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ELECTRONIC AND RADIATION DAMAGE PROPERTIES OF RUTILE

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PROGRESS REPORT

FOR PERIOD ENGING 15 AUGUST 1973

to

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ELECTRONIC AND RADIATION DAMAGE PROPERTIES OF RUTILE

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I. HYDROGEN DIFFUSION - THEORETICAL ANALYSIS AND CALCULATIONS:

The basic theory and equations describing diffusion of charged ions in a semiconductor (or insulator) such as TiO_2, in the presence of electric fields induced by variation of the concentration of these ions, was outlined in the last progress report.

The resulting coupled differential equations (which are non-linear) cannot be solved analytically, except for certain limiting cases which are not particularly helpful, and hence must be treated numerically. A major portion of our effort during this period has been devoted to developing a computer program to handle this problem. It is worth noting that this is a very important problem, with application to a wide variety of systems; our results could have quite far-reaching implications. While the problem is not completely solved, our results to date are very gratifying and, in certain respects, rather startling. We anticipate that at least a partial treatment of the problem will be submitted for publication during the current reporting period, so we will only summarize our results here.

The first breakthrough on the problem was achieved when we were able essentially to eliminate one of the coupled equations, thus simplifying the calculations enormously. This step essentially consisted of replacing Poisson's Equation (Eq. 19 of our previous Technical Report) by a simple requirement of local charge neutrality. This is only approximately correct, of course, but we have established detailed criteria for applicability of the approximation and have been able to place upper bounds on the error introduced; the approximation is extremely accurate for a wide variety of situations, including virtually all experimental conditions amenable to accurate measurement.

Even with this major simplification, however, this problem has proved to be an extremely difficult one. Numerical solution essentially requires a double numerical integration, over a spatial coordinate and a time coordinate, of functions which can vary rapidly with both time and position. In order to keep the running time finite, it was necessary to program variable increments in the time coordinate. For some choices of parameters (electron trap concentrations, initial and final concentrations of H and D), the program is now running well. For an isotope exchange measurement, where the solubilities and diffusion coefficients of H and D are not grossly different, quite accurate calculations are possible. The behavior is quite close to Fick's Law, particularly for the out-diffusing ion, with a small enhancement of the diffusion coefficient. This agrees with our experimental results (see Section II), and we are presently in the process of obtaining the best fit to our experimental results.

However, for other choices of H, D, and trap concentrations, and in spite of successively more sophisticated criteria for choosing increments for the integration variables, we found that the calculations is simply beyond the capacity of a rather large computor. We now understand the nature of this difficulty; it does not, in fact, result from a mathematical artifact, but reflects a real and rather surprising physical situation. The problem can arise either for double diffusion (i.e., D replacing H), or for the more general case of single diffusion (i.e., an impurity such as H diffusing either in or out). The anomaly arises in any case in which the total concentration of donor impurities (for the case of diffusion of positively charged interstitials) is greater than the total electron trap density in some part of the crystal and less in another, at any time during the diffusion process.

The details of the behavior depend on trap density and trapping energy, conduction band density of states, etc., but the general features are similar, and are perhaps easier to understand in terms of a specific example. We will use the parameters appropriate to the crystal used for the single diffusion measurements to be described in Section II. The dominant trapping level is due to Al substitutionals and is located ~ 2 eV below the conduction band - the Al concentration, n_{Al}, was approximately $(0.9 \times 10^{19})/\text{cm}^3$. The initial (n_{HO}) and final (n_{HF})H concentrations were $(1.0 \times 10^{19})/\text{cm}^3$ and $(0.7 \times 10^{19})/\text{cm}^3$, respectively. Under these conditions, our calculations predict dramatic departure from the behavior described by Fick's Law. First, the diffusion proceeds at a much more rapid rate - diffusion rates may be enhanced by a factor of 100 or more. Second, the H concentration profile is dramatically different from that predicted by Fick's Law (see Fig. 1).

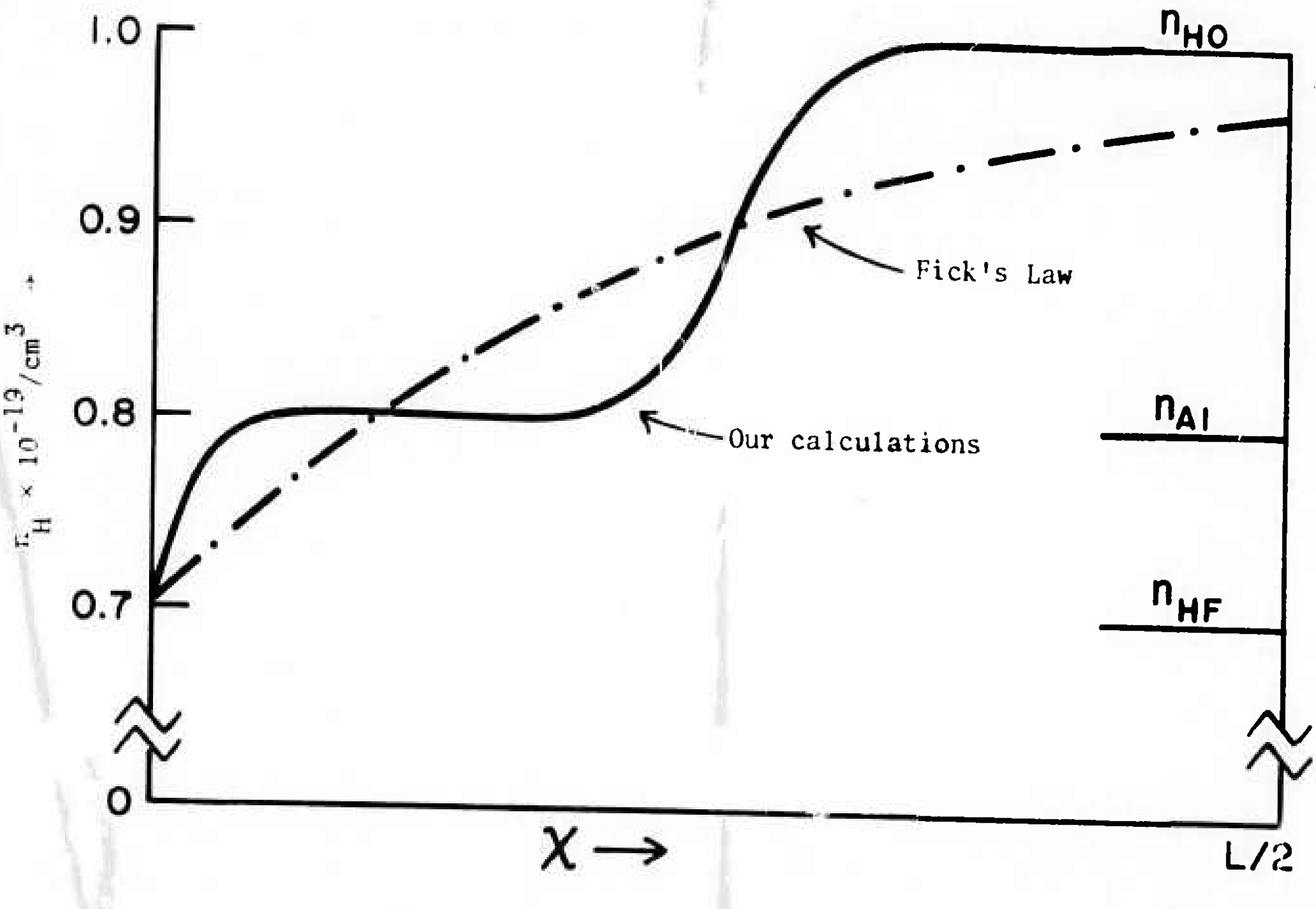

FIG. 1. H concentration as a function of position in specimen, as predicted by Fick's Law, and as predicted by the theory outlined in the text (the latter at a much earlier time than the former).

Figure 1 compares the profile predicted by Fick's Law with the results of our calculations. (The profiles shown would occur at different times. The figure is intended only to indicate the general features.) While we have not yet been able to make precise calculations for a case such as this, the general features are clear and it is also understood why the peculiar behavior occurs. It is possible to define an "effective" (local) diffusion coefficient, D_{eff}, which depends only on the concentrations of H and Al; formulated in this way, diffusion proceeds according to Fick's Law, but with a variable diffusion coefficient. The general behavior of D_{eff}/D_0 (where D_0 is the Fick's Law diffusion coefficient) is indicated in Fig. 2.

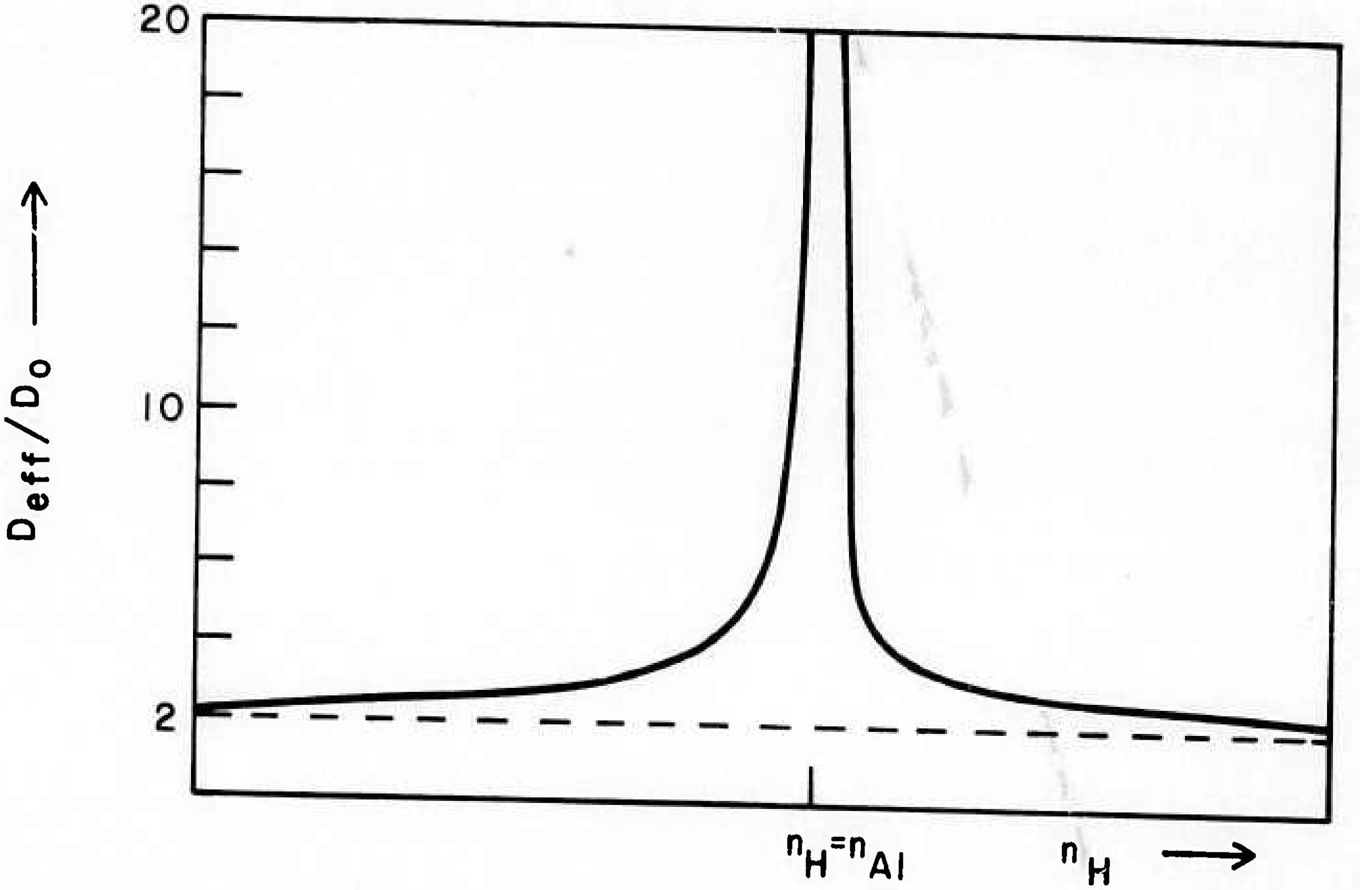

FIG. 2. Normalized "effective diffusion coefficient" as a function of H concentration for the parameters given in the text. The maximum value of D_{eff}/D_0 is > 8,000.

The important feature of the behavior of D_{eff} is an abrupt increase when $n_H = n_{Al}$. For the case under consideration, the maximum value of D_{eff}/D_0 is $> 8,000$. Thus, when n_H is $\sim n_{Al}$ in Fig. 1, D_{eff} is very large and only a very small concentration gradient is required to maintain the flow of ions. Qualitatively, the reason for this behavior is simply that when $n_H = n_{Al}$, the Fermi level is far away from both the conduction band and the Al trapping and an even small gradient in n_H results in rapid shifts of the crystal energy levels and hence, large electric fields. In Fig. 1, all of the H ions except those near the "plateau" are diffusing in a more or less normal fashion (but at least twice as fast as predicted by Fick's Law). After n_H has fallen below n_{Al} everywhere, the diffusion slows down substantially, and the behavior is much closer to Fick's Law. The initial stages of diffusion, however, can be extremely rapid.

It may not be possible to obtain precise solutions to this problem, although several promising schemes are presently being tested. A qualitative understanding of the process is probably more important, in any event, and we feel this has been achieved, particularly in view of the experimental verification of the dramatic enhancement of diffusion rate to be described in the next section.

II. HYDROGEN DIFFUSION - EXPERIMENTAL

The experimental work on H-D diffusion has progressed extremely well in the past 6 months. The problems initially encountered in the double-diffusion (H in -D out and vice versa) have been overcome and the measurements are nearing completion. This work will be described in detail in a forthcoming report; the work has progressed far enough, however, to justify a brief summary of our results. The measurements for diffusion || to the c-axis are essentially complete and only these are described below. The measurements for diffusion $\perp$ to the c-axis are about 50% completed. The diffusion coefficients shown in Fig. 3 for H and D in the high temperature region [$(1000/T) \lesssim 1.2$] were obtained from these measurements. (Only a portion of our data is indicated - several other runs produced results consistent with the data presented here.) The values indicated will probably need to be revised (downward), perhaps by as much as 30%, after the computer analysis is completed, since these points were obtained from the raw data, assuming Fick's Law is obeyed; as discussed in the previous section, this assumption is not strictly valid, even for the double diffusion case, due to slightly different solubilities and diffusion coefficients for the two isotopes. Even with the raw data, we obtained quite good agreement with other measurements described below, and corrections to the raw data promise to make the agreement even better.

Since the double diffusion measurements necessarily extend over a relatively narrow temperature range, it was felt that these measurements should be supplemented by data obtained using different techniques, if possible, to extend the temperature range. Several possiblities were considered; the most direct and unambiguous data would be ionic conductivity measurements. Previous attempts to make such measurements have been unsuccessful, but our progress in understanding the thermodynamics of the rutile system in the past year suggested that the experiment might now be possible. The basic difficulty with such a measurement (aside from problems of blocking layers,

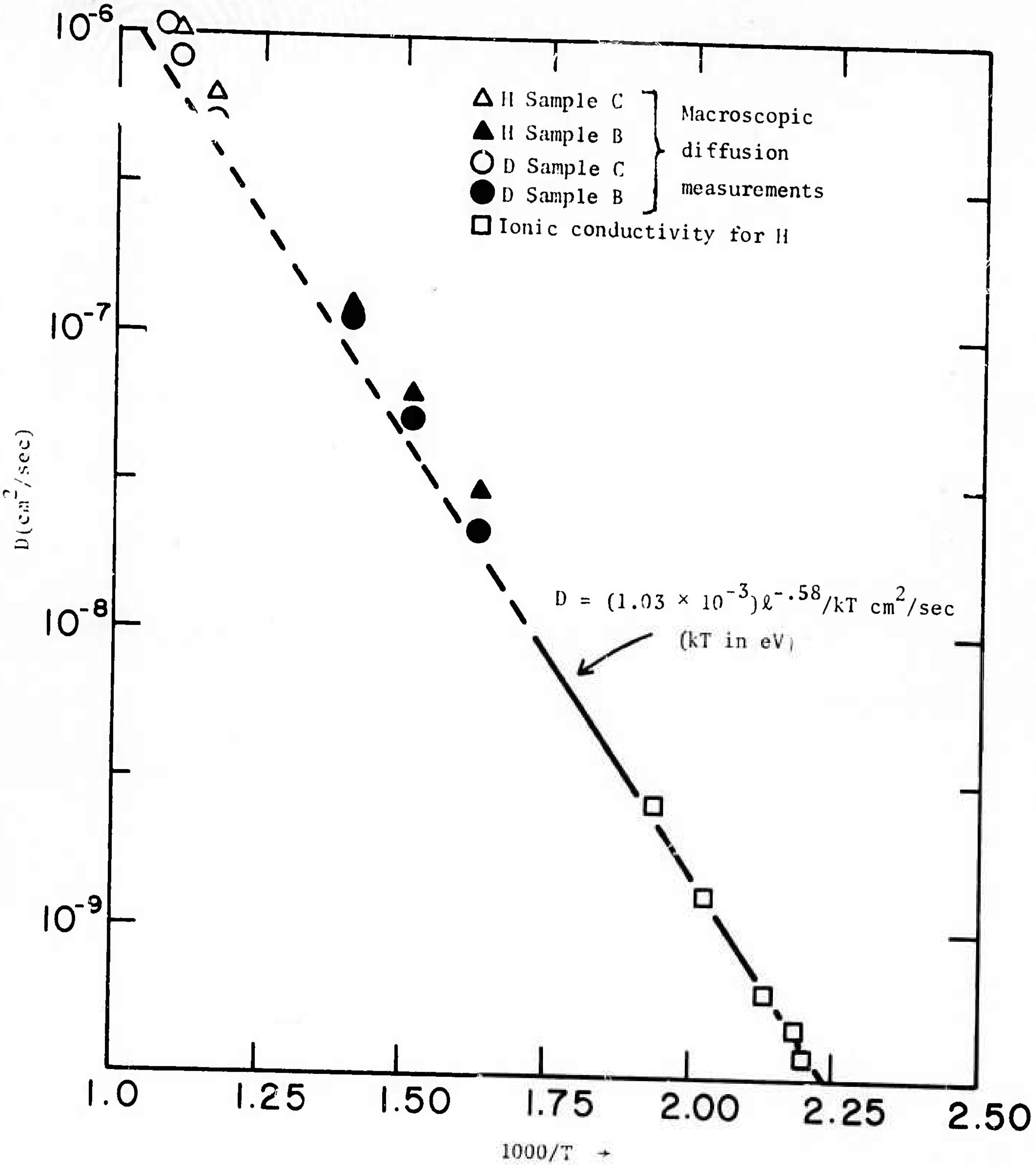

FIG. 3. Measured diffusion coefficients for H and D. High temperature measurements were analyzed assuming Fick's Law was obeyed - these points are systematically too high due to departures from Fick's Law and will be much closer to the extrapolated behavior based on the ionic conductivity measurements when computer analysis is completed.

etc., which are readily overcome by making AC rather than DC measurements) is fairly obvious. The mobility of the H ion is smaller than that of a conduction electron by a factor of ~ 10^5. Hence, to make accurate measurements of ionic conductivity of H, we must have the conduction electron concentration, $n_e \lesssim 10^{-7} n_H$. The problem is further complicated by the substantial impurity band conduction often observed in these crystals. Thus, the Fermi level must be controlled rather precisely. In addition, n_H should be as high as possible (preferably $> 10^{19}/cm^3$), which requires an equivalent concentration of acceptors to avoid electron conduction. In spite of these very stringent requirements, it appeared that it should be possible to put an appropriately doped crystal in the required state, and indeed, this was readily achieved (with, perhaps, a bit of luck) in an Al-doped crystal ($n_{Al} = 1.2 \times 10^{19}/cm^3$). The data points in the low temperature range in Fig. 3 ($1/T \gtrsim 1.2$) were obtained from AC conductivity measurements (at 1 kH) on this sample. The possibility exists, of course, that the conductivity measured was electronic rather than ionic; this possibility cannot be ruled out by direct measurement of electron concentration, since only about 10^{12} electrons/cm^3 would be required to produce the observed conductivity. However, even in the absence of the good agreement with the high temperature diffusion results (which would be a truly remarkable coincidence), electron conductivity can be rather conclusively ruled out because of the observed temperature dependence. It is quite easy to show that under these conditions (i.e., a single dominant trapping level ~ 2 eV below the conduction band, with E_F well above the trapping level), the conduction electron concentration is essentially independent of temperature in this range, and the temperature dependence of the conductivity should be essentially that of the electron mobility, which is very weak in this range. Other less likely possibilities (impurity band conduction, other trapping levels, etc.) can be ruled out by similar arguments. Thus, it seems almost certain that the observed conductivity is indeed due to H in the lattice, and that the diffusion parameters indicated in Fig. 3 are quite accurate.

The diffusion measurements have been extended in another way as well, in order to verify the general features of the theoretical calculations outlined in Section I for the single diffusion case. As indicated there, if the concentration of a dominant trapping level lies between the initial and final H concentrations, the observed diffusion rate (either in or out) should be substantially enhanced - by a factor of 100 or more in our case ($n_{H0} = 1.0 \times 10^{19}/cm^3$, $n_{HF} = 0.7 \times 10^{19}/cm^3$, $n_{Al} = 0.9 \times 10^{19}/cm^3$). The precise behavior has not been worked out in detail, but because of the excellent agreement of the results previously described, we felt confident that we could detect an enhancement by a factor of 2 quite readily, and the much large enhancement predicted by the theory should be convincingly demonstrated. The measurements of H concentration were made optically as described in previous reports. The specimen was doped with H by heating to ~ 900°C in 20 Torr of H_2O and quenched to room temperature. The out diffusion was carried out at 250°C in 100 Torr of O_2, in a recirculating glass system with a liquid nitrogen cold trap. (It is interesting to note that the quite high final H concentration apparently represents equilibrium of the sample with an H_2O partial pressure of ~ 10^{-11} Torr!) The conduction electron concentration was also monitored optically. The results of these measurements are presented in Figs. 4 and 5. The "Fick's Law" curves were calculated

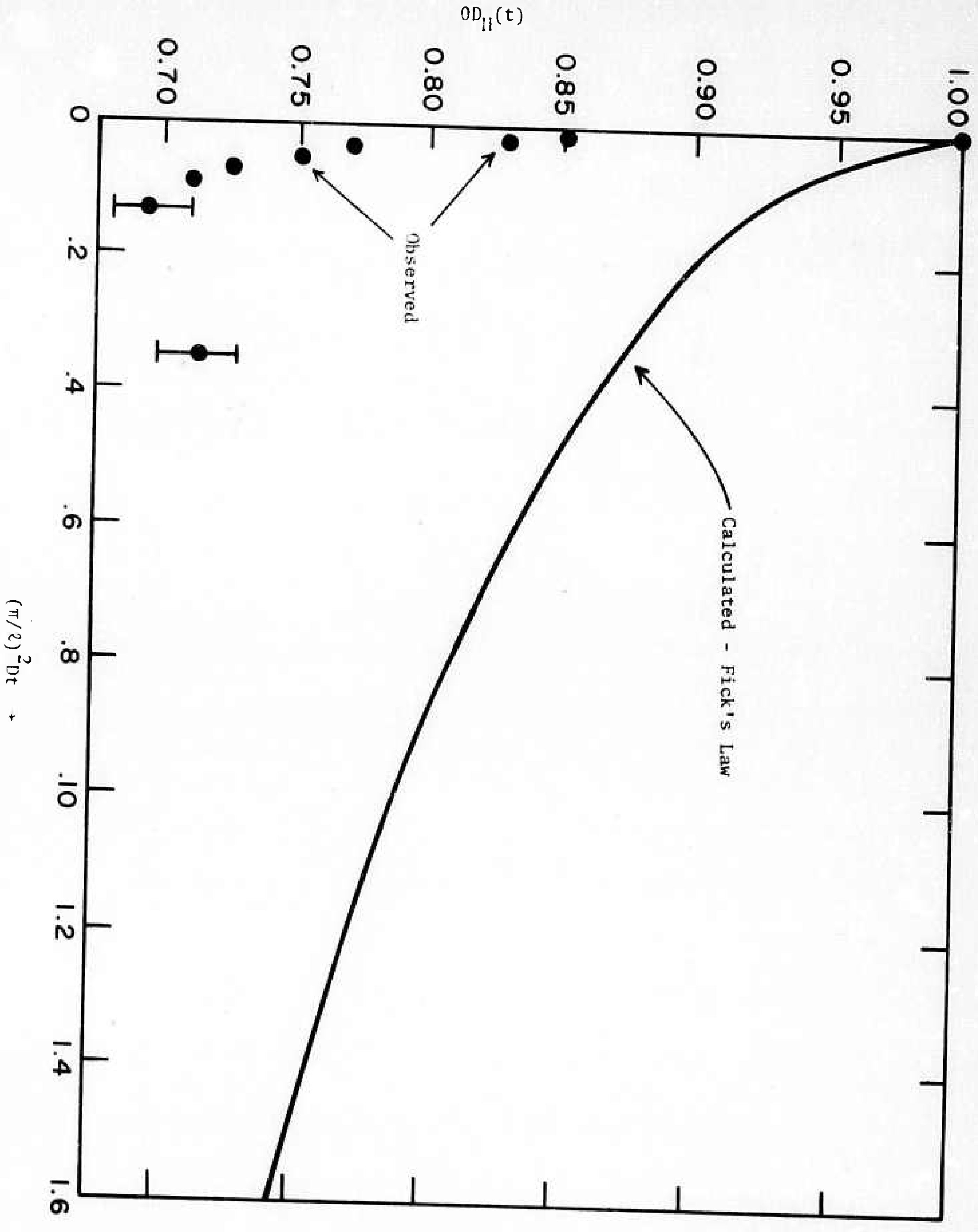

FIG. 4. Relative optical density at the H^+ absorption peak (proportional to total H^+ in crystal), as a function of $(\pi/\ell)^2Dt$, where ℓ is the sample thickness, D is the diffusion coefficient (taken from Fig. 3), and t is time. The curve marked "Fick's Law" shows the behavior which would be expected in the absence of electronic effects for the observed initial and final H concentration.

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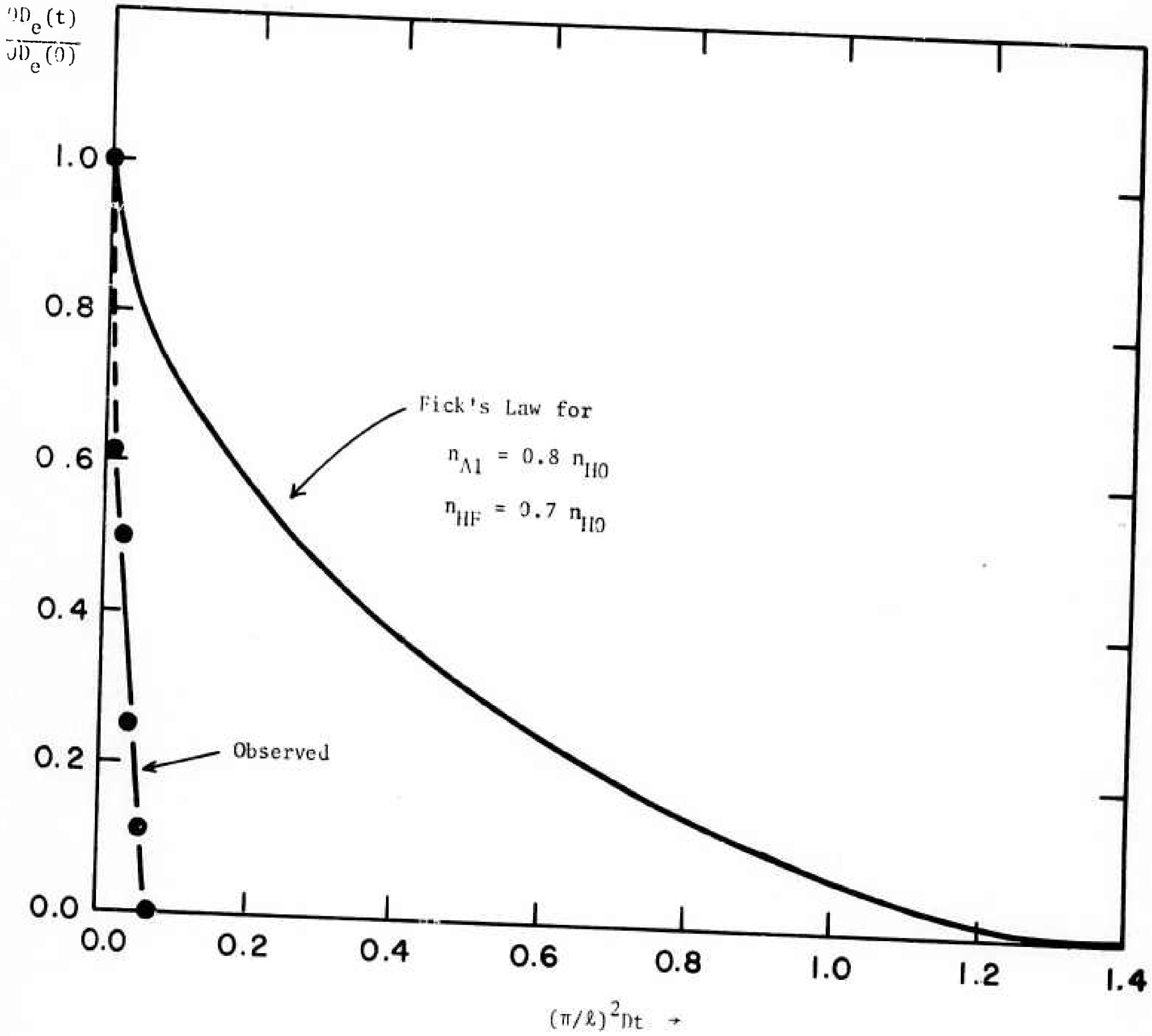

FIG. 5. Relative optical density due to conduction electrons (at 1.55 microns) as a function of $(\pi/\ell)^2Dt$ (see Fig. 4).

assuming the diffusion parameters in Fig. 3. We consider these results to be quite impressive, though not yet quantitative, verification of the theory outlined in Section I. A detailed concentration profile (as in Fig. 1) would perhaps be even more compelling; we will attempt to obtain such a profile during the next few months. All in all, the results of the diffusion project have been extremely gratifying. It has been possible to do a thorough and quite definitive study, which we feel was well worth the time and effort, even though it required postponement of certain other work. Since our results are of quite wide applicability, it may well be that this work will turn out to be the most important part of the project.

III. ESR MEASUREMENTS:

While a considerable number of spectra associated with impurities in TiO_2 have been catalogued and identified during the past few years, very little progress has been made in sorting out and identifying a group of spectra originally observed by Chester,[1] which presumably are associated with lattice defects or impurities always present in the lattice, since they are observed in both "pure" and doped crystals. These spectra, which Chester simply labeled alphabetically (A through G, some with subscripts!), come and go with various heat treatments in a complicated manner. In a previous publication,[2] we presented evidence which seemed to indicate that the "A spectrum" was associated with Ti^{3+} interstitials. Aside from this tentative identification (which in fact was incorrect), very little progress has been made in understanding these spectra since Chester's original work.

The basic problem has been that until our work on the thermodynamics of the rutile system,[3] there had been no way of controlling or measuring the concentration of either donor lattice defects (Ti interstitials or O vacancies, both of which may well be present) or H, which is sufficiently ubiquitous that it is essentially always present. Hence, there had been no way of reliably controlling the Fermi Level, or even of determining where it was, in many cases. Thus, without knowledge as to what defects or impurities were present, little progress could be expected in identifying these ESR spectra, particularly since comparison between different samples is essentially meaningless unless the Fermi levels are known.

With the insight gained from our thermodynamic studies, it is now possible to both control and to measure H concentration and Fermi level and to control or eliminate the lattice defects which are mobile below 1000°C. Presumably, these are Ti interstitials, although this has never been conclusively demonstrated. There appears to be a second lattice defect, presumably the O vacancy, which is essentially immobile below 1000°C, but can nonetheless be important in determining the electronic properties of a given crystal. Considerable work remains to be done to achieve a good understanding of this whole problem, particularly as regards the high temperature defect. This is the general area on which we are concentrating at present, and considerable progress has been made during the past few months. In the discussion which follows, we will refer to the low temperature lattice defect as the Ti interstitial merely to avoid excess verbage, even though the identification is not absolutely certain. None of our conclusions would be altered if it should turn out that this defect were an O vacancy.

A. The "A-Center":

As previously mentioned, this had been tentatively identified as being due to a Ti^{3+} interstitial. However, certain observations cast doubt on this conclusion and a careful study was initiated. The general approach was to observe the ESR spectrum (at liquid He temperatures) of a "pure" specimen as a function of Fermi level, first with H used as the donor impurity and Ti interstitials eliminated, then to repeat the measurements over the same range of E_F using Ti interstitials as donors, with H eliminated. The A spectrum was observed only when H was present, and then only when E_F was high enough to assure that shallow traps would be populated at He temperatures (i.e., significant concentration of conduction electrons at room temperature). Thus, one can conclude that the A spectrum is definitely not associated with Ti interstitials, but rather with a shallow trapping level which involves H. (Li was also used as a donor dopant; only a very weak A spectrum was observed, consistent with the known residual concentration of H.) The microscopic details of the center responsible for the observed spectrum remain to be elucidated, and ENDOR studies are planned for this purpose, since we have been unable to resolve any hyperfine structure in the spectrum.

At sufficiently high H concentration (with $n_H \gtrsim 10^{19}/cm^3$ with correspondingly high E_F), we found that the A spectrum was transformed into Chester's B spectrum. Again, the details remain to be worked out, but this constitutes substantial progress on a rather refractory problem.

B. "The "E-Center":

This center is less frequently encountered, and may well involve an impurity, since we have observed it only in a V-doped crystal also containing Ti interstitials but not significant H. It is not entirely clear that the center necessarily involves V, since we have again been unable to resolve a hyperfine structure, but this seems to be a quite common occurrence in TiO_2. It seems likely that this center is a complex involving both V and Ti.

C. The "G_1-Center":

This spectrum is probably also an impurity-Ti complex, in this case involving Al, since we have observed it only in crystals containing Al, as well as Ti interstitials, and in which E_F is fairly high ($\gtrsim$ .4 eV below the conduction band). The ESR spectrum apparently results from a center or complex which also gives rise to a specific optical absorption spectrum, which is quite similar to the free electron absorption but shifted to shorter wavelength. Neither the ESR nor the optical spectrum are observed in these crystals when the Ti interstitials are replaced with H. Both spectra are observed in the majority of samples (even "pure" samples), if they are treated to produce Ti interstitials and the correct E_F, so this center is much more common than the E center. This is not surprising, however, since Al is found in quite high concentrations in virtually all commerically available crystals (see Section IV), and the strength of the spectrum appears to correlate well with Al concentration.

D. The H-Fe Center:

This center, and the ESR spectrum associated with it was discussed in a previous report. Briefly, our studies show that when Fe and H are both present in high concentrations, a spectrum similar to the previously identified Fe^{3+} spectrum appears. The occurrence and strength of this spectrum correlates well with a shifted H^+ ir absorption spectrum. The center involves an ion which is somewhat mobile in the range above - 25°C, since the strength of both spectra can be significantly enhanced by slow cooling through the range from room temperature to - 25°C. The H diffusion data are consistent with H^+ being the mobile ion. Again, we have been unable to observe a hyperfine splitting appropriate to H^+, nor can we detect any difference in the ESR spectrum when D is substituted for H; ENDOR measurements are also planned for this center. The identification with Fe is conclusive, however, since we were able to observe the appropriate hyperfine structure in a crystal which we doped with Fe^{57}. A rather nice bonus of this work was an accurate measurement of the Fe hyperfine interaction of the normal (unperturbed) Fe^{3+}. Only one rough (and probably incorrect) measurement has been reported in the literature.[4] The Fe^{57} doping, incidentally, required development of a Cl_2 transport technique, which is probably also applicable to several other impurities and may prove to be quite helpful in future work.

The four-fold multiplicity of the H-Fe ESR spectrum suggests an approximately (0, 1/2, 0) site for the proton, although a shift toward one of the neighboring O ions cannot be ruled out. Positive identification of the H^+ site in the lattice would be very desirable; it should be possible to obtain this information from the ENDOR measurements.

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E. Other Work:

In addition to examination of specific spectra, we are also devoting some further attention to the so-called "vacuum-reduction" process. As discussed in a previous report, we have shown that "vacuum reduction" does not occur below ~ 1100°C, contrary to numerous reports in the literature, which in fact were based on changes in the crystal resulting from contamination of the vacuum system. Heating above 1100°C, even in a clean vacuum, however, apparently does induce an oxygen deficiency, possibly associated, at least in part, with O vacancies. Elucidation of the defect behavior of TiO_2 certainly will require resolving the question of the roles of Ti interstitials and of O vacancies. More sophisticated sample treatment facilities have been constructed; it is hoped that careful study of the defects produced at high temperature in a very clean vacuum will cast some light into this murky area.

IV. CRYSTAL GROWTH AND CHARACTERIZATION:

A total of 81 full-scale runs (not including calibration runs and various test runs in which crystal growth was not attempted) have been completed, each of which involved extensive pretreatment of the quartz ampoule, starting material and seed, as well as the transport agents. In one sense, the results have been disappointing, since we are still not growing useful crystals. In retrospect, however, considering the number of unanticipated problems which have had to be solved, steady progress has been made, and a great deal of knowledge has been obtained, much of it applicable to a wide variety of systems other than rutile. Furthermore, none of the problems encountered has proved to be insoluble (although several looked like good candidates for a while). The most important and encouraging point is that we have found no fundamental limitations to this technique; prospects for producing high purity strain-free crystals look even more promising than they did at the outset.

The main reason for optimism at this point resulted from one of those rare accidents which turns out to be beneficial. During a recent run the seed was inadvertently etched completely away. Rather than abort the run, it was decided to attempt to nucleate a small number of crystals on the wall of the ampoule. This was successful, and several milimeter-size crystals of apparently very high quality were obtained. One of these was subjected to mass spectrographic analysis by Dennis Walters at the Columbus Laboratories of Battelle Institute. The results are listed in Table I. While the overall impurity level is not terribly impressive, this is not significant, since no attempt has yet been made to purify the starting material. Most of the impurity levels are consistent with those expected for the starting material. The crucial point is the low Si content. This is the main impurity which has been a source of concern to us, because of the possibility of transport from the ampoule walls. Even 20 PPM would be a very satisfactory level for this impurity since it is unlikely to seriously disturb the lattice, having the same valence and approximately the same ionic radius as Ti. Optimization of the growth parameters will doubtless enable us to achieve even lower levels for both Si and Te. Thus, it appears almost certain that we will be able to make an order of magnitude improvement over currently available crystals.

TABLE 1. Mass Spectrographic Analysis of TiO_2

(ppmw)

Element	Sample Number 59
B(a)	< 50
F	2
Na	(b)
Mg	≤ 50(b)
Al	50
Si	20
P	0.5
S	5
Cl	5
K	0.1
Ca	3
V	0.3
Cr	0.3
Mn	0.1
Fe	5
Co	3
Ni	5
Cu	< 5
Zn	≤ 5
Ge	< 3
As	< 3
Se	< 50(c)
Pd	≤ 5
Te	20
La	< 20(b)
Ta	< 5
Au	< 3
Pb	0.3

(a) Contamination from boron carbide mortar
(b) Interference from Ti
(c) Memory from previous samples

The inadvertent loss of the seed on this run also resulted in a clue as to the nature of what we hope was our last major problem. As discussed in the last report, we had previously achieved atleast a good qualitative understanding of the SiO_2 transport problem during growth, and largely eliminated this as a source of contamination. This is quantitatively verified by the mass spectrographic analysis. However, we had not considered the possibility of SiO_2 transport and deposition while the seed was being etched. Examination of the ampoule in which the unseeded growth took place revealed a tenuous skeleton of white material closely corresponding to the original size and shape of the seed which had been etched away. The material doubtless was SiO_2. Several of the previously grown crystals have since been sectioned and examined under the microscope, and in all cases, we have found a thin layer of inclusions corresponding to the original seed surface. Again, these inclusions are undoubtedly SiO_2. In spite of the fact that the crystal grew around and over these inclusions, the structure in many cases is quite good and there is every reason to believe that elimination of the contamination during etching will finally permit us to obtain the high quality crystals we have been striving for, particularly since microscopic examination of the spontaneously nucleated crystals revealed no trace of inclusions or disturbances of the crystal structure.

The SiO_2 transport apparently occurs as a result of the TiO_2 seed being at a slightly lower temperature than the surrounding ampoule walls. This temperature differential was due to intentional cooling by use of an extension of the ampoule as a light pipe, as described in a previous report. This ingenious idea has proven to be quite useful for several other systems; unfortunately, it has turned out to be a disaster for the system for which it was developed. We originally adopted this technique as a means of establishing conditions in the ampoule which would eliminate spontaneous nucleation on the walls. We have found, however, that entirely adequate transport rates are readily attainable at a sufficiently small supersaturation that spontaneous nucleation does not occur anyway. Thus, by elimination of the light pipe, and by exercising care in maintaining isothermal conditions during heatup and etching, we should be able to eliminate this problem, at which point the only remaining difficulty would be purification and processing of the starting material, which we do not anticipate will be particularly difficult, for the reasons outlines in our original proposal.

The continuing need for high purity crystals is illustrated by our experience with two boules of TiO_2 which we recently purchased from a source which we had not used for several years. We had reason to believe, as a result of conversations with this crystal grower and with other research groups which who had used his material, that he could supply us with somewhat better crystals than were available elsewhere, particularly with respect to Al content, which is very troublesome. Since this also provided an opportunity to test the optical sample analysis techniques which grew out of our thermodynamic studies, a fairly detailed examination of these crystals has been made. Basically the technique consists of heavily oxidizing the crystal in the presence of H_2O to eliminate Ti interstitials and other possible mobile donors such as Li and Na. If done at appropriate temperature and partial pressures, this treatment results in a Fermi level high enough to fill all electron traps. This is assured by the presence of a significant concentration of conduction electrons, which concentration is measured by monitoring the optical absorption at 1.55 microns. The H^+ concentration is also measured optically. We thus obtain quite accurately the net acceptor concentration, as the difference of the H^+ and e^- concentrations. Since almost all of the important impurities are acceptors under these conditions, this is an excellent gauge of total impurity concentration. In addition, certain of these impurities can be monitored directly because the association of H^+ with the impurity produces a shifted ir absorption. Thus, for example, the ratio of the Al-H^+ peak to the unassociated H^+ peak gives a direct measure of the Al concentration. We have only done an approximate calibration of the scale factor involved, but our results are accurate to within 25%. At present we are only monitoring Al and Mg, since these are the most important impurities at present, but several others are also possible by measuring at low temperatures in order to resolve the impurity-associated peaks. Actually, it appears that many of the important impurities can be directly monitored in this way, including Fe, Ni, Ga, Cr, and probably Co, and Mn and possibly others. Those not directly detected still show up as part of the net acceptor concentration. In any event, measurements were made at various locations in these two boules: Location A was on the axis of the first boule near the cap end. B was Boule 1, cap end, near surface. C was on axis, cap end, Boule 2. D was on axis, near the center of Boule 2. E was on axis, near seed end of Boule 2. Results are listed in Table II. (N.D. → not determined).

These discouraging results have been transmitted to the grower, but significant improvement is unlikely. It is interesting to note that for location A at least, the net acceptor concentration is less than the sum of M_{Al} and M_{Mg}. This indicates compensating donors, which could be either cation substitutional impurities or donor lattice defects not removed by

TABLE II.

Location	n_{Al}	n_{Mg}	n_{acc}
A	38 ppm	76 ppm	65 ppm
B	250	low	430
C	40	100	N.D.
D	55	29	N.D.
E	125	21	N.D.

the heat treatment. The only known possibilities for these impurities are W, Mo, Ta, and Nb. It is not likely that these are present in the required 50 ppm concentration. It is more likely that the donors are the high temperature lattice defects discussed in Section II (presumably O vacancies), since the heat treatment should have removed the Ti interstitials. The work described in Section II should provide more information on this point. With a bit more development, this technique will prove very useful in future sample evaluation studies.

V. OTHER WORK:

Not much effort has been devoted to other areas during the past few months, mainly due to the necessity of concentrating on the diffusion measurements. More careful evalution of the H solubility parameters is of high

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priority and it should be possible to return to this problem shortly. Use of the Fourier transform spectrometer has been delayed as a result of default by the contractor for one of the computer interface components; minor redesign and use of alternative components has solved this problem and the spectrometer should go into operation shortly.

Preliminary survey runs on the Department's recently completed Raman spectrometer were rather disappointing. Results were in excellent agreement with published measurements and the spectrometer is functioning very well. We were, however, primarily interested in obtaining additional information on the vibrational modes of H^+ and [illegible]; no emission lines were observed which could be identified with these impurities. It is anticipated that the instrument will prove useful for other measurements, however, perhaps to extend the analysis techniques described above, and for detailed study of excited states of impurities, both by Raman scattering and fluorescence spectroscopy.

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