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ELECTRONIC AND RADIATION DAMAGE PROPERTIES OF RUTILE

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TECHNICAL REPORT

FOR PERIOD ENDING 15 MARCH 1973

to

ADVANCED RESEARCH PROJECT AGENCY

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Title

ELECTRONIC AND RADIATION DAMAGE PROPERTIES OF RUTILE

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The following report covers the period from 1 August 1972 to 15 March 1973. During this period effort has been concentrated in the following areas:

I. Crystal Growth
II. Magnetic Resonance Study of Defects
III. Hydrogen Diffusion Experimental
IV. Hydrogen Diffusion Theoretical
V. Determination of Conduction Band Parameters by Use of Hydrogen Solubility Theory Developed in Previous Report
VI. Far I.R. Spectrometer

The four preprints included in the last progress report have all been accepted for publication and will appear shortly. In addition, three papers dealing with work in progress were presented at the San Diego APS Meeting.

I. Crystal Growth

The relation between the actual temperature profile inside the chemical vapor transport ampoule and the temperature distribution of the exterior heat source has been followed further. The temperature gradient at the growing crystal determines to a large extent the interface stability. Hence this investigation is basic to CVT crystal growth in general. Precious little had been known before our measurements, concerning temperature oscillations and profiles in this crystal growth technique. By expanding the study from $TeCl_4$ to iodine, that is also frequently used as CVT transport agent, we were able to verify chemical convective instability on a broader basis, leading to a publication that will be basic for future CVT studies. (See the attached Preprint I that has been submitted to the Journal of Crystal Growth; an invited talk on this subject will be presented at the Gordon Research Conference on Crystal Growth in July.)

The crystal growth efforts are summarized in the enclosed thesis (Preprint II) of M. C. DeLong. Beyond this thesis, further insight has been obtained into the actual transport chemistry of the process. In former progress reports it had been pointed out already that the transport reaction assumed by earlier workers

$$TiO_{2(s)} + TeCl_{4(g)} \rightleftarrows TiCl_{4(g)} + TeO_{2(g)} \qquad (1)$$

is at best a crude overall equation for a chain of subreactions. One of these reactions, thermal dissociation of $TeCl_4$ has been identified earlier in this work. Quantitative measurements of the dissociation kinetics are now under way. In addition, thermo-chemical calculations predict that TeO_2 should also dissociate to a large extent in the employed temperature range. This species will be included into the kinetic studies which will result in better defined thermo-chemical data for the various tellurium compounds involved, than are currently available. Furthermore we found that SiO_2 of the quartz container is also transported in the system, leading under certain conditions to a sizeable contamination of the TiO_2 crystals. We assign the observed SiO_2 transport preliminarily to the coupled reactions [that are also coupled to (1)].

$$SiO_{2(s)} + TiCl_{4(g)} \rightleftarrows SiCl_{4(g)} + TiO_{2(s)} \qquad (2)$$

$$SiCl_{4(g)} + O_{2(g)} \rightleftarrows SiO_{2(s)} + 2Cl_{2(g)} \qquad (3)$$

Further experiments are planned to verify the role of (2) and (3) which are of general interest since various other workers employ quartz ampoules in CVT processes that involve $SiCl_4$.

II. Magnetic Resonance

Work in this area has centerd on investigation and identification of various charge states of impurities in rutile. See attached preprints III and IV. In addition to the work discussed in the preprints we are studying W-doped and V-doped material and are attempting to identify the site of interstitial **protons** in the rutile lattice.

III. Hydrogen Diffusion Experimental

A large **effort** has been made in this area because of the importance of H as a probe in the study of electron trapping levels as discussed in IV. This has proved to be an extremely difficult project both experimentally and theoretically (Sec. IV). In order to avoid large electric field effects it is necessary to perform the experiments at nearly constant Fermi Level. This has been achieved by simultaneously diffusing Hin and Dout or vice versa in such a way that the total concentration of H + D remains nearly constant. Problems of vacuum contamination at the elevated temperatures required have been severe, as have surface effects. Thus far satisfactory results have not been obtained but we feel that the problems are nearly under control.

IV. Hydrogen Diffusion Theoretical

A. Introduction

Diffusion in insulators is generally accompanied by changes in the Fermi Level, which in turn results in electric fields which influence the diffusion rate in the material. Since the electric field present may vary greatly with the sample and the experimental conditions one cannot expect a unique diffusion coefficient or even that the system will obey Fick's Law. The observed diffusion will be the result of many factors including microscopic jump rates in the absence of fields, impurities, and nearby diffusing ions etc.; distribution of impurities and defects; in addition to internal electric fields. Yet experimentally what is measured is simply concentration vs. time - indeed, often only total integrated concentration vs time. The purpose of this study (consisting of the theory of this paper and the experimental work of Sec. III) is to identify precisely what can be determined from diffusion measurements.

As a prototype system we will consider the simultaneous diffusion of H and D in rutile in such a fashion that the total concentration of H plus D remains nearly constant. As will be shown, this permits a quantitative treatment of the effects of both concentration gradients and electric fields in a self-consistent manner, and determination of an effective diffusion coefficient in the absence of a field.

In summary, the goal of this study if to indicate the conditions under which Fick's Law is valid and to determine the meaning of the measured diffusion coefficient if these conditions are met.

B. Diffusion Equation

We begin by deriving an equation describing diffusion in the presence of both a concentration gradient and electric fields, in a form suitable to the present problem as indicated in the Introduction. We shall not be concerned with a first principles calculation of diffusion rates and in fact we wish to formulate the problem is a manner which is as model independent as possible. We assume that the concentration n of a given species can be represented as a continuous function of position which is sufficiently slowly varying that $\Delta n/n << 1$ (where Δn is the change in n) over a region large enough that a macroscopic electrostatic potential can be used, i.e., over a region of several ($\sim$ 5-10) atomic planes. We suppose further that the macroscopic potential, ϕ, is sufficiently slowly varying over the same region that $q\Delta\phi << kT$ (where q is the charge of the diffusing species and $\Delta\phi$ is the change in ϕ), and that the local concentration influences the average (over the above region) probability that a particular ion will jump out of the region only through the macroscopic potential gradient.

The latter is an assumption that the concentration is low enough that "most" hops of "most" ions are not influenced by the presence of others. The fact that they may be influenced occasionally is covered by the averaging process, but we are ignoring any dependence of the average jump frequency on concentration. Considering the normal concentration range of $\sim 10^{18}$-$10^{19}/\mathrm{cm}^3$ this should be a good approximation.

Using these assumptions, and considering one-dimensional diffusion, it is readily seen that the time rate of change of concentration is given by:

$$\frac{\partial n(x,t)}{\partial t} = n(x + \Delta x,t)\, F_L(x + \Delta x) + n(x - \Delta x,t)\, F_R(x - \Delta x) \qquad (1)$$

$$- n(x,t)[F_L(x) + F_R(x)] \quad ,$$

where x is the position, t is the time, F_L and F_R are the average probabilities of an ion leaving the region by hopping to the left and right respectively. The relation between F_L and F_R can be found by considering a concentration profile corresponding to equilibrium in the presence of a macroscopic potential, $\phi(x)$. (Note that equilibrium requires a uniform chemical potential, not a uniform concentration.) Since the F's depend on n only through ϕ (as assumed above) the relation found at equilibrium will be valid for all n. The equilibrium concentration is given by Boltzmann statistics as:

$$n(x) = n_0 e^{-q\phi(x)/kT} \quad , \qquad (2)$$

where n_0 is a constant, k is Boltzmann's constant, and T is the absolute temperature.

Since in equilibrium the net number crossing any plane must be zero we have:

$$n_0 e^{-q\phi(x+\Delta x)/kT}\, F_L(x + \Delta x) = n_0 e^{-q\phi(x)/kT}\, F_R(x) \quad .$$

Expanding the exponents and rearranging, we find:

$$F_L(x + \Delta x) \approx F_R(x) \left[1 + \frac{q}{kT} \frac{d\phi(x)}{dx} \Delta x\right] \quad .$$

Substituting (3) in (1) we find, after some manipulation, the equation:

$$\frac{\partial n(x,t)}{\partial t} = (\Delta x)^2 \frac{\partial}{\partial x}\left[F_R(x)\,\frac{\partial n(x,t)}{\partial x} + \frac{q}{kT}\,F_R(x)\,n(x,t)\,\frac{\partial \phi(x,t)}{\partial x}\right], \qquad (4)$$

where Δx is the width of the region. Δx takes the place of the lattice constant in the normal derivation of Fick's Law. In our case Δx is not the lattice constant and $F_R(x)$ is not the probability of jumping from one plane to the next. We can, however, combine them into an effective diffusion constant as shown below. For the moment we simply let

$$(\Delta x)^2\, F_R(x) = g(x). \qquad (5)$$

What we have done is consider a region large enough that local fluctuations (e.g., is there another impurity or lattice defect near the diffusing ion?) average out. Hence Δx does not correspond to a single jump but rather to many jumps. Exactly how many is not important so long as it is enough to eliminate local perturbations. Similarly F_R is not the usual jump frequency but rather $1/t$ where t is the average time required for a particular ion to leave the region, Δx, by jumping to the right. In the ideal case of a completely homogeneous crystal, with low concentration of diffusing ions, and in which only single jumps occurred, we would have:

$$a^2 F = (\Delta x)^2\, F_R = D\ , \qquad (5a)$$

where a is the lattice constant, F is the microscopic jump frequency, and D is the usual diffusion coefficient. In general, however, none of these conditions are met and $g(x)$ is not related to a and F in any simple fashion. We will see later (in Sec. D) the significance of $g(x)$. Thus:

$$\frac{\partial n(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[g(x)\,\frac{\partial n(x,t)}{\partial x} + \frac{q}{kT}\,g(x)\,n(x,t)\,\frac{\partial \phi(x,t)}{\partial x}\right] . \tag{6}$$

To proceed further we suppose that $g(x)$ is constant. If the crystal is homogeneous - save for the diffusing species - this assumption amounts to restricting the macroscopic electric field to values too small to effect the jump probability. This corresponds to the assumption that $ga\,\frac{d\phi}{dx} \ll W$ where a is the lattice constant and W is the barrier height if the jumps are thermally activated. If tunneling predominates the situation is considerably more complicated and model dependent. Experimentally, however, this appears to be a good approximation at least at high temperatures. With this simplification the diffusion equation becomes:

$$\frac{\partial n(x,t)}{\partial t} = g\,\frac{\partial^2 n(x,t)}{\partial x^2} + \frac{qg}{kT}\,\frac{\partial}{\partial x}\left[n(x,t)\,\frac{\partial \phi(x,t)}{\partial x}\right] . \tag{7}$$

C. MACROSCOPIC Field Equations

To determine $\phi(x,t)$ we impose the boundary condition that $\phi = 0$ at the surface and make use of Poisson's equation in CGS units.

$$\frac{d^2\phi}{dx^2} = -\,\frac{4\pi\rho}{\varepsilon} . \tag{8}$$

where ε is the dielectric constant and ρ is the charge density. The interpretation of (8) requires some care in that the potential needed in (2) and (3) is the potential at the equilibrium sites of the diffusing ion, and hence is a local potential which may be subject to a local field correction. If so, we would have:

$$\vec{E}_{Loc} = \vec{E}_M + \alpha\vec{P} \quad ,$$

where $\vec{E}_{Loc}$ is the field at the ion site, $\vec{E}_M$ is the macroscopic field, $\vec{P}$ is the polarization, and α is the appropriate Lorentz local field factor. Now in our case $\vec{P}$ is not being produced by the diffusing ions themselves and hence $\vec{P}$ is not proportional to $\vec{E}_{Loc}$, but rather to $\vec{E}_M$. The proportionality constant will not be just the susceptibility but will involve Lorentz local field factors appropriate to the system. The net result, however, is that:

$$\vec{P} = \gamma\vec{E}_M \quad ,$$

where γ is a constant.

Hence:

$$\vec{E}_{Loc} = (1 + \gamma)\vec{E}_M \quad .$$

Thus:

$$\frac{d\phi_{Loc}}{dx} = (1 + \gamma)\,\frac{d\phi_M}{dx}$$

and

$$\phi_{Loc} = (1 + \gamma)\,\phi_M + \delta \quad ,$$

where ϕ_M is macroscopic potential given by (8), ϕ_{Loc} is defined by $-\frac{d\phi_{Loc}}{dx} = E_{Loc}$, and δ is a constant. The requirements of charge neutrality for the crystal as a whole means ϕ_M and ϕ_{Loc} both equal 0 at the surface. Hence:

$$\phi_{Loc} = (1 + \gamma)\, \phi_M \quad .$$

Thus ϕ_M as obtained from (8) can be used in (7) by simply replacing q in (7) by q_{eff}. However, in the absence of experimental evidence to the contrary we shall suppose that $\gamma = 0$ so that $q_{eff} = q$, and $\phi_{Loc} = \phi_M = \phi$.

The total charge density is made up of the following terms:

ρ_L = Charge density due to Lattice Ions;
$\rho_c = - n_c e$ = Conduction electrons;
$\rho_T = - n_T e$ = "Trapped" electrons;
$\rho_n = nq$ = Diffusing ions;
ρ_I = Non-diffusing Ions;
ρ_V = Valence electrons;

where -e equals the charge of an electron. Noting that $\rho_L + \rho_V = 0$, for an insulator we have:

$$\rho = \rho_I + nq - e(n_c + n_T) \quad . \tag{9}$$

In the absence of electric fields,

$$n_T = \sum_i \frac{N_i}{e^{\beta(E_i - \mu)} + 1} \quad , \tag{10}$$

where N_i is the concentration of traps with trapping level E_i, $\beta = 1/kT$, and μ is the electron Fermi level. Similarly:

$$n_c = \int_{E_c}^{\infty} D(E) \frac{dE}{e^{\beta(E-\mu)} + 1} \quad , \tag{11}$$

where E_c is the energy of the bottom of the conduction band and $D(E)dE$ is the number of states/cm^3 between E and E + dE.

In the presence of a macroscopic electrostatic potential, equations (10) and (11) take the form:

$$n_T(x) = \sum_i \frac{N_i}{e^{\beta[E_i - e\phi(x) - \mu]} + 1} \quad , \tag{12}$$

$$n_c(x) = \int_{E_c(x)}^{\infty} D(E) \frac{dE}{e^{\beta[E - e\phi(x) - \mu]} + 1} \quad . \tag{13}$$

In practice, $n_c(x)$ is always small enough that (13) can be approximated by:

$$n_c(x) = N_0\, e^{-\beta[E_c(0) - \mu - e\phi(x)]} \equiv N_s\, e^{\beta e\phi(x)} \quad , \tag{14}$$

where N_s is the conduction electron density at the surface of the crystal (where $\phi(x)$ is taken to be zero).

We now consider a special case of particular experimental interest. We suppose that, in addition to the conduction band (and shallow traps which can be lumped with it), we have deep filled traps and one trapping level near the Fermi level. This case can be made to fit nearly all experimental situations by appropriate choice of parameters. The concentration of electrons on the trap near the Fermi level is:

$$N_T = \frac{N_{T0}}{e^{\beta(E_T-\mu_e)}\, e^{-\beta e\phi} + 1} = \left[\frac{N_{T0}}{e^{\beta(E_T-\mu_e)} + 1}\right]$$

$$\times \left[1 + \frac{\left[e^{\beta(E_T-\mu_e)}\right]\left(e^{-\beta e\phi} - 1\right)}{e^{\beta(E_T-\mu)} + 1}\right]^{-1} \qquad (15)$$

where N_{T0} is the density of the trap, E_T is the energy of the trap at the surface of the crystal, and N_T is the concentration of electrons on the trap. Hence:

$$\rho(x) = \rho_I + n(x)q - eN_s{}'e^{\beta e\phi(x)} - e(N_D + N_T) \quad , \qquad (16)$$

where N_D is the concentration of filled traps and $N_s{}'$ is the concentration of electrons, in the conduction band and in shallow traps, at the surface of the crystal. Note that we have ignored any contribution due to surface states. These can be included by an additional δ function term at the surface if needed.

At this point it is useful to note some of the special cases covered by (16). In a perfect crystal $\rho_I = N_D = N_T = 0$ and (16) becomes:

$$\rho(x) = n(x)q - eN_s{}'e^{\beta e\phi(x)} \quad . \qquad (16a)$$

In the case of several deep traps well below the Fermi Level (16) becomes:

$$\rho(x) = n(x)q - eN_D - eN_s{}'e^{\beta e\phi(x)} \quad . \qquad (16b)$$

Similarly, most experimental situations can be described by (16).

D. Two Component Diffusion Equation with Macroscopic Field

We are now in a position to write down a system of equations governing the simultaneous diffusion of H and D in the presence of a macroscopic electric field they help to produce. We assume that no other electrically active species is diffusing. From (7) and (8) we have:

$$\frac{\partial n_H(x,t)}{\partial t} = g_H \frac{\partial^2 n_H(x,t)}{\partial x^2} + \frac{q_H g_H}{kT} \frac{\partial}{\partial x} \left[n_H(x,t) \frac{\partial \phi(x,t)}{\partial x} \right] , \tag{17}$$

$$\frac{\partial n_D(x,t)}{\partial t} = g_D \frac{\partial^2 n_D(x,t)}{\partial x^2} + \frac{q_D g_D}{kT} \frac{\partial}{\partial x} \left[n_D(x,t) \frac{\partial \phi(x,t)}{\partial x} \right] , \tag{18}$$

and

$$\frac{d^2 \phi(x,t)}{dx^2} = -\frac{4\pi\rho(x,t)}{\varepsilon} , \tag{19}$$

where ρ is given by equation 16. Equations 17 and 18 are valid in the interior of the sample but not at the surface. This is best seen by considering the limit $\frac{\partial[\ ]}{\partial x} \equiv 0$ in (17) and (18) above (Fick's 2nd Law). The situation of interest experimentally is one in which the concentration at the surface is constant. Hence the solution of Fick's 2nd Law is of the form

$$n(x,t) = A_0 + \sum_{n=1}^{\infty} A_n(t) \sin(n\pi x/\ell) ,$$

where ℓ is the thickness of the sample. Now, strictly speaking, Fick's Second Law is not valid at the surface due to the fact that the crystal ends and hence there is a discontinuity in the physical parameters. Mathematically we add an "anti-crystal" at the surface and extend the solution to negative x and to $x > \ell$. Since $n(x,t) - A_0$ is odd at $x = 0$, the effect is to make both $[n(x,t) - A_0]$ and $d^2n/dx^2 = 0$ at $x = 0,\ell$. Hence the discontinuity can either be removed by adding the anti-crystal or can simply be ignored since both give precisely the same answer for n and d^2n/dx^2 at $x = 0,\ell$. In other words, the symmetry is such that the discontinuity at the surfaces can be neglected. However, in the case of Eqs. 17-19, this is no longer true. $(n - A_0)$ and ϕ are odd at the surface, but $\partial/\partial x[n(d\phi/dx)]$ is not. Thus the discontinuity cannot be ignored and we must simulate the surface by adding the term required to make $\partial n/\partial t = 0$ at $x = 0,\ell$.

This source term which accounts for the injection (or ejection) of ions at the surface by the electric field is:

$$- \frac{qg}{kT} \frac{d}{dx} \left[n(x) \frac{d\phi(x)}{dx} \right] [\delta(x) + \delta(x - \ell)] \quad , \tag{20}$$

where δ is the Dirac δ Function. With this modification, Eqs. 17-19 describe the physical system.

We now need appropriate boundary conditions. We shall be interested in the case in which the initial concentrations of H and D are constant throughout the sample except at the surface, and the surface concentrations are constant in time. For example, we will have conditions of the type:

$$\begin{aligned} &n_H\,(x,0) = N_H && 0 < x < \ell \\ &n_D\,(x,0) = N_D && 0 < x < \ell \\ &n_H\,(0,t) = N_{H_0} = n_H\,(\ell,t) && \\ &n_D\,(0,t) = N_{D_0} = n_D\,(\ell,t) && \\ &\phi(0) = \phi(\ell) = 0 \quad . && \end{aligned} \tag{21}$$

Note that the condition on ϕ is simply a statement of overall charge neutrality for the crystal.

E. Small Potential Approximation

The system (17)-(19) is in general nonlinear because of the dependence of ρ on ϕ. However, if $\beta e\phi << 1$, the system can be linearized. The resulting equations admit solutions for which $\beta e\phi >> 1$. Hence, if the solution does indeed satisfy the condition $\beta e\phi << 1$. the approximation is satisfactory. In this spirit we now consider ρ in this limit. Referring to Eq. (16) we find:

$$N_T = \frac{N_{T_0}}{e^{\beta(E_T-\mu)}+1}\left[1 - \beta e\phi \frac{e^{\beta(E_T-\mu)}}{e^{\beta(E_T-\mu)}+1}\right]^{-1}$$

$$\approx \frac{N_{T_0}}{e^{\beta(E_T-\mu)}+1}\left[1 + \beta e\phi \frac{e^{\beta(E_T-\mu)}}{e^{\beta(E_T-\mu)}+1}\right] \equiv G + H\phi \ , \qquad (22)$$

where

$$G = \frac{N_{T_0}}{e^{\beta(E_T-\mu)}+1} \ ; \quad H = \left[\frac{\beta e N_{T_0}}{e^{\beta(E_T-\mu)}+1}\right]\left[\frac{e^{\beta(E_T-\mu)}}{e^{\beta(E_T-\mu)}+1}\right] \ . \qquad (23)$$

Hence

$$\rho(x) \approx \left(\rho_I - eN_s' - eN_D - eG\right) + n_H(x)q_H + n_D(x)q_D$$
$$- \phi\left(eH + \beta e^2 N_s'\right) \equiv M + q_H n_H(x) + q_D n_D(x) - N\phi(x) \ , \qquad (24)$$

where

$$M = \left(\rho_I - e\, N_s' + N_D + G\right) \ ; \quad N = eH + \beta e^2 N_s' \ . \qquad (24)$$

F. Solution in the Small Potential Approximation

To solve the system (17)-(19) we expand the concentrations and potential in Fourier Series as follows:

$$n_H(x,t) = A_0 + \sum_{n=1}^{\infty} A_n(t) \sin(n\pi x/\ell) \quad , \tag{25}$$

$$n_D(x,t) = B_0 + \sum_{n=1}^{\infty} B_n(t) \sin(n\pi x/\ell) \quad , \tag{26}$$

$$\phi(x) = \sum_{n=1}^{\infty} C_n(t) \sin(n\pi x/\ell) \quad . \tag{27}$$

Note that the requirement of constant n and ϕ at the surface excludes cosine terms from Eqs. 25-27. Substituting (25)-(27) into (19) we find:

$$-\sum_{n=1}^{\infty} C_n \left(\frac{n\pi}{\ell}\right)^2 \sin\left(\frac{n\pi x}{\ell}\right) = -\frac{4\pi}{\varepsilon}$$

$$\times \left[M + \sum_{n=1}^{\infty} \{q_H A_n + q_D B_n - NC_n\} \sin\left(\frac{n\pi x}{\ell}\right) + q_H A_0 + q_D B_0\right] . \tag{28}$$

Hence:

$$q_H A_0 + q_D B_0 = -M \quad ; \quad C_n \left(\frac{n\pi}{\ell}\right)^2 = \frac{4\pi}{\varepsilon} \left[q_H A_n + q_D B_n - NC_n\right] . \tag{29}$$

Therefore

$$C_n = \frac{(4\pi/\varepsilon)(q_H A_n + q_D B_n)}{(4\pi/\varepsilon)N + (n\pi/\ell)^2} \quad . \tag{30}$$

Next, substituting (25) and (27) into (17) we find:

$$\sum_{n=1}^{\infty} \frac{\partial A_n}{\partial t} \sin\left(\frac{n\pi x}{\ell}\right) = -g_H \sum_{n=1}^{\infty} A_n \left(\frac{n\pi}{\ell}\right)^2 \sin\left(\frac{n\pi x}{\ell}\right) + \frac{q_H g_H}{kT} \frac{\partial}{\partial x}$$

$$\times \left[\sum_{n,m=1}^{\infty} A_n(+C_m) \frac{m\pi}{\ell} \sin\left(\frac{n\pi x}{\ell}\right) \cos\left(\frac{m\pi x}{\ell}\right) + A_0 \sum_{m=1}^{\infty} C_m\left(\frac{m\pi}{\ell}\right) \cos\left(\frac{m\pi x}{\ell}\right)\right]$$

$$= - g_H \sum_{n=1}^{\infty} A_n \left(\frac{n\pi}{\ell}\right)^2 \sin\left(\frac{n\pi x}{\ell}\right) + \frac{q_H g_H}{kT}$$

$$\times \left[\sum_{n,m=1}^{\infty} \left\{A_n C_m \left(\frac{m\pi}{\ell}\right) \left\langle\left(\frac{n\pi}{\ell}\right) \cos\left(\frac{n\pi x}{\ell}\right) \cos\left(\frac{m\pi x}{\ell}\right) - \left(\frac{m\pi}{\ell}\right) \sin\left(\frac{m\pi x}{\ell}\right) \sin\left(\frac{n\pi x}{\ell}\right)\right\rangle\right\}\right.$$

$$\left. - A_0 \sum_{m=1}^{\infty} C_m \left(\frac{m\pi}{\ell}\right)^2 \sin\left(\frac{m\pi x}{\ell}\right)\right] \quad . \tag{31}$$

Note that (20) insured that $(dA_0/dt) = 0$. Now:

$$\cos\left(\frac{n\pi x}{\ell}\right) \cos\left(\frac{m\pi x}{\ell}\right) = \frac{1}{2}\left\{\cos\left[(n + m) \frac{\pi x}{\ell}\right] + \cos\left[(n - m) \frac{\pi x}{\ell}\right]\right\} , \tag{32}$$

and

$$\sin\left(\frac{n\pi x}{\ell}\right) \sin\left(\frac{m\pi x}{\ell}\right) = \frac{1}{2}\left\{\cos\left[(n - m) \frac{\pi x}{\ell}\right] - \cos\left[(n + m) \frac{\pi x}{\ell}\right]\right\} . \tag{33}$$

Substituting (32) and (33) into (31), multiplying by $\sin(n\pi x/\ell)$ and integrating over x from 0 to ℓ, and setting $q_H = q_D = e$, we find:

$$\frac{\partial A_n}{\partial t} = - g_H A_n \left(\frac{n\pi}{\ell}\right)^2 - \frac{e g_H}{kT} A_0 C_n \left(\frac{n\pi}{\ell}\right)^2$$

$$+ 2g_H \left(\frac{n\pi}{\ell}\right)^2 \frac{e}{\pi n} \sum_{\substack{pm \\ \text{odd}}} m A_p C_m \left|\frac{p + m}{n^2 - (p + m)^2} + \frac{p - m}{n^2 - |p - m|^2}\right| . \tag{34}$$

Similarly,

$$\frac{\partial B_n}{\partial t} = - g_D B_n \left(\frac{n\pi}{\ell}\right)^2 - \frac{e g_D}{kT} B_0 C_n \left(\frac{n\pi}{\ell}\right)^2$$

$$+ 2 g_D \left(\frac{n\pi}{\ell}\right)^2 \frac{e}{\pi n} \sum_{\substack{pm \\ \text{odd}}} m A_p C_m \left| \frac{p + m}{n^2 - (p + m)^2} + \frac{p - m}{n^2 - |p - m|^2} \right| . \qquad (35)$$

The system (30), and (34)-(35) cannot be solved analytically but it is very easily done numerically. Thus as soon as experimental numbers (work of Sec. III) are available for the parameters the problem will be completed.

V. Determination of Conduction Band Parameters

Considerable experimental work has been done on applying the theory of hydrogen solubility of the last progress report to the determination of conduction band parameters, trapping levels, etc. The difficulties encountered in this work demonstrate quite compellingly precisely why these measurements are so essential. The first parameters which must be determined are the proton binding energy and the conduction band density of states. After these have been determined to sufficient accuracy, it will then be possible to measure the Ti interstitial binding energy and to start measuring thermal trapping energies for electrons on various defects and impurities, and to calculate the equilibrium concentration of both <H> and <Ti> (H and Ti interstitials). Determination of <H> binding energy and conduction band density of states requires measurement of equilibrium concentration of <H> and conduction electrons, over a fairly wide temperature range, with P_{H_2} and P_{H_2O} held constant, in a concentration range where the electron Fermi level is high enough that we can be sure that all electron traps are filled. In order for our results to be meaningful, however, we must simultaneously hold the concentration of <Ti> at a very low level, since we have no quantitative means of measuring their concentration. Fortunately, the theory is sufficiently detailed to provide a variety of checks to determine whether or not this requirement is being met. So far, we have encountered considerable difficulty in selecting operating conditions which yield adequate <H> concentrations without significant <Ti> concentrations. This same difficulty has been the source of many incorrect interpretations in published work. The most recent measurements indicate that we now have the problem under control, however, and quantitative results should be obtained in the next few weeks.

Because of the extreme importance of these measurements (several other projects can be done properly only after these measurements are completed), most of our efforts recently have been devoted to this problem. If we are successful in completing these determinations, it will be the first time, to our knowledge, the defect and impurity thermodynamics of a system such as rutile have been worked out theoretically and the necessary experimental parameters obtained. This will make possible a wide variety of experiments that could not previously have been done, and will be a major step forward in obtaining a useful characterization of this system.

VI. Far IR Spectrometer

The spectrometer is essentially complete and the first experiments are now being planned. We will begin with a general survey of transmission and reflection properties with special attention being devoted to looking for the plasma frequency.