditions of this investigation. Then,

$$\left[\frac{\partial D(t,T)}{\partial t}\right]_{T,\omega} = J_D(t,T) + J_i(t,T). \qquad (2.12)$$

Relaxation in a Model Electrical Circuit

When a dielectric is made into a parallel plate capacitor, and a time dependent voltage V(t) is applied across the two plates, the charge Q on the plates will vary with time, and a current I will flow. Electrically, dielectric relaxation is concerned with the timing of electrical response, that is with the relationships of V(t), Q(t), and I(t). For dielectric relaxation, these relationships obey the same mathematical formalism as the relationship of V(t), Q(t), and I(t) for the passive electrical networks. One of the simplest of these networks that is often employed to represent a capacitor with a high degree of leakage as a pure capacitor and a pure resistor in parallel connection. The electrical impedance $Z^*(\omega)$ for this R-C parallel circuit is

$$Z^{*}(\omega) = \frac{R_{P}}{1 + i\omega C_{P}R_{P}} , \qquad (2.13)$$

where C_p and R_p represent the pure capacitance and resistance in parallel. For this investigation, the observed quantities are the currents through R_p and C_p , denoted by I_{R_p} (t) and I_{C_p} (t); the total current flow at time t due to applied a.c. voltage $V^*(t)$ is

$$I^{*}(t) = I_{R_{p}}(t) + I^{*}_{C_{p}}(t) = \frac{V^{*}(t)}{R_{p}} + C_{p}\frac{dV^{*}(t)}{dt}$$

for constant ω and at a given temperature. This expression can be converted into an expression, which is physically more representative of the system of this investigation, by using the relations

$$V^{*}(t) = I^{*}(t)Z^{*}(\omega) , \text{ and}$$
$$\frac{dV^{*}(t)}{dt} = Z(\omega) \frac{dI^{*}(t)}{dt}$$

The resulting expression is

$$R_{p}V^{*}(t) = I^{*}(t) + C_{p}R_{p}\frac{dI^{*}(t)}{dt}$$

This is in the form of a characteristic linear differential equation for a relaxing system. The general form of such an equation is

$$\tau \frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t} + \mathbf{x} = \mathbf{y} \tag{2.14}$$

where y is the stimulating force, x is the response, and τ is the relaxation time which characterizes the process.

Thermodynamical Considerations of Dielectric Relaxation

The equilibrium thermodynamics does not by itself give information on relaxation, because relaxation is a process involving the approach to equilibrium of a system which is initially out of thermodynamical equilibrium. The extent to which the system is out of equilibrium will determine the rate at which entropy is created in the system, and this rate of creation of entropy can be studied by the methods of irreversible thermodynamics. Irreversible thermodynamics operates on a system of forces, or stimuli, and fluxes, or responses. For dielectric relaxation, the stimulus is the electric field, and the responses are the delayed polarization and the current flow. The effect due to the electric field is small enough that it can be considered as a slight perturbation on the thermal equilibrium of the dielectric system. Hence, the equilibrium thermodynamic functions in the system are still defined within close limits.

An energy term relating to the change of entropy is TdS; under the influence of a time dependent field it will become $T\frac{dS}{dt}$, the rate of dissipation of energy. Correlating the thermodynamical and the electrical notions of the rate of energy dissipation, the expression

$$\frac{-T \frac{dS}{dt}}{\text{unit volume of}} = \vec{E}(t) \cdot \vec{J}(t, T)$$

is formulated. For periodic field $E(t) = E_0 \cos \omega t$ and J(t, T) is given by Equation (2.10). On averaging over a cycle of time, W, the power dissipated per volume of dielectric, can be expressed as

$$W(\omega, T) = -\frac{\omega}{2\pi} \int_{0}^{2\pi} T \frac{\partial S}{\partial t} dt = \frac{\omega}{2\pi} \int_{0}^{2\pi} (E \cos \omega t) (J_{s} + \frac{\partial D(t T)}{\partial t}]_{T, \omega} dt$$
(2.15)

for constant ω and T. Combining Equations (2.2), (2.6), and (2.7), the resulting expression is

$$D(t) = \epsilon_1 E_0 \cos \omega t + \epsilon_2 E \sin \omega t$$

and the derivative of it with respect to t gives

$$\begin{bmatrix} \frac{\partial D(t)}{\partial t} \end{bmatrix}_{T,\omega}^{T} = -\epsilon_{1}E_{0}\omega\sin\omega t + \epsilon_{2}E_{0}\omega\cos\omega t \qquad (2.16)$$

Substituting Equation (2.16) and the relation

$$Js(T) = O_{dc}(T) E$$

into Equation (2.15), the resulting equation can be easily integrated to yield

$$W(\omega, T) = \frac{\sigma_{dc} E_{o}^{2}}{2\pi} [\pi] + \frac{\omega \epsilon_{o} \epsilon_{1} E_{o}^{2}}{2\pi} [o] + \frac{\omega \epsilon_{o} \epsilon_{2} E_{o}^{2}}{2\pi} [\pi] (2.17)$$

This result indicates that the dissipated power per unit volume of dielectric is related to the imaginary dielectric constant. Equation (2.17) can be expressed as

$$W(\omega, T) = \left[\sigma_{dc}(T) + \sigma_{diel}(\omega, T)\right] \frac{E_o^2}{2} = \sigma_{ac}(\omega, T) \frac{E_o^2}{2} \qquad (2.18)$$

through the use of Equation (2.9) and the relation

$$\sigma_{ac}(\omega, T) = \sigma_{dc}(T) + \sigma_{diel}(\omega, T).$$

A linear differential equation having relaxation characteristics can be derived from the principles of irreversible thermodynamics. The polarization P(t) of the dielectric will become time dependent after the continuous application of an ac field E(t) across the dielectric for some time which is long comparing to T. If P_s is the equilibrium polarization, P_s - P(t) represents the extent to which the system is out of equilibrium. It is usual to assume that $\frac{dP(t)}{dt}$ is proportional to P_s - P(t) and in mathematical form,

$$\tau \frac{\mathrm{dP}(t)}{\mathrm{dt}} = P_{s} - P(t)$$

where T, the relaxation time is here viewed as a proportionality constant.

Molecular Model with a Single Relaxation Time

Charge Displacements and Polarization

A dielectric substance can be considered as consisting of charged particles with charges e. If the substance contains no net charge, $\sum_{i=1}^{n} e_i = 0$. Under the influence of an electric field, these charged particles will undergo a certain degree of displacement from their equilibrium positions. For a dielectric there are, in general, two characteristic types of charge displacement: 1. the displaced charged particle is bound elastically to an equilibrium position; and 2. a charged particle has several equilibrium positions each of which it occupies with a probability which depends on the strength of an external field. The elastic type of charge displacement characterizes the atomic polarization and ionic displacement under the influence of periodic field of low frequency. Here, the term "atomic polarization" is used in order to avoid possible confusion with the hopping electronic displacement which will be introduced later. The models of displacing a charged particle to another equilibrium position are often used to explain the behavior of dipolar relaxation.

Polarization $\overrightarrow{P}(t)$ is the macroscopic field quantity which has a direct relation with a microscopic property, the dipole moment, for it is defined as the net dipole moment per unit volume of dielectric. The dipole moment $\overrightarrow{\mu}$ of a charge e, bound to a fixed point of opposite charge is defined by a vector

$$\mathbf{\hat{\mu}} = \mathbf{e}_{\mathbf{i}} \mathbf{\hat{l}}_{\mathbf{i}}$$
(2.19)

if 1_i is the radius vector from the fixed point to e_i .

Description of the Bistable Model

The simplest and the most often used molecular model for the case of charge displacement to another equilibrium position is the bistable model. This model assumes that a particle of charge e_i may be located in one of the two available sites, 1 or 2, at a distance of b apart. These sites are defined as minima of the potential energy, and they are separated by a potential barrier of height H. Figure 1 shows the potential energy as a function of distance: the solid and the dashed lines indicate the absence and the presence of an applied field \vec{E} respectively. According to Equation (2.19), the magnitude of the dipole moment for this model is

$\mu = 1/2 \text{ eb}$

when the charge opposite to e_i is located at x = o. This microscopic assembly of bistable dipoles are imagined to be in a heat reservoir which consists of spontaneously active particles. These particles exchange energy with each other and with the dipoles through the process of collision.



Figure 1. Bistable model: the potential energy as function of distance. The solid and dashed lines indicate the absence and the presence of an applied field $E(t_1)$ respectively

$$\phi_1 = \phi_2 = \frac{1}{2} e b E(t_1)$$

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Debye Equations from the Bistable Model

In the absence of an applied electric field $\vec{E}(t)$, statistically an equal number of the dipoles will oscillate about each of the equilibrium positions and will constantly collide with the active particles. The average thermal energy of these dipoles is of the order of kT where k is the Boltzmann constant. From statistical thermodynamics, W_{12} , the frequency or the probability of a dipole to change orientation from 1 to 2, is small if H>> kT, and the same can be said about W_{21} . At equilibrium

$$W_{12} = W_{21} = A_{1} \exp^{-H/kT} = W$$
 (2.20)

where A_{l} is a factor which may or may not be dependent on temperature. Under the influence of $\vec{E}(t)$ and at the moment when $t = t_{l}$ with the field in site l direction, the potential energy of each site will be changed slightly, and the total change between the two sites will be

$$\phi_2 + \phi_1 = e b E_1(t_1) = 2\mu E(t_1)$$

by assuming all dipoles are either parallel or anti-parallel to the applied field. The frequency of jump in both directions will be effected, and they are now given by

$$W_{12} = A_1 \exp\left[\frac{-H + \mu E(t_1)}{kT}\right], \text{ and}$$
$$W_{21} = A_1 \exp\left[\frac{-H - \mu E(t_1)}{kT}\right].$$

These expressions can be simplified by assuming $kT \gg \mu E(t_1)$; expanding the exponentials and retaining only the first two terms, these expressions are resulted

$$W_{12} = W \left[1 + \frac{\mu E(t_1)}{kT} \right] \text{ and}$$
$$W_{21} = W \left[1 - \frac{\mu E(t_1)}{kT} \right].$$

Based on the fact that the change in dipolar density occupancy of site 1, N_1 , is equal to the difference of outflow to 2 and inflow from 2, the generalized time dependence of the difference in occupancy of the two sites, $N_1 - N_2$, can be expressed as

$$1/2 \frac{d(N_1 - N_2)}{dt} = -N_1 W_{12} + N_2 W_{21}$$
 (2.21)

Substituting the derived expressions for W_{12} and W_{21} and multiplying through by μ , Equation (2.21) will become

$$T_{\rm D} \frac{dP_{\rm D}(t)}{dt} + P_{\rm D}(t) = \frac{N\mu^2}{kT} E(t)$$
 (2.22)

where P_D is defined as $\mu(N_1 - N_2)$. Equation (2.22) is now in the form of the characteristic linear differential equation for a single relaxation process. In this expression, T_D is the time constant for the relaxation process which is dependent on temperature only. Mathematically, T_D is given by

$$\tau_{\rm D} = \frac{1}{2W} = \frac{1}{2A_{\rm l}} \exp(H/kT) = \tau_{\rm o} \exp(\frac{H}{kT})$$
 (2.23)

where τ_0 may also be temperature dependent, but H is assumed to be temperature independent.

Considering Equation (2.22), if the right hand side is equal to zero, the resulting equation can be solved for $P_D(t)$, and it is found to be proportional to $\exp(-t/\tau_D)$. Physically, this resembles the decay of $P_D(t)$ for an equilibrium system when the field is suddenly removed. Therefore, a polarization decay function, X (t), is defined in the form of

$$X(t) = C \exp(-t/\tau_D)$$
 (2.24)

where C is a proportionality constant.

The solution of Equation (2.22) in terms of the quantities relating to the experimental measurements is

$$\epsilon^* - \epsilon_{\infty} = \frac{\epsilon - \epsilon_{\infty}}{1 - i\omega \tau_{D}}$$
(2.25)

Equating the corresponding (real and imaginary) components of both side of Equation (2. 25), the results are the two Debye equations

$$\epsilon_1(\omega) - \epsilon_{\infty} = \frac{\epsilon_s - \epsilon_{\infty}}{1 + \omega^2 \tau_D^2}$$
, and (2.26)

$$\epsilon_{2}(\omega) = \frac{(\epsilon_{s} - \epsilon_{\omega})\omega \tau_{D}}{1 + \omega^{2} \tau_{D}^{2}}, \qquad (2.27)$$

where ϵ_s is the static dielectric constant and ϵ_{∞} is the real dielectric constant measured at a frequency much greater than that of the dipolar

reorientation. It should be emphasized that the basic assumptions for the derivation of these Debye equations are low dipole concentration and constant activation energy for the dipolar reorientation process.

III. THEORY OF DEBYE TYPE OF RELAXATION LOSS DUE TO TRAPPED ELECTRONS

Description of the Center

The described classical microscopic model would encounter difficulties when it is used to explain the observed Debye type of dielectric loss, which was attributed to trapped electrons, in certain ionic crystals. Fröhlich (16) proposed a structural unit, known as the <u>center</u>, corresponding to the classical dipolar unit. This center is a charge carrier, electron or hole, which is trapped in the field of a crystalline defect or of an impurity atom or ion. He then proceeded to investigate the condition that must be imposed on the center, in order to have Debye loss.

The two basic requirements for Debye loss are: 1. at least two available levels, transitions between which result in the reorientation of the electric moment of the center and 2. a spread of these energy levels of the order of kT or less. The second condition guarantees that the electron may be considered localized on a given ion. According to Fröhlich (16) and Sewell (50), strong electron-phonon coupling tends to reduce the spread of energy levels. Compared to the spread in the absence of the coupling, the reduction is by a factor of the order of

$$F = \exp(-\Delta^2/\alpha^2)$$

where Δ is the displacement of an ion due to a neighboring electron, and α is the ion's zero point amplitude. If the condition F << 1 is fulfilled, the electron would behave quasi-classically, in the sense that it can be assumed localized at a positive ion near a defect with a chance of jumping to an equivalent neighboring positive ion.

Electronic Hopping Model

Fröhlich, Machlup, and Mitra (18) quantitatively proposed the electronic hopping model through outlining the relevant theoretical methods of calculation. The following qualitative physical interpretations from these theoretical considerations were drawn by the authors. The strong electron-phonon interaction causes displacement of the neighboring ions of the defect, and the results of this displacement are the decrease of the probability of charge transfer through tunneling process and the increase of the probability of the phonon collision assisted jumping process. The localized electronic wave functions become relatively stable, and they consist of relatively small electronic orbits centered on a positive ion. Jumping of the electron to a neighboring positive ion must be accompanied by a The transition corresponding change in the lattice displacement. matrix elements were shown to depend in a sensitive way on the distance between the ion on which the electron is centered and its neighbors; a distance which is influenced by temperature.

Sewell (51) considers a simple idealized two-sites model with small polaron properties. For this model, the exact transport properties were calculated quantum mechanically. The derived polarization response function to an applied classical periodic field is

$$K(t) = -\frac{e_{0}^{2} a}{kT} \frac{d}{dt} \left[\exp(-\gamma t) \cos \Omega t \right]$$
(3.1)

where e_0 is the electronic charge, a is half of the direct distance separating the two sites, γ is twice the polaron jump frequency between the two sites, and Ω is its tunneling frequency. He defined a critical temperature, T_c , such that if $T > T_c$, the exponential term will dominate. Then, Equation (3.1) becomes

$$K(t) = \frac{e_{o}^{2}a^{2}}{\gamma kT} \exp(-\gamma t) \qquad (3.2)$$

Comparing this expression to Equation (2.24), the quantum mechanically derived K(t) and the classically defined X(t) are in the similar form. Therefore, Sewell concluded that his model shows the features of Debye relaxation at temperature $T > T_c$. Hence, the classical Debye equations can be used to describe the dielectric properties of the crystal which are due to the small polarons in the field of defects.

Polarization Mechanism

Klinger and Blakher (32) made an extensive study on the polarization mechanism of absorption of electromagnetic waves by small polaron. Their center consists of a central impurity ion or vacancy

with z equivalent nearest neighbors. The ground state energy levels of the charge carrier of the center are split by the presence of the field-induced polarization current within the center. The energy split, W_{D} , between the neighboring sites of the center is small compared to kT. Quantum mechanical calculations were made with a single particle Hamiltonian which describes the linear coupling of the charge carrier with some boson collective excitation. The constructed wave functions were the ortho-normal localized states which also described the Bloch-type coherent tunneling motion through zsites. The calculation was done with z = 2. Kubo's fluctuation dissipation theorem, which was also used by Sewell, was used to correlate the time dependence of the spontaneous thermal fluctuations of the dipole. The derived time corrector K(t) is in the same form as the response function derived by Sewell from the hopping mechanism. The calculated results show that for this polarization mechanism, the system will display an absorption peak of Debye-type at "high" temperature.

Dipolar Center Without Small-Polaron Formation

According to Sussmann (54), Debye relaxation loss can occur in a rigid or near rigid lattice providing the dipolar center meets a certain symmetry condition. Similarly, in this model, the element that binds the electron to the center is either a vacancy or a
substitutional impurity atom. The trapped electron is described by a linear combination of atomic orbitals centered on the nearest neighbors to the vacancy or on the impurity atom and its nearest neighbors. In relation to the binding element, when there are three equidistant nearest neighbors or four equidistant nearest neighbors, tetrahedrally disposed, the electric dipole states will exist. These states could be the ground degenerate states of the trapped electron.

In an electric field, transition between dipole directions are caused by optical accoustical phonon scattering processes. At temperatures greater than the Debye temperature, θ_D , both scattering mechanisms will lead to $\tau \alpha T^{-2}$. At $T < \theta_D$, the acoustical phonon and the optical-phonon scatterings will lead to the relations that τ is proportional to T^{-7} and to exp (E_{op}/kT) respectively where E_{op} is the minimum optical phonon energy for the crystal lattice of interest.

IV. EXPERIMENTAL

Preparation: from V₂O₅ Powder to V₂O₅ Capacitor

Crystals Grown from the Melt

The crystals used in this study were grown from the melt in an air atmosphere using a modified method which was originally due to Arsen'eva and Kurchatov (3) and was supplied to this laboratory by Boros in a private communication. The starting powder was the certified reagent grade powder, claiming an assay content of 100.4% V_2O_5 , from Fisher Scientific Company; the Company's analysis also revealed 0.005% chloride and 0.008% iron. This powder was packed into a round platinum crucible whose diameter was about four centi-This platinum crucible was cemented in an Alundum crucible meters. placed in a Hevi-Duty type 86 furnace. The temperature within the furnace was monitored by a chromel-alumel thermocouple which was in contact with the inside rim of the Alundum crucible. The furnace temperature was regulated and recorded by a Leeds and Northrup Micromax recording potentiometer. The system was designed such that when a relay was in the "off" position some current was still heating the furnace due to a resistance in parallel with the relay. This provided a more stable temperature control in the furnace than a simple "on-off" arrangement.

The powder V_2O_5 was heated to its observed melting point of 680° C. After the oxide was completely melted, the melt was then seeded with a small piece of microtome shaving from a previously The placing of the seed was usually aimed at the grown crystal. center of the platinum crucible where the temperature was the lowest. Immediately after seeding, the melt generally solidified rapidly around the seed due to the sudden drop in temperature, because heat was lost through convection when the cover pieces of the furnace opening were removed for seeding. The cover pieces were replaced and arranged to allow minimal heat loss, but to allow observation of the crystal growth. The temperature of the melt was then raised very slowly to melt all the solidified mass except a small single crystallite. When a very small single seed was obtained, the temperature of the furnace would then be held constant for about 20 minutes before cooling at an approximate rate of 1° C per every five minutes by changing the controller setting initially and by shifting the cover pieces to allow more heat loss through convection at the later stage of the growth. The crystal was allowed to grow to an approximate size of 20 X 15 mm before it was lifted out of the melt with a stainless steel spatula. The spatula was dipped into the melt near the grown crystal which become quickly frozen onto the spatula along with the melt surrounding the spatula.

During all the time in the growing process, the crystal was floating at the surface of the melt. Perhaps it was being held by the surface tension of the melt. The crystals grew with the (010) crystallographic plane parallel to the surface of the melt. The c-axis direction grew faster than the a-axis direction, especially so when the cooling rate was high. Initially, the habit of the small crystallite was a distorted hexagonal plate, the distortion being elongation of the edges parallel to the c-axes. As the crystal grew, the four short edges would round off into two arc-like edges. The grown crystals had a dark red-brown color with a platelet, layer type of structure, and the surfaces of the (010) plane were highly reflective. The latter observation was also true for the other plane surfaces inside the crystal when a good cleavage perpendicular to the b-axis was obtained.

Singularity of the Grown Crystal

Considering the size of the grown crystal, it would be a difficult task for proving its singularity in the sense of the idealized definition. X-ray diffraction patterns of a small crystal showed that V_2O_5 belongs to the orthorhombic crystal system. (4, 10) Since the grown crystals are transparent to white light, microscopic study using polarized light is feasible. Under microscopic observation between crossed Nicol prisms, a transparent anisotropic substance.

such as an orthorhombic crystal, will appear colored in most positions and only in certain definite orientations will become dark like the crossed Nicol field, or extinguish. Using low magnification, the microtomed crystal of an approximate uniform thickness for capacitance measurement was placed on a microscope slide, which was in turn mounted on the rotating stage of the microscope. The stage was rotated until an extinction position was located. Considering this as the initial position, the stage was rotated again to locate the other extinction positions, and three other extinction positions were found before return to the initial position. The angular difference between the consecutive extinction positions was always 90°, and the extinction is sharp to within $\pm 4^{\circ}$ for the whole crystal. The sharpness of the extinction indicates that layers or the platelets were packed with not more than $\pm 4^{\circ}$ of misorientation for the regions where a clear alternation of illumination and extinction existed. Most of the crystals used in this investigation were studied microscopically between crossed Nicol prisms after microtoming and before gold evaporation. The location of the guarded electrode was usually at the part of the crystal surface where a clear alternation of nearly complete, uniform illumination and extinction was observed.

The most conclusive evidence of singularity of a crystal is shown by its X-ray transmission diffraction pattern. This pattern indicates not only the degree of crystallinity but also the crystal symmetry with respect to the axis of oscillation. However, due to the smallness of the cross-section of the X-ray beam, in the order of 0.5 to 1.0 mm in diameter, this method is actually not suitable for a large crystal because conclusive information is obtained only for the region where the beam penetrated. However, combining the knowledge gained from polarizing microscopy observation and from X-ray sampling of the appropriate representative parts of a region of the large crystal, the degree of single crystallinity of the sampled region can possibly be inferred with some certainty.

An ordinary melt-grown crystal which was microtomed to an approximate uniform thickness of 0.52 mm was clamped to a goniometer head for oscillation around the c-axis. The source of radiation was a molybdenum-target tube, and a zirconium filter was used when monochromatic radiation was desired. The diffracted radiation struck a luminescent screen, and the pattern was then recorded on a Polaroid type 57 camera using 3000 speed film after the X-ray was turned off. For unfiltered radiation, the crystal was irradiated for approximately one minute; it was oscillated around the c-axis with an amplitude of $\pm 20^{\circ}$. When the crystal was irradiated with filtered radiation, both the time of irradiation and the angle of oscillation were increased to approximately 2 minutes and to $\pm 30^{\circ}$ respectively. Figure 2 shows a film recording of a diffraction pattern of filtered radiation. The presence of distinguishable spots and well defined diffraction pattern



Figure 2. Transmission X-ray diffraction pattern. The source of radiation was Mo - K_{α} , and the crystal was oscillating around c-axis with an amplitude of $\pm 30^{\circ}$.

indicates the existence of a well ordered crystal. The evidence for the existence of a mirror plane perpendicular to the c-axis is revealed by the pattern. The comparatively large spot size can be explained by the thickness of the crystal. The lattice constant along the c-axis can be calculated from an expression for a perpendicular incident beam (9)

$$l_{c} = \frac{n\lambda}{\sin \tan^{-1}(y_{n}/r)}$$
(4.1)

where l_{c} is the lattice constant, n is the order of lattice reflection, $\boldsymbol{\lambda}$ is the wavelength of the radiation, \boldsymbol{y}_n is the distance measured on the film between the zeroth and the nth levels, and r is the distance between the camera and the crystal. The calculated lattice constant, c = 3.58 Å, agrees well with the reported value of 3.563 Å (4) from analysis of a small crystal. Figure 3 illustrates the different locations on the crystal surface at which transmission X-ray diffraction photographs were taken. All of the photographs display an almost identically well-defined pattern. Position (5) was actually near the center of the original crystal. The photograph in Figure 2 was taken at position (4). The distances between locations (5) and (2) and between locations (1) and (4) exceeded 0.5 cm. Hence, both the microscopic examinations between crossed Nicol prisms and the transmission X-ray diffraction patterns gave strong indications that the region of the crystal between the guarded and the unguarded electrodes have



Figure 3. The locations on the crystal surface at which transmission X-ray diffraction photographs were taken.



Figure 4. Three-terminal capacitor: 1. Guarded electrode, 2. Guard electrode, and 3. Unguarded electrode.

a high degree of single crystallinity, with not more than a $\pm 4^{\circ}$ misorientation in its layer.

Geometry of the Capacitor

The use of Equation (2.8) imposed two geometrical constraints on the capacitor, and they are: 1. the plates, or the electrodes, of the capacitor must be parallel to each other; and 2. the dimension of the smaller plate must be much greater than the separation of the two parallel plates. The second constraint will be less important when the edge effect is minimized by a guard electrode. Parallel plates implies as near uniform thickness as possible for the crystal. To achieve this condition, an American Optical Company microtome model 86C was used to slice the crystal. This instrument allowed a parallel alignment between the cutting edge of the razor blade and the surface of the pedestal upon which the crystal rested.

Since the observed growth mechanism of the crystal is by the formation of a new layer or the addition to the formed layers, the large smooth surface of the crystal, as grown, was assumed to be nearly planar. The back side of the crystal was shaved first by mounting the crystal on a microscope slide with Apiezon W wax. A small amount of the wax was heated to its melting point on the slide, and the crystal was placed on top of the melted wax. A small amount of pressure was added to the crystal to ensure an even spread of the

wax between the two surfaces. After cooling to room temperature, the crystal was cleaved with the razor blade to the approximate thickness of interest. Then the slide was in turn mounted on the prealigned pedestal with metallic liquid solder adhesive and again pressure was exerted to ensure an even spread of adhesive. After standing over night for the adhesive to dry, the sample was sliced ten microns on each cut until a shiny smooth surface was obtained. The number of cuts was kept to a minimum because after a certain number of cut, the cutting edge of the razor blade became dull and roughened the surface. A rough surface may introduce an error, which will be discussed later along with evaporation of gold as electrode. After slicing, trichloroetylene and acetone was used to dissolve the Apiezon W wax and the liquid solder adhesive respectively in that order. The wax dissolved readily and left a clean surface, but that was not true for the adhesive. After cleaving the crystal to a rectangular shape, the other surface of the crystal was shaved by the same procedure. The purposes for shaving the other surface were that the evaporated gold adhered better on a slightly roughened surface, and a possible source of a Wagner type of relaxation was reduced. The thickness and the uniformity, which is measured by a micrometer caliper with a Vernier, of the shaved crystals were in the range of 0.4 to 0.9 mm and of ± 1.0 to $\pm 3.0\%$ respectively for the regions to be used.

After measuring the thickness of the crystal, gold was evaporated onto the crystals to provide low resistance contacts and as electrodes. The methods used for cleaning the crystal surfaces and for evaporation of gold were modifications of those used by McCulloch (7, pp. 9-14). The crystal surfaces were cleaned by boiling the crystal for approximately 15 minutes in each of these organic solvents and according to the order in which they are listed: trichloroethylene, petroleum ether, 95% ethanol, and acetone. The evaporation of gold was done in a Mikros VE-10 vacuum evaporator. This apparatus consisted of bell jar which was readily evacuated with a fore-pump and an oil diffusion pump. The current source was modified to provide current to heat either the crystal or the gold-vapor source. The crystal was heated by means of a small ceramic heater. The goldvapor source was a small aluminum oxide crucible molded around a tungsten wire.

The bell jar was pumped to a pressure of approximately 0.08 micron before current was allowed to flow through the heater. The heating of the crystal to 100° to 150° C usually took one to one and a half hours. This heating under vacuum further cleaned the surface and released some of the adsorbed gases and water. While the crystal was at 100 to 150° C, gold was evaporated onto the surface slowly to allow for an even layer of deposition. A highly roughened surface and a fast, uneven deposition of gold layer would possibly create some voids

between the crystal surface and the gold layer. Under an applied potential, these voids would distort the applied electric field and would reduce the effective areas of the plates from the macroscopically measured value. The slow evaporation usually required 10 to 15 minutes to give a thick layer. The crystal was allowed to cool in the vacuum for a few minutes before air was leaked into the bell jar. The evaporation process was repeated on the other side of the crystal. The first evaporated side of a crystal was sectioned by microtoming, and the sectioned surface was examined under low power reflection microscope for highly reflective metallic particle. The estimate penetration of the gold is less than 0.01 mm.

The gold deposited on the edges of the crystal was removed by cleaving or scraping with a razor blade to avoid a short circuit across the edges. Using a template as a guide, a sharp, thin pointer was used to scribe a guard ring on one of the gold plate forming the guard and the guarded electrodes. Along with the unguarded electrode which was parallel to the other two, a three terminal capacitor, as shown in Figure 4 on p. 31, was thus formed. The sectioning later by microtoming revealed an estimated maximum depth of less than 0.02 mm for the scribe. The diameter of the guarded electrode was measured by a traveling microscope which give an accuracy of five significant figures. The roundness of the guard ring was checked by making at least two measurements at positions 90^o apart. These measurements

agreed to the fourth significant figure with a difference of $\pm 0.5\%$. The average width of the guard ring was measured to be in the range of 0.015 to 0.020 cm. The width of the guard electrode was at least twice the crystal thickness.

McCulloch (37) has found that the combination of cleaning the gold surface with small amount of 85% lactic acid and the use of indium solder would make a non-rectifying and mechanically stable contact between the gold plate electrode and copper wire. After cleaning the gold plate with the application of a minimum amount of lactic acid, a small amount of indium solder was placed on the cleaned spot. Simultaneously touching the solder with the "tinned" copper wire and a low-power soldering iron, the solder on the gold plate melted quickly. Upon cooling, the resistance of the contact was measured by means of a vacuum tube volt-ohm meter.

Non-ohmic contact implies the existence of a rectifying barrier layer at the contact between metal electrode and the semiconducting sample. The non-ohmic behavior of a system is usually represented by a non-linear plot of current as function of applied voltage. Figure 5 shows a linear relationship of current and applied voltage for a V_2O_5 capacitor with gold plates as electrodes at room temperature. The ohmic nature of the contact between metal and sample was studied for every V_2O_5 capacitor used in this investigation.



Figure 5. Ohmic nature of the contacts in the system at room temperature.

The Measuring Circuits

The Impedance Bridge

The impedance bridge used in this investigation was constructed by Lewis (36, pp. 84-89); it was based on a design by McGregor <u>et al.</u> (38). The values of its components were chosen to conform to those suggested by the designers for the frequency of 10^3 Hz. This bridge includes a resistance compensating network to balance the shunted resistance around the unknown capacitance. The entire assembly and the resistance compensating network are shown achematically in Figure 6 and Figure 7 respectively. All leads and terminals were well shielded to eliminate noise from external radiation and stray capacitance due to connection error. Therefore, the capacitance of a three terminal capacitor, measured with this bridge, depends solely upon the construction of the capacitor, and the accuracy of measurement would be limited only by the bridge or the reference standard used. (23)

The components of the bridge network and the parts used to construct the range shifter circuit were calibrated precisely or measured accurately by the manufacturers or by Lewis. The alternating current generator and detector unit was an Electro Scientific Industries model 861A. This unit provides a continuous frequency variation in three ranges from 20 to 20,000 Hz, and the detector has a



Figure 6. Bridge network with the transformer arms in 1:1 ratio. The ac signal generator and detector were the ESI model 861A generator and detector unit, the transformer was the ESI model CA-719 standard decade transformer, C_s was the General Radio model 1422 CD standard capacitor, and FC was a Hewlett-Packard model 5232A electronic counter. The parallel circuit of C_u and R_u with C_g indicated the three-terminal capacitor. The network with R, C_T C₁, and C₂ was the resistance compensating network.



Figure 7. Resistance compensating network showing the arrangement of the capacitors used to change the conductivity range. For the drawing arrangement, the C_1 and C_2 of Figures 6 are equal to C_6 and $C_3 + C_4 + C_5$ respectively.



Figure 8. The dc circuit: the power supply was the Keithley model 241 regulated high voltage supply, and A was either the Keithley model 610 electrometer or Keithley model 150A microvoltammeter.

sensitivity of l_µ V full scale on its most sensitive range. Accurate voltage division was provided by an Electro Scientific Industries model CA 719 standard decade transformer. The range multiplication factors of this transformer are 1:1, 1.2:1, 10:1 and 12:1 by the arrangement of its taps. The reference capacitor was a General Radio model 1422 CD three-terminal standard capacitor with worm gear corrections. With this standard capacitor, direct capacitance measurements were possible over the range of 0.050 ± 0.002 to 11.00 ± 0.01 pf at the transformer taps to give 1:1 multiplication factor. The upper value can be extended to 110.0 ± 0.1 pf by using the combination of transformer taps labelled 1.0 and -0.1. The capacitance can further be extended, by using the model 1422 CD standard capacitor to 12,300 pf. From the analysis of the current flow around the different loops and of the balance conditions for the bridge, Lewis (36) derived the expressions for the unknown capacitance and conductance in terms of the experimentally measured quantities and the variable and the , fixed parameters of the bridge network for the transformer taps at 1.0 and -1.0. The derived expressions are

$$\frac{1}{Ru} = \frac{S\omega^2 C_1 R [2(C_1 + C_2) + C_T]}{\left[1 - R^2 \omega^2 C_T (C_1 + C_2)\right]^2 + R^2 \omega^2 [2(C_1 + C_2) + C_T]^2},$$
(4.2)

a nd

$$C_{u} = C_{s} + \frac{SC_{1}\left[1 - R^{2}\omega^{2}C_{T}(C_{1} + C_{2})\right]}{\left[1 - R^{2}\omega^{2}C_{T}(C_{1} + C_{2})\right]^{2} + R^{2}\omega^{2}\left[2(C_{1} + C_{2}) + C_{T}\right]^{2}}.$$
(4.3)

Substituting the fixed parameters of the bridge network, Equations (4.2) and (4.3) become

$$\frac{1}{R_{u}} = \frac{1.112 \times 10^{-14} S \omega^{2} C_{1}}{\left[1 - 2.833 \times 10^{-8} \omega^{2}\right]^{2} + 1.236 \times 10^{-4} \omega^{2}}, \text{ and } (4.4)$$

$$C_{u} = C_{s} - \frac{SC_{1}(1 - 2.833 \times 10^{-8} \omega^{2})}{\left[1 - 2.833 \times 10^{-8} \omega^{2}\right]^{2} + 1.236 \times 10^{-4} \omega^{2}}$$
(4.5)

When the arrangement of the transformer taps is at 1.0 and -0.1, the measured conductance and capacitance will be given by

$$\frac{1}{R_{u}} = \frac{1.112 \times 10^{-13} \text{ su}^{2} \text{ C}_{1}}{\left[1 - 2.833 \times 10^{-8} \text{ su}^{2}\right]^{2} + 1.236 \times 10^{-4} \text{ su}^{2}}, \text{ and} \quad (4.6)$$

$$C_{u} = \left[C_{s} - \frac{\text{SC}_{1}(1 - 2.833 \times 10^{-8} \text{ su}^{2})}{(1 - 2.833 \times 10^{-8} \text{ su}^{2}) + 1.236 \times 10^{-4} \text{ su}^{2}}\right] 10 \quad (4.7)$$

respectively. In these expressions C_s , the value of the standard capacitor in pf, and S, the reading in the transformer, are the experimentally measured quantities of which the data of this investigation consisted; ω , the angular frequency in rad/sec, and C_1 , the value of the range shifting capacitor in pf, are the experimental variable parameters; C_u , the unknown capacitance in pf, and R_u , the unknown

resistance in ohms, are the two physical quantities to which the data must be converted.

For the frequency of 1000 Hz, Lewis (36) calibrated the bridge network for the accuracy of its capacitance and resistance measurements. The 'dummy' model of a leakage capacitor was a parallel connection between a variable standard capacitor and a shielded resistance box with Victoreen carbon films as resistors. For all the capacitance and resistance ranges examined, he found a complete agreement for the capacitance after the calibration correction was applied. He established the bridge's effectiveness of resistance measurement as a range of $10^5 - 10^{10}$ ohms. Since the values of the capacitors used in this study were in the range of 5 to 20 pf, a portion of his calibrations was repeated. The results were in complete agreement.

As described in Chapter II, this impedance bridge is actually a current measuring instrument, and the simplest model circuit used to represent a capacitor with large loss is a pure capacitor in parallel with a pure resistor. The current ratio through these components will set the limit of the bridge's effectiveness in measuring the values of the resistor and the capacitor.

A new 'dummy' capacitor was formed by connecting a constant capacitor of approximately 10 pf in parallel with the resistance box. Using this new 'dummy' capacitor, the range shifter circuit was calibrated for accuracy in measuring the conductance and capacitance

components at constant frequency. This calibration was done for all frequencies used in this investigation. For a particular frequency, the calibration results indicated a difference of as much as 3% between resistance measurements using the different ranges in the range shifter circuit. On the average, the range with $C_1 = 10^5$ pf gave the lowest current at the null-point, and the best agreement with the resistance values measured by the dc method for the frequency and resistance ranges of interest. For this reason $C_1 = 10^5$ was used for all measurements reported here. Intercomparing the ac values for all frequencies and the dc values, the bridge's effective resistance ranges for the different frequencies were established. The measured capacitances for the frequencies other than 1000 Hz were compared with that for 1000 Hz, and the results showed good agreement within the experimental error which is set by the standard capacitor. A Hewlett-Packard model 5232A electronic counter was used to count the frequency for the calibration as well as for the experimental work with the samples. The frequency fluctuation rarely exceeded 1.0% after the generator unit had sufficient time to warm up. The generator's output voltage range of 0 to 2 V was kept constant throughout the course of this study.

The dc Circuit

The dc conductivity measurement was made with a two-probe

current measuring system. For the purpose of this study, this method is probably the most suitable because the whole arrangement within the three terminal cell must be the same as that for the ac measurements. The circuit is shown in Figure 8 of p. 40. The power source was the Keithly model 241 regulated high voltage supply which, the manufacturer claims, has an accuracy of $\pm 0.05\%$ or ± 1 mV. The dial settings of the power supply provide a continuous change of voltage from 0.01 to 1000 volts. The lower extreme of the voltage settings were useful for ohmic contact study. These values were calibrated by means of a Keithly model 150A microvolt-ammeter, and if necessary small corrections were made. The current was measured by either a Keithly model 610 electrometer or the microvolt-ammeter depending on the magnitude of the applied potential. The multiplier and the range dials of the electrometer were calibrated by measuring the currents through the standard resistors in the resistance box. For low applied voltage, these measured values of the resistors were compared with those measured by the ac impedance bridge and by another dc method. All three sets of values agreed with each other within the accuracy limits set by the instruments. The same circuit was used for ohmic contact studies except that the microvolt-ammeter was used to measure the current.

Cryostat

The vacuum cell included a standard taper joint which allowed the convenience of easy sample changing and provided for a good vacuum system. Five capillaries with glass-to-metal seals of either Kovar or copper were located at the top part of the cell to provide lead inputs for thermocouple and the three terminals of the capacitor. Small coaxial cables, suitable for low frequency ac work, were used as leads from the three-terminal sample holder to the capillary for the high and low terminals. Since the seal at the Kovar was metal-tometal with solder, the outer and inner insulations and radiation shield of the cable must be stripped. To prevent a short across to ground, the stripping of the radiation shield was a little beyond the Kovar and glass contact point. The surface of the Kovar where the contact was made with 60/40 tin and lead solder was cleaned with 85% lactic acid. At this point, a larger cable for the lead to the bridge was also soldered. Soldering by itself did not give a good enough vacuum seal, and melted Apiezon W wax was added. For added mechanical strength, the whole capillary and a small part of the outside cable was enclosed in a short nylobraid tubing. Thin aluminum foil was wrapped around the tubing to serve as radiation shield which was connected to the central ground of the bridge. The combination of solder and Apiezon W wax was also used as seal for the other three capillaries. For the

thermocouple wires, the insulation was only stripped at the metal-tometal sealing point which was later enclosed in a small tygon tube for added mechanical strength. The cryostat was able to hold a vacuum of less than 0.1 micron of Hg under pumping.

A long glass tubing, which extended from the top half to the lower half of the vacuum cell, with a Kovar to glass seal served as a "cold finger." A brass block was silver-soldered to the Kovar. The upper part of a closed, cylindrical shaped radiation shield was screwed to the brass block. Four well-positioned holes were drilled through the top of the radiation shield to provide for the extension of the cables and the thermocouple leads inside the shield. The lower, and much longer, portion was connected to the upper portion by a screw-and-slide type of hook which provided for an easy access to the sample holding unit. This radiation shield was machined from aluminum tubing to give a highly reflective surface; it was directly connected to the ground input capillary. The glass wall of the vacuum cell was not silver plated because most of its lower portion was immersed in a one-liter dewar containing liquid nitrogen.

The arrangement of the three-terminal sample holder is shown in Figure 9. The possible thermal gradient across the sample was minimized by sandwiching the sample between BeO disks which served as thermal conductor and electrical insulator between the sample and the brass unit. Beryllium oxide has a unique set of Figure 9. The arrangement of the sample holding unit: 1. the V_2O_5 three-terminal capacitor, 2. the brass-nut soldered to a C_u -foil, 3. BeO disk, 4. brass block, 5. thermocouple bead pressed against a teflon block, 6. brass shoulder, 7. swing bridge, 8. coaxial cable, 9. cold finger, 10. aluminum radiation shield, 11. vacuum cell, and 12. felt plunger.



properties: under the experimental conditions it has a high thermal conductivity and a low electrical conductivity. The two top BeO disks rested on the two vertically movable shoulders extending from the arms of the swinging brass bridge. The combination of the shoulders and the bridge held the two BeO disks tightly against the brass block. The bead of the iron-constantan thermocouple, which was wrapped in copper foil, was pressed between the surface of the lower disk and the teflon block by one of the brass shoulders. The positions of these BeO disks and the thermocouple were kept constant throughout the course of this investigation after they were set at the beginning. The thermocouple was calibrated at the normal boiling point of liquid nitrogen and the normal freezing points of pentane, ethyl acetate, carbon tetrachloride, and H_2O . All organic solvents were analytical grade. The electromotive force of the thermocouple was measured with a Biddle Gray Compact portable potentiometer with the reference junction in ice-water. The brass nut, which was cleaned with dilute HCl, provided thermal contact between the guarded electrode and the surface of the lower BeO disk through pressure exerted by hand-tightening of the screw at the bottom of the swinging bridge. The brass disk on top of the screw was self-adjustable to provide for an even exertion of pressure. Hence, in this position, the thermocouples probably registered the temperature closest to that of the sample. Electrically, solder contacts were made between the brass nut and the high

terminal cable, between the unguarded electrode and low terminal, and between the guard electrode and the grounded brass unit.

The cryostat was examined for any extraneous source of noise. A pure KC1 crystal was used as dielectric material for a three terminal capacitor whose electrode material, guard ring, and solder contacts were the same as that for a V_2O_5 sample. The capacitances of this capacitor were measured as the function of temperature at a constant frequency of 1000 Hz, between 78° and 200° K. The result is shown in Figure 10, and the slope of the plot shows no steep rise, as expected. In addition, the room temperature capacitance was measured. The calculated real dielectric constant for the room temperature and the average temperature coefficient for the temperature range of 80° K to 200° K are 4.94 and 2.49 x 10⁻⁴ K⁻¹ respectively. These values agree well with the recent reported values of 4.81 and 2.59 x 10⁻⁴ K⁻¹ by Robinson and Hollis Hallet (47)using an impedance bridge having a similar design.

Procedures of Making Measurements

Slowly Warming

The cryostat was evacuated with the combination of a mechanical fore-pump and a mercury diffusion pump to a pressure of less than 0.1 micron of Hg. After this continuous evacuation for at least two



Figure 10. Capacitance of a KCl-capacitor as function of temperature measured at constant frequency of 1000 Hz.

hours, liquid nitrogen was added to the outer dewar flask. The cooled wall of the vacuum cell not only served as a cooler for the sample, but also acted as a condenser for water and other condensible vapors. Later, the radiation shield served as another condenser. After thermal equilibrium between the outer wall and the liquid nitrogen bath was established, liquid nitrogen was poured into the "cold finger" slowly. The temperature of the cooling sample was monitored by checking its resistance between the high and low terminals. When the resistance reached 10^9 ohms, the cryostat was sealed from the evacuation system. The continuing addition of liquid nitrogen to the "cold finger" cooled the sample to the lowest attainable temperature. Then the sample was allowed to warm via heat exchange between the "cold finger" and the atmosphere. When a porous felt plunger of 0.5 to 1.0 cm thick was inserted in the "cold finger" the warming rate was reduced significantly by pouring liquid nitrogen into the plungered glass tubing. Hence, the sample warming rate was controlled by judiciously adding liquid nitrogen to the plungered glass tubing or to the outside dewar or to both.

As the sample was warming, the measurements were made. Before balancing the impedance bridge, the approximate electromotive force of the thermocouple was found. The null point of the bridge was sought by compensating the slowly changing component first and then the other component. The null point was represented

by the lowest meter reading in the most sensitive range of the detector. After the bridge was balanced, the electromotive force of the thermocouples was measured again, and this measurement taken to give the temperature. This whole operation of taking a single datum usually required about one minute at the sample warming rate of approximately 1°K per three minutes. In the temperature region where the real current component was significantly larger than the imaginary current component, the null points were difficult to locate. The warming rate of the sample would be reduced to allow for an accurate compensation of the individual components. The procedure of making measurements was continued until no null point could be found for the bridge due to the increase of conductivity with temperature. An approximate warming rate of 1[°] K per three minutes for the range from 78° to 200° K and a lower rate for the higher temperature region were generally used for dc measurements.

Constant Temperature

The cryostat was designed mainly for use in slowly warming experiments. However, the sample could be held at constant temperature for many hours through the use of a low temperature slush bath of organic solvent and the continuous addition of small amount of liquid nitrogen to maintain the slush. The cryostat was pumped and cooled by the procedure as described in the previous section. When the system was cooled to the approximate desired temperature, well stirred slush was introduced into the "cold finger." The felt plunger was inserted into glass tubing with part of the plunger's handle extended into the slush. When liquid nitrogen was added, this part of the plunger would serve as a cold finger for the slush. Liquid nitrogen was poured into the "cold finger" when a change in the density or the color of the slush was detected. The system was allowed at least 30 minutes to attain thermal equilibrium. A stable thermal equilibrium would not be attainable when the cryostat was not continuously under evacuation.

When the system had attained thermal equilibrium, the conductance and the capacitance of the sample were measured as function of frequency. As described in Chapter II, the ac conductivity is the sum of the dc conductivity and the dielectric conductivity. Hence, accurate measurement of the dc value is necessary. Starting from the lowest frequency, the dc conductance was measured before and after the ac measurement. After the measurements at the highest frequency were made, the measurements of the lower frequencies were repeated at random. The comparison between the earlier and the later measurements revealed close agreement. After a change of frequency was made, at least five minutes were allowed for the generator to become stabilized. If the two dc values were not significantly different, the later value was used in the calculation. Otherwise, the average value of the two was accepted.

V. RESULTS AND INTERPRETATION

Data Evaluation and Results

The Presence of Debye Type of Relaxation Losses

For the melt grown V_2O_5 crystal, a typical set of measurement of capacitance as a function of temperature, $C(T)_{0}$, taken at constant frequency of 1000 Hz is displayed in Figure 11. Contrary to Figure 10, $C(T)_{0}$ for V_2O_5 crystal undergoes a sharp increase from 11.10 pf at T = 125° K to a possible leveling-off value of 17.85 pf at T = 173° This observation may be due to a phase change or to some dielec-K. tric relaxation process or processes in the crystal. Dmitrieva, Ioffe, and Patrina have concluded from NMR studies of their crystals that there was no phase change in the temperature range of 77° K to room temperature (14). Their crystals were grown by a similar method that used in this investigation. Hence, a dielectric relaxation process was the more likely cause of the steep increase in the measured cacacitance. Since the geometry of the capacitor was kept constant, the only variable parameter was the real part of the dielectric constant $\epsilon_1(\omega, T)$. Considering the different contributing components to the $\varepsilon_1\left(\omega,\,T\right)$ and assuming its linear separation:

$$\epsilon_1(\omega, T) = \epsilon_{atomic}(\omega, T) + \epsilon_{ionic}(\omega, T) + \epsilon_{dipolar}(\omega, T).$$
 (5.1)



Figure 11. Capacitance of a V_2O_5 -capacitor as function of temperature measured at constant frequency of 1000 Hz.

For the frequency of 10^3 Hz and the size of the temperature range, ϵ_{atomic} and ϵ_{ionic} are essentially constant. Then $\epsilon_{dipolar}$ is the only possible temperature variable component, and the chief relaxation process is related to dipolar relaxation. A more concise form of Equation (5.1) is

$$\epsilon_1(\omega, T) = \epsilon_{\infty} + \epsilon_D(\omega, T);$$

Therefore, for this investigation ϵ_{∞} is taken to equal to $\epsilon_{1}(\omega, T)$ at the T value when $\epsilon_{D}(\omega, T)$ contribution is negligibly small.

Equation (2.26) and (2.27) are the two Debye equations which indicate only an explicit frequency dependence for ϵ_1 and ϵ_2 . However, they are implicitly dependent on temperature through $\epsilon_s - \epsilon_{\infty}$ and T_D . Since this study is concerned only with the dipolar relaxation time, T_D will be represented by τ . At constant temperature, these quantities become constant. A new quantity Z is defined as

$$Z = \ln\omega\tau = \ln\omega + \ln\tau \qquad (5.2)$$

Then, Equations (2.26) and (2.27) can be expressed as

$$\frac{\epsilon_1 - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}} = \frac{e^{-Z}}{e^{Z} + e^{-Z}}, \text{ and} \qquad (5.3)$$

$$\frac{\epsilon_2}{\epsilon_s - \epsilon_{\infty}} = \frac{1}{e^{Z_{+e}} - Z}$$
(5.4)

respectively. Figure 12 illustrates the frequency dependence of ϵ_1 at constant temperature. Considering Equation (5.4) when Z varies continuously from negative to positive, $\frac{\epsilon_2}{\epsilon_s - \epsilon_{\infty}}$ or ϵ_2 would be


Figure 12. Dielectric dispersion of V_2O_5 crystal measured at $T = 142^{\circ}$ K.

a symmetric function of Z with the existence of a maximum at Z = 0. The physical meaning of this maximum will be revealed by the application of the ordinary method of calculus to Equation (2.27)

$$\begin{bmatrix} \frac{\partial \epsilon_{2}(\omega)}{\partial \omega} \end{bmatrix}_{T} = \begin{cases} \frac{\partial}{\partial \omega} \left[\frac{\omega t}{1 + (\omega t)^{2}} \right] \end{cases}_{T} \quad (\epsilon_{s} - \epsilon_{\infty}) = 0$$
$$w_{max} = \frac{1}{T(T)} \quad (5.5)$$

Therefore, when the frequency of the applied field is equal to twice the natural jumpicing frequency of the dipole (in the absence of the field), the measured ϵ_2 would be a maximum value for that particular temperature at which the system was maintained. This provides for a method of determining $\tau(T)$ and $\epsilon_s - \epsilon_{\infty}$ as functions of T, because at ω_{max}

$$\epsilon_2(\omega_{\text{max}}) = 1/2(\epsilon_s - \epsilon_{\infty}).$$
 (5.6)

Substituting the determined quantities, T(T) and $\epsilon_s - \epsilon_{\infty}$, into Equation (2.27), $\epsilon_2(\omega)$ can be calculated as the function of frequencies. Such a curve is plotted along with the experimental data points as a function of log ν in Figure 13. The experimental curve is wider but has the same shape as the calculated one; therefore, the melt grown vanadium pentoxide crystal behaves approximately like a Debye dielectric. The degree of deviation from the idealized Debye dielectric can possibly be estimated from the consideration of the quantity $\epsilon_s - \epsilon_{\infty}$. From Equation (5.6), it is equal to 2.4 which is calculated on the



Figure 13. Comparison of the measured and the calculated dielectric losses of V_2O_5 crystal for T = 142°K. The solid and the dashed lines are for the measured and the calculated curves respectively.

basis of Debye equation. While from the extrapolation of the dispersion curve, its value is estimated to be 3.1. The difference between these values is attributable to the deviation between the actual dielectric crystal and the simple Debye model dielectric.

Relaxation Times and Activation Energy

Both of the Debye equations are function of the relaxation time T; however, according to Equation (2.17) only ϵ_2 yields information on the relaxation process. Equation (2.18) expresses the relationship between the dissipation of energy/unit time/unit volume of dielectric and the experimentally measurable quantity $\sigma_{ac}(\omega, T)$ which, in turn, is a linear sum of $\sigma_{dc}(T)$ and $\sigma_{diel}(\omega, T)$. Furthermore, $\sigma_{diel}(\omega, T)$ is related to $\epsilon_2(\omega, T)$ through Equation (2.9). Therefore, ϵ_2 as function of T for a constant frequency, $\epsilon_2(T)_{\omega}$, can be obtained through suitable mathematical analysis of $\sigma_{ac}(T)_{\omega}$.

One of the simplest but accurate enough method is the graphical subtraction of $\sigma_{dc}(T)$ from $\sigma_{ac}(T)_{\omega}$. From the previous work done in this laboratory (37), the Arrhenius type of relation

$$\sigma_{dc}(T) = \sigma_{o} \exp\left(-\frac{E}{dc}/kT\right)$$
(5.7)

was found to be valid in the temperature range of 297° K to 125° K with the addition of a guard electrode to minimize the surface conduction. The $\sigma_{dc}(T)$ was obtained either through direct dc measurement or through graphical extrapolation of the linear section of the

superimposed plots of $\sigma_{ac}(T)_{\omega}$ against reciprocal of T for all ω used. Figure 14 shows three plots of log σ_{dc} against the reciprocal temperature. These curves are linear from a high of room temperature for Crystal 13 down to less than 125° K, and the calculated activation energy for the conduction is 0.27 ± 0.01 eV. The linearity to this low temperature could be taken as an indication that only one mechanism of dc conduction operates throughout the entire temperature range of interest. The calculated activation energy of dc conduction from the slope of the extrapolated ac curve in Figure A 4, in Appendix II, was 0.26 ± 0.01 eV. The difference between the calculated activation energy values from extrapolated curve and that from dc curve is within the estimated uncertainties.

The log $\sigma_{ac}(T)_{\omega}$ was plotted against T^{-1} on an expanded 5 cycle semilog graph paper, and the appropriate section of the $\sigma_{dc}(T)$ was superimposed. A sample of such a plot is shown in Figure 15. A set of results from graphical interpretation of the two curves in Figure 15 is given in Table 1. From these results, $\sigma_{diel}(T)_{\omega}$ and $\epsilon_2(T)_{\omega}$ with their respective propagated errors, which were calculated on the basis of the estimated uncertainties in the graphical readings, were calculated. These calculated results are also given in Table 1. The plots of $\sigma_{diel}(T)$ against T^{-1} and of $\epsilon_2(T)$ against T are shown in Figures 16 and 17 respectively. The condition for, and the physical meaning of, the existence of a maximum in Figure Figure 14. The dc conductivities of three crystals. The ordinate refers to Crystal 13, and for Crystal B and C 1 and 2 should be subtracted from the log respectively.

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Figure 15. The ac conductivity of Crystal 13 measured at constant frequency of 500 Hz.

т, ^о к	$\frac{10^{3}}{T, o_{K}}$ -1	$\sigma_{ac}, \Omega^{-1} cm^{-1}$	$\sigma_{\rm dc}, \Omega^{-1} \rm cm^{-1}$	$\sigma_{diel}, \Omega^{-1} cm^{-1}$	¢2
152.5	6.60	(5.35±0.05)X10 ⁻⁹	(5.15±0.05)X10 ⁻⁹	(0.20±0.1)X10 ⁻⁹	0.72 <u>+</u> 0.36
149	6.70	(3.95±0.02)	(3.73 <u>+</u> 0.02)	(0.22 <u>+</u> 0.04)	0.79 <u>+</u> 0.14
147	6.80	(2.98+0.02)	(2.73 <u>+</u> 0.02)	(0.25 <u>+</u> 0.04)	0.90 <u>+</u> 0.14
145	6.90	(2.28 <u>+</u> 0.02)	(2.00±0.02)	(0.28±0.04)	1.0 <u>+</u> 0.14
143	7.00	(1.77±0.02)	(1.47 <u>+</u> 0.02)	(0.30±0.04)	1.1 <u>+</u> 0.14
141	7.10	(1.38±0.01)	(1.07±0.01)	(0.31±0.02)	1.1±0.08
139	7.20	(1.13 <u>+</u> 0.01)	(0.79 <u>+</u> 0.02)	(0.34 <u>+</u> 0.03)	1.2±0.11
137	7.30	(0.89±0.01)	(0.57 <u>+</u> 0.02)	(0.32 <u>+</u> 0.03)	1.2 <u>+</u> 0.10
135	7.40	(0.68 <u>+</u> 0.01)	(4.25±0.1)X10 ⁻¹⁰	(0.25 <u>+</u> 0.02)	0.90±0.07
133	7.50	(0.54 <u>+</u> 0.01	(3.12±0.1)	(0.23±0.02)	0.83±0.07
131.6	7.60	(4.25 <u>+</u> 0.05)X10 ⁻¹⁰	(2.30 <u>+</u> 0.05)	(0.195±0.01)	0.70±0.04
130	7.70	(3.30 <u>+</u> 0.05)	(1.70±0.05)	(0.16±0.01)	0.57 <u>+</u> 0.03

Table 1. Results from graphical interpretation of Figure 15 and the calculated values of σ_{diel} and ϵ_2 .

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Figure 16. Dielectric conductivity of Crystal 13 measured at constant frequency of 500 Hz.



Figure 17. Temperature dependence of ϵ_2 measured at constant frequency of 500 Hz on Crystal C.

17 can be learned through the application of ordinary method of calculus to Equation (2.27). Since $\epsilon_{\rm s} - \epsilon_{\infty}$ is generally also function of temperature, ideally the quantity $\epsilon_2^{/\epsilon} - \epsilon_{\infty}$ should be plotted against T.

$$\begin{bmatrix} \frac{\partial}{\partial T} \begin{pmatrix} \frac{\epsilon_2(T)}{\epsilon_s - \epsilon_{\infty}} \end{pmatrix} \end{bmatrix}_{\omega} = \begin{bmatrix} \frac{\partial}{\partial T} \begin{pmatrix} \omega \tau(T) \\ 1 + \omega^2 \tau^2(T) \end{pmatrix} \end{bmatrix}_{\omega} = 0 \quad (5.8)$$

Hence, the condition for the existence of a maximum is

$$\tau(T_{\max}) = \frac{1}{\omega}$$

and the physical meaning of this maximum is the same of that in Figure 13. However, when the data is in the form of $\epsilon_2(T)_{\omega}$, and $\epsilon_s - \epsilon_{\infty}$ as function of temperature is not known; it is essential to find the condition such that

$$\begin{bmatrix} \frac{\partial \epsilon_2(T)}{\partial T} \end{bmatrix}_{\omega} = 0 = \frac{\partial}{\partial T} \begin{bmatrix} \frac{\epsilon_2(T)}{\epsilon_s - \epsilon_{\infty}} \end{bmatrix}_{\omega} \text{ at } T = T_{\max}$$
(5.9)

Expanding the right hand side of Equation (5.8) and assuming $\epsilon_{s} - \epsilon_{\infty}$ is inversely proportional to temperature, the condition for Equation (5.9) to hold is that $T_{max} \gg \epsilon_{2}(T_{max})$.

This condition is fulfilled for the melt-grown V_2O_5 crystal used in this investigation because $\frac{\epsilon_2(T_{max})}{T_{max}} < 0.01$ and 0.01 is beyond

detection in the $\epsilon_2(T)$ against T curve. Then, from Figure 17, the estimated relaxation time at $141^{\circ} \pm 2^{\circ}$ K is 3.18 x 10^{-4} sec. Referring to Figure 13, the $\epsilon_2(max)$ values measured at T = 141° and

 $\omega = 3.142 \times 10^3$ rad/sec by the methods of either varying ω or slowly warming agree well within the estimated experimental uncertainties.

The described process of deducing the relaxation time as function of temperature τ (T), from the conductance measurements is long, tedious, and often inaccurate. The values of τ (T) can also be deduced from the capacitance measurements. When the conditions to give $\omega = \frac{1}{\tau(T)}$ were reached, Equation (2.26) becomes

$$\epsilon_1(\omega) - \epsilon_{\infty} = \frac{\epsilon - \epsilon}{2}$$
 (5.10)

For the experimental condition of constant frequency and slowly increasing temperature, Equation (5.10) become

$$\epsilon_1(T_m)_{\omega} - \epsilon_{\infty} = \frac{\epsilon_s - \epsilon_{\infty}}{2}$$

and the T_m is the temperature at which $\tau (T_m) = \frac{1}{\omega}$. Figure 18 displays the data sets of ϵ_1 as function of T at constant ω , $\epsilon_1(T)_{\omega}$, for different ω . For a particular ω_p , by assuming ϵ_s to have the ϵ_1 value at the high temperature leveling-off region and ϵ_{∞} to be equal to that at the lowest temperature, $\epsilon_s - \epsilon_{\infty}$, and $\tau(T_m)$, can then be estimated from the appropriate plot of Figure 18. This process of deducing $\tau(T)$ was applied to the plots in Figure 18, and the results with the estimated uncertainties are given in Table 2. The deduced temperature at which $\tau = 3.18 \times 10^{-4}$ sec agrees well within the estimated uncertainties with that deduced from conductance measurements.



Figure 18. Temperature dependence of ϵ_1 measured at constant frequency for different frequencies on Crystal 13.

v,kHz	¢ s	ε ∞	$(\epsilon - \epsilon)/2$	Т _т , К	٤l	$\frac{10^3}{T_m} K^{-1}$
0.2	8.70	5.15	1.80	1 38+2	6.95	7.25
0.5	8.68	5.10	1.79	144 <u>+</u> 2	6.89	6.94
1.0	8.68	5.10	1.79	1 50 ± 2	6.89	6.67
1.5	8.66	5.10	1.78	153 <u>+</u> 2	6.88	6.54
2.0	8.58	5.08	1.75	155 <u>+</u> 2	6.82	6.41
3.0	8.58	5.04	1.77	159±2	6.81	6.29
5.0	8.26	5.04	1.61	162+2	6.65	6.17
10.0	8.10	5.02	1.54	169+2	6.56	5.92

Table 2. T(T) deduced from Figure 19.

On the basis of the Debye theory of dielectrics, the activation energy, H, for the relaxation process can be determined from Equation (2.23). Assuming the temperature dependence of τ_0 to be small compared to the exponential factor, H can be calculated from the slope of the plot of log τ (T) against T⁻¹. Then, using any of τ (T) value and the determined H, τ_0 can be calculated. The τ (T) in Table 2 were plotted in Figure 19; the figure also displays for comparison another two sets of τ (T) which were deduced from both capacitance and conductance measurements of the same crystal. The appropriate plots from which the latter two sets of τ (T) were deduced are given in the Appendix I. For Crystal C the values of every relaxation time deduced by the two respective methods agree well within the estimated experimental uncertainties. The calculated values of H from Figure 19 are 0.26 + 0.03 eV.

The described method of determining H can be applied when there are at least three T(T) values whose range represents a sufficient spread. Based on the symmetrical properties of $\epsilon_2(\omega T)$ in the Debye equation, Reads and William (46) derived an expression to calculate H from the half width, $\delta_{1/2}$, of the curve ϵ_2 versus T^{-1} . Their derived expression is

$$H = \frac{1}{\frac{1}{T_{r}} - \frac{1}{T_{m}}} k \ln (r + \sqrt{r^{2}} - 1)$$
 (5.11)



Figure 19. Log Tas function of reciprocal temperature. The ordinate refers to Crystal 13, and for Crystal C, the upper curve, subtracts 1 from the log. The symbols • and A designate data points deduced from capacitance and conductance measurements respectively.

where T_m and T_r are the temperatures at which the values of ϵ_2 are ϵ_2 (max) and $\frac{1}{r} \epsilon_2$ (max) respectively, and k is the Boltzmann constant. From the curve in Figure 16, these values are estimated: $\frac{1}{T_m} = 7.18 \times 10^{-3} \text{ K}^{-1}$ and $\frac{1}{T_r} = 7.68 \times 10^{-3} \text{ K}^{-1}$ where r = 2, and the calculated activation energy is $0.23 \pm 0.02 \text{ eV}$. This agrees well with the previous value of $0.26 \pm 0.3 \text{ eV}$. This method was applied to one of the samples, and the appropriate plots and calculation are given in the Appendix II.

Averaging over four samples whose H's were determined through either the shift or the half-width method, the calculated average activation energy was 0.24 ± 0.03 eV. Using this value for H, and the $T(169^{\circ} \text{ K}) = 1.59 \times 10^{-5}$ sec, the value of T_{\circ} was calculated to be equal to 1.1×10^{-12} sec. This value of T(T) was chosen because it was consistent for three samples. The calculated τ_{\circ} is within three orders of magnitude of the frequency of the lattice modes (30).

The Possible Relaxation Processes

Electrode Effects

When gold was evaporated on the crystal surfaces as electrode, a thin layer with conductivity different from that of the bulk crystal may be formed. This inhomogeneous conductivity through the sample is often a source of Maxwell-Wagner type of relaxation process (60). Volger (56) discussed the four possible cases of the simplest two layer model, and only the case of good conducting layers would behave like a Debye dielectric. The condition for this case is $\rho_1 / \rho_2 << d_1 / d_2$ where ρ_1 , ρ_2 , d_1 and d_2 are resistivity and thickness for layers 1 and 2 respectively. Assuming the permittivity $\epsilon_0 \epsilon_1$ of the two layers to be equal, the expression for tan δ was derived

$$\tan \delta = \frac{d_1}{d_2} \frac{\omega \tau_{\delta}}{1 + \omega^2 \tau_{\delta}^2}$$
(5.12)

where tan δ is defined as the ratio of imaginary dielectric constant to real dielectric constant and τ_{δ} is the relaxation time. Then, the increase in static dielectric constant becomes a function of the thickness of the two layers such as

$$\epsilon_{s} - \epsilon_{\infty} = \left(\frac{d_{1}}{d_{2}}\right) \epsilon_{i}$$
 (5.13)

For the samples used in this study, the conductivity of the layer immediately under the deposited electrode could be increased due to the presence of gold atoms which diffused in during the evaporation. If ρ_1 and d_1 represented the resistivity and thickness of this layer, and ρ_b and d_b represented that of the bulk, the condition $\rho_1 / \rho_b \ll$ d_1 / d_b could possibly be fulfilled. In the new notation, Equation (5.13) becomes

$$\frac{\frac{\epsilon_{s} - \epsilon_{\infty}}{\epsilon_{i}}}{\epsilon_{i}} = \frac{d_{1}}{d_{b}}$$

Under similar electrode deposition conditions, d_1 can be assumed constant for the samples used in this study. The values of $\epsilon_s - \epsilon_{\infty}$ and $\epsilon_1(T_m)_{\omega}$ can be estimated from the $\epsilon_1(T)_{\omega}$ against T plots as described earlier. Assuming ϵ_i is equal to $\epsilon_1(T_m)_{\omega}$, the quantity $\frac{\epsilon_s - \epsilon_{\infty}}{\epsilon_i}$ can be plotted against the reciprocal thickness of the crystals. The conformation of the plotted points to a straight line through the origin can be taken as an indication of the presence of the Maxwell-Wagner relaxation process. A plot of such is shown in Figure 20, and the points do not conform to a straight line through the origin. However, they seem to indicate $\frac{\epsilon_s - \epsilon_{\infty}}{\epsilon_i}$ is independent of thickness of the crystal. The data for this plot were all taken at $\omega = 2\pi \times 10^3$ rad/sec. It is concluded thereby that Maxwell-Wagner losses are not responsible for the observed relaxation.

Dielectric Losses Due to Local Movements of Ions

Dielectric losses can be caused by two possible types of local movements of ions around imperfections in the crystal lattice. The two types of ionic movements are the jumping over interatomic distances and the slow deformation of not greater than 0.5 Å. The ionic jump process has been used extensively to explain the observed dielectric loss in alkali halide crystals doped with a divalent cation. This process requires an activation energy of the order of 0.5 to



Figure 20. $\frac{\epsilon}{s} - \epsilon_{\infty}$ as function of reciprocal crystal thickness. The numeral or letter at each ϵ_{i} point is the crystal identification.

l eV, and it takes place at temperature exceeding 400° K. The process of slow deformation around the imperfection is possible because the imperfection may perturb the lattice to the extent to allow the probability of small displacements of ions or atoms near the imperfection. This mechanism was used to explain the observed dielectric losses at low temperature, below 100° K, in single crystals of clear quartz (58) and glasses (53, 57). The reported activation energies were in the order of 0.05 to 0.1 eV. It is not likely, therefore, that either of these processes is responsible for the relaxation observed in V_2O_5 .

Dielectric Loss Due to Trapped Electrons in Donor Center

The general model of the hopping charge carrier, electron or hole, described in Chapter III was used to explain most of the observed dielectric relaxation phenomena of transition metal oxides. The centers consisted of either an impurity ion or a vacancy, and they were added either as dopant or through reduction by increasing the nonstoichiometry of the original material. A wide range of activation energy, from 0.001 to 0.43 eV, has been reported, and the absorption peaks were observed in the temperature range of 7^o K to 215° K. Many of the studied samples were ceramic materials, and some exhibited absorption curves showing good approximation to that of Debye dielectric. As an example of particular interest, Bosman and Crevecoeur (7) showed that the ceramic samples of CoO doped with low concentration of either Li or Na behaved approximately like a Debye dielectric. These authors proposed the existence of dipolar units such as $(\text{Li}^{1+} - \text{Co}^{3+})$ and $(\text{Na}^{1+} - \text{Co}^{3+})$ to explain the observations, and the movement of the hole around the Na⁺ and Li⁺ was thought to be corresponding to the reorientation of the dipoles. This movement of the hole was proved to be a thermally activated hopping process with an activation energy of 0.20 eV and 0.25 eV respectively for Li⁺ and Na⁺ dope. The activation energies were determined from a shift method as described earlier.

On the basis of the experimental results and considering all these possible relaxation processes, the most probable or the dominant process which can be used to explain the dielectric measurements of the melt-grown V_2O_5 crystal is the hopping of trapped electrons in the donor centers. Chemical and electrical considerations can further justify this proposal of the relaxation process. Vanadium pentoxide is a transition metal oxide. Milan (39) has shown that molten vanadium pentoxide at temperature just above the melting point dissociates according to

$$V_2O_5 = V_2O_5 - x + \frac{x}{2}O_2$$

where x increases with increasing temperature. For every atom of oxygen evolved, two electrons are left behind, and these electrons

can be singly or doubly trapped in a structure unit. Thermoelectric power (41, 42) and Hall coefficient (37, 29) measurements on V_2O_5 crystals grown from the melt have established that the charge carrier is the electron. The nature of the donor center, including the number of electrons per center, the type of defects, and the number of V^{+5} ions with which the charge carrier is interacting can in principle be deduced from ESR studies.

Proposed Dipolar Centers and Calculations

Dipolar Centers

In the literature, there are two schools of thought in the interpretation of the ESR spectra, and the two models proposed in the representative papers will be briefly discussed. Gilles and Boesman (19) proposed a vacancy model of $V^{+5} \boxed{O_v} V^{+4}$ to explain the observed fifteen-line spectra of their crystals which were grown from material purified by zone-refinement and under oxygen atmosphere. The nuclear spin of $5^{11}V$ is 7/2, so that if the electron is shared by two nuclei, the number of hyperfine lines is $2\left(\frac{7}{2}\right) + 1 = 15$. In this model, the electron interacts equally with two V^{+5} ions through an oxygen vacancy, $\boxed{O_v}$, because of a supposed physical improbability of overlapping electronic orbitals between vanadium atoms which are separated by an oxygen atom. From symmetry considerations, the authors concluded that only two units, $u \ F v$ and $u \ U u$, are geometrically possible, and their orientations with respect to the crystallographical axes are indicated in Figure 21 which shows a three dimensional drawing of a unit cell according to the structure given by Byström, et al (10).

Neither $u \mathbf{F} \mathbf{v}$ nor $u | \overline{U} | u$ possesses a significant amount of dipole moment because the electron in the unit is bound about equally to both V^{+5} ions. From molecular orbital theory, Goodenough (21) proposed the existence of $v^{+5}Ov^{+5}$ as an electron trapping unit, and the electron is shared between the two V^{+5} ions through a process of superexchange. Then, a dipolar center can be formed to include a v^{+5} $\boxed{O_v}$ v^{+5} unit and the surrounding four v^{+5} O v^{+5} units as shown in Figures 22 and 23. In the absence of an applied field, the four electronic energy levels, one for each of the $V^{+5}OV^{+5}$ units, of the center are equal. The applied electric field will lift this directional degeneracy. For an applied electric field along [010] direction, the jumping of the electron between Land L_2 directly or through L_3 or L_4 as intermediate represents a 180 ° reorientation of the "dipole" because the net charge at O_v is 2+ due to its immediate neighbors of $V^{\pm5}$ ions. Similarly, the hopping of the electron from L, or L_2 to L_3 or L_4 represent a 90° rotation of the "dipole." From Equation (2.19), the calculated moment of this "dipole" is 4.4 debye.



Figure 21. Crystal structure of vanadium pentoxide (10), and the possible ESR units $(u \cup u)$ and $u \vdash Fv$ proposed by Gilles and Boesman (19). The unit cell is indicated by the heavy broken line.



Figure 22. The possible locations of the two proposed dipolar centers in the V_2O_5 structure projected along (001) (10). The symbols I⁺ and I₁ and I₂ are the impurity ion and the two electronic levels respectively for the impurity center, and similarly O_v , L₁, and L₂ designate the oxide-ion vacancy and the two electronic levels respectively for the vacancy center. The heavy lines indicate the unit cell.



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Figure 23. The possible locations of the two proposed dipolar centers in the V_2O_5 structure projected along (010) (19). For the impurity ion center, I^+ is the impurity ion and the numbers 1, 2, 3, and 4 designate the possible ions, either part or all of them interact with the trapped electron. For the vacancy center, O_v , L_3 , and L_4 designate the oxideion vacancy and the two energy levels respectively. The heavy lines indicate the unit cell, and the dashed lines indicate the atoms lie below the ac plane.

According to the polaron theory, the carrier gets self-trapped in a polaron state through polarizing the surrounding medium (25). Then, the activation energy for the dipolar reorientation can be interpreted as the energy needed to overcome the polarization field of the original level.

From the study of ESR spectra of V_2O_5 crystals grown from starting materials with different degree of purity and under either air or oxygen atmosphere, loffe and Patrina (29) proposed an impurity model. The localization of the electron carriers was thought to be due to the coulombic fields of the compensating impurities which eliminate the overlap of the $|x^2 - y^2|$ ground-state orbitals. These authors proposed that a univalent metal, such as Li, Na, and Cu which are non-paramagnetic and form compounds of the type $M_{x}V_{2}O_{5}$, penetrates the structure between the layers as a univalent positive ion whose charge would compensate the electron transferred to the vanadium sublattice. This electron may interact with two or four V^{+5} neighboring ions of the same layer depending on the nature of the impurity; these V^{+5} ions are at the same potential, which is different from that of the other nearest neighbors. The suggested locations of these impurity ions in the lattice are shown in Figures 22 and 23.

A dipolar center can be formed according to this impurity model. If the impurity is located at equal distances from the adjacent layers, it can be viewed as the positive pole of the "dipole." The hopping motion of the electron between these two layers represents the reorientation of this "dipole." Similarly, the energy of reorientation can be interpreted as above for the vacancy model. This "dipole" would have a moment of 2.2 debye.

A small sample was cleaved from a large grown crystal for ESR measurements. Spectra were taken at 77° K and at room temperature with a Varian model E9 ESR spectrometer equipped with a Varian model E101 microwave bridge as modulation and detection unit. Figure 24 shows a spectrum taken at 77° K with the crystal orientation with respect to the magnetic field \vec{H} of $\vec{H}b = 35^{\circ}$ and $H\perp c$. The observed hyperfine spectra for V^{+4} agreed well with that reported by Gilles and Boesman for zone refined V_2O_5 (19). However, where Gilles and Boesman found 15 lines with a splitting of 93 Oe (at $\vec{H}b = 30^{\circ}$ and $H\perp c$), for the sample used in this study, there are apparently two or three additional lines which may arise from impurities. The hyper-fine splitting between the major lines was found to be 98 Oe.

The principal impurity was identified to be Fe^{+3} by comparison with the spectra of V_2O_5 doped with 0.05% Fe_2O_3 given by loffe and Patrina (28). These authors found at room temperature, for the orientation H\\a, three lines, which were calculated (for frequency 9.52 G Hz) to lie at 1124, 1379 and 1748 Oe. For the sample used in this study, at the same temperature, orientation, and frequency, lines were observed at 1120, 1394 and 1768 Oe, as shown in Figure 25.







At room temperature, when the angle between H and b-axis decreased from 90° to 0°, the g value for the Fe⁺³ lines decreased and approached the value of 2.00, as observed by Ioffe and Patrina (28).

The weight of the above ESR measurements gives strong support to a model of the dipolar centers in which the unpaired electron is shared between two vanadium ions. It cannot be concluded, however, which defect (e.g. the oxide-ion vacancy or an interstitial alkali metal ion) serves to bind the electron to the center. Since the dielectric relaxation observed did not conform exactly to the Debye model, implying at least two different relaxation times, it may be that both types of centers exist together.

Intracenter Mobility and Concentration of Dipolar Centers

It may be inquired whether other means exist to differentiate between the two dipolar models. For a two-site model, Sewell (51) derived, through application of quantum mechanics, the expression for dielectric conductivity in terms of T(T), the concentration of dipolar center N_o, the dipolar separation a, and the physical constants electronic charge e and Boltzmann constant k. This expression is

$$\sigma_{\text{diel}}(\omega) = \left(\frac{N_{\text{o}}e^2}{kT}\right) \frac{a^2}{2\tau(T)}$$
(5.14)

when ω is equal to $\tau^{-1}(T)$. From Equation (5.14), the intracenter

mobility μ_{intra} can be expressed as

$$\mu_{intra}(T) = \frac{ea^2}{2kT \tau(T)} .$$
 (5.15)

Assuming the process of 180[°] reorientation is the dominant one at ω equal to $\tau^{-1}(T)$, the vacancy model of dipolar center becomes a two-site model.

If the activation energy of the dipolar reorientation for one type of center is much greater than that of another type, the measured T(T) within the experimental temperature range is that of the center with the lower activation energy. From Equation (5.15), for $T(142^{\circ} \text{ K}) = 3.18 \times 10^{-4} \text{ sec}$, μ_{intra} for the vacancy and impurity dipolar centers is 3.2×10^{-10} and $8.1 \times 10^{-11} \text{ cm}^2/\text{V}$ sec respectively. From Equations (5.14) for σ_{diel} ($\tau = 3.18 \times 10^{-4} \text{ sec}$) = 3.3×10^{-10} $\Omega^{-1} \text{ sec}^{-1}$, the corresponding N_{0} of $6.5 \times 10^{18}/\text{cm}^{3}$ and 2.6×10^{19} cm³ respectively for the vacancy and impurity dipolar centers were calculated.

While order-of-magnitude determinations of unpaired electron concentration are possible by means of ESR (19,27), these clearly will not distinguish between the two types of centers on the basis of their calculated concentrations.

The mean separation between the neighboring centers, $2r_m$, can be calculated from N_o through

$$r_{\rm m} = (\frac{3}{4\pi N_{\rm o}})^{1/3}$$

For $N_o = 6.5 \times 10^{18}/cm^3$, r_m would have the value of 34 Å, and this value of N_o represents a molar concentration of 0.01 mole of dipolar centers per 1000 cc of V_2O_5 material or a concentration of 0.1 mole %, which is calculated on the assumption that 1 dipolar center per unit cell is the maximum concentration. Hence, the assumption of low dipolar concentration in the Debye theory of dielectric is fulfilled. According to Schnakenberg (48), the resonance integral between the neighboring dipolar centers, which become donor centers in electrical conduction, is exponentially decreasing with the mean separation between neighboring centers. The calculated large value for r_m coupled with the observed linearity of the log σ_{dc} against T^{-1} curves down to temperature of less than 125° K implies the existence of localized dipolar centers in the V_2O_5 crystals used in this study.

D C Conduction Mechanism and Activation Energy

The activation energy of dc conduction may consist of contributions from carrier production and from the transport process. According to Holstein, (25), for temperature below one half of the Debye temperature, θ_D , the mobility of a small polaron is not thermally activated, and above $\theta_D/2$ the mobility would vary exponentially with temperature. The θ_D of V_2O_5 is not known, and the present published data on V_2O_5 is not sufficient to establish the mobility behavior of the ionized carrier for the temperature range of interest. Therefore, the dominant carrier transport process is assumed to be the non-thermally activated tunneling over most of the temperature range of interest. Then, the main contribution to the activation energy for dc conductivity is the energy required to produce a free carrier from a donor center.

McCulloch (37) considered the process of carrier production as an equilibrium ionization reaction of the donor center to give a free carrier and an ionized donor center. An equilibrium constant K was defined as

$$K = \frac{{n e^{n} (d^{+})}}{{n (d)}} = \exp(-\Delta G/kT)$$
 (5.17)

where n_e , $n_{(d^+)}$, and $n_{(d)}$ are the concentrations of the free carrier, ionized donor center, and the donor center respectively, and ΔG is the reaction potential of the process. Assuming

$$n_{e} = n_{(d^{+})}$$

and

$$n_{e} < < n_{(d)}$$

Equation (5.19) can be rewritten as

$$n_{e} = [n_{(d)} \exp(\frac{\Delta S}{k})]^{-1/2} \exp(-E_{i}/2 kT)$$
 (5.18)

where E_i and ΔS are the enthalpy and entropy changes for the process of charge carrier production. A similar expression for n_e can be derived through the application of quantum statistics to a model of a non-degenerate n-type semiconductor with very low impurity compensation and $n_e << n_{(d)}$ (6).

For the presence of one dominant type of charge carrier, $\sigma_{dc}(T)$ is given by

$$\sigma_{dc}(T) = n(T)e\mu(T)$$
 (5.19)

where n(T) is the concentration of dominant charge carrier, e is the charge, and $\mu(T)$, the mobility, is assumed constant for the temperature range of interest. From Equation (5.18), Equation (5.19) can be expressed

$$\sigma_{dc}(T) = \sigma_{o} \exp\left(-E_{i}/2kT\right)$$
(5.20)

where

$$\sigma_{o} = e\mu \left[n_{(d)} \exp\left(\frac{\Delta S}{k}\right) \right]^{1/2}$$

Comparing Equations (5.20) and (5.7), the relationship

$$\mathbf{E}_{i} = 2\mathbf{E}_{dc} \tag{5.21}$$

is obtained.

Assuming the defect and the electron to be point charges, the order of magnitude for the ionization energy, E_{ic} , can be calculated from

$$E_{ic} = \frac{q_e^{q}q_D}{\epsilon_m^{R}}$$

where q_e and q_D are the charge of the electron and the defect respectively, ϵ_m is the dielectric constant of the medium, and R is the separation between the two charges. For the oxide-ion vacancy as
defect model q_e and q_D are equal to 1 and 2 electronic charge unit respectively, ϵ_m is equal to 5.1, and R is 4.4 Å. The calculated value for E_{ic} is 1.3 eV which is more than twice the value calculated from Equation (5.21). The difference could be explained in terms of the contributions that are not included in this crude electrostatic model. One of the major unaccounted contributions is the polarization energy of the crystal lattice which relaxes after the ionization of the electron.

After ionization from the donor center, the carrier will be trapped by its self-induced polarizing field at some normal site of the lattice. For the temperature range used in this study, this freed carrier will move through the lattice from one V^{+5} ion to another by a dominant process of non-thermally activated tunneling.

Summary

Through the evaluation of the ac conductance and capacitance measurements, the presence of Debye type of dielectric relaxation in V_2O_5 crystals was established. Then, on the basis of the Debye theory of dielectric, the relaxation times were deduced, and the activation energy for the dipolar reorientation was calculated to be 0.24 \pm 0.03 eV. A value for τ_0 was estimated to be 1.1 x 10⁻¹² sec.

The three possible relaxation processes considered are the inhomogeneous conduction, the movements of ions around a defect in the lattice, and the hopping of the trapped electron in a donor center.

9.3

Based on the experimental results and chemical and electrical considerations, the process was concluded to be the hopping of a trapped electron in a donor center.

Two models of dipolar centers, with either an oxide-ion vacancy or a univalence interstitial impurity ion as defect, were proposed. The reorientation of the "dipole" was achieved by the hopping of the electron along the direction of the applied field and between the available electronic energy levels in the center. The activation energy for the reorientation process was interpreted in terms of the polaron theory.

ESR measurements on the crystal and calculations of the intracenter mobility and the dipolar concentration, N_0 , on the basis of the proposed dipolar models can not prove their exclusive existence. However, the possibility of simultaneous existence of both types of centers in the same crystal provides an explanation for the observed deviation from the Debye model. The value of N_0 confirms the assumption of low dipolar concentration. Furthermore the large mean separation between the neighboring centers, calculated from N_0 , coupling with the fact that the curves of log σ_{ac} vs T⁻¹ is linear down to temperature less than 125[°]K implies that the centers are localized.

For dc conduction, the ionization energy of the electron from the center was shown to be approximately twice the value of the activation energy calculated from the slope of the log σ_{dc} vs T⁻¹ plots.

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After ionization from the center, the electron will be transported through the crystal via a dominant process of non-thermally activated tunneling for the temperature range of interest.

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APPENDICES

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APPENDIX I

The processes of deducing $\tau(T)$ from the conductance and capacitance measurements have been described in the text. For a particular crystal, a set of plots of log σ_{ac} vs T^{-1} for five frequencies was presented in Figure A1. Graphical interpretations were applied to these curves, and the calculated results of ϵ_2 as function of T for the different frequencies are plotted in Figure A2.

For the same sample, a set of plots of ϵ_1 as function of temperature at constant frequency for the use frequencies is shown in Figure A3. The deduced T(T)'s with the estimated uncertainties from both processes are tabulated in Table 3.

$2\pi T(T)$, 10^{-3} sec	T ^{**} _{max} , ^o K	Т [*] , ^о к	
10	134 <u>+</u> 2	134 <u>+</u> 2	
2	145 <u>+</u> 2	146 ± 2	
1	149 <u>+</u> 2	152 <u>+</u> 2	
0.2	164 + 2	163 <u>+</u> 2	
0.1	168 ± 2	169 <u>+</u> 2	

Table 3. Tabulation of the T(T) values deduced from conductance and capacitance measurements of Crystal C.

* Results from capacitance measurement

** Results from conductance measurement



Figure A1. The ac conductivities for Crystal C measured at constant frequency for different frequencies. The ordinate at the right is for the curves of $v = 5 \times 10^3$ Hz and $v = 10^4$ Hz.

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Figure A3. Temperature dependence of ϵ_1 for Crystal C measured at constant frequency for different frequencies.

APPENDIX II

As described in the text, one way to determine the σ_{dc} as function of temperature for a sample is through graphical extrapolation of the linear sections of the superimposed plots of $\log \sigma_{ac}(T)$, at a frequency, against T^{-1} for all the frequencies used. Such plots are shown in Figure A4. The calculated activation energy of conduction from the slope of the extrapolated curve is 0.26 ± 0.01 eV. After establishing the $\sigma_{dc}(T)$ curve, graphical subtraction between $\sigma_{ac}(T)$ and $\sigma_{dc}(T)$ curves to give $\sigma_{diel}(T)$ is possible. Figures A5 and A6 show the plots of σ_{diel} as function of T^{-1} , and from these plots the corresponding half widths, $\delta_{1/2}$, are estimated to be $0.46 \times 10^{-3} \text{K}^{-1}$ and $0.47 \times 10^{-3} \text{K}^{-1}$ for frequencies 5×10^2 and 2×10^2 Hz respectively. The average of the H calculated from these two using Equation (5.11) is 0.24 ± 0.02 eV.



Figure A4. Superimposed plots of ac conductivity for Crystal 14 measured at constant frequency for different frequencies.



Figure A5. Dielectric conductivity as function of temperature for crystal 14 measured at constant frequency of 500 Hz.



Figure A6. Dielectric conductivity as function of temperature measured for Crystal 14 at constant frequency of 200 Hz.

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