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TECHNICAL REPORT

FOR PERIOD ENDING NOVEMBER 30, 1971

to

ADVANCED RESEARCH PROJECT AGENCY

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Title

ELECTRONIC AND RADIATION DAMAGE PROPERTIES OF RUTILE

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The work done during the first 17 months under this grant, through November, 1971, will be discussed in terms of the proposal for the period June 71 - June 72. In the proposal the work was divided into the following areas:

A. Crystal Growth
B. Dielectric Loss
C. Devices
D. Hall Effect
E. Radiation Damage
F. Theory and Data Analysis
G. Optical Absorption Spectroscopy
H. Photoconductivity and Photoemission
I. Review Paper
J. Ultrasonic Attenuation

In what follows each area will be discussed, plus work not anticipated in the original proposal. In each area a brief review of the proposal expectation is given, followed by a description of what has been accomplished.

A. Crystal Growth

1. As described in more detail in our previous proposal, the plans for the crystal growth project were as follows:
   a.) Establishment of the technique and novel equipment for crystal growth of rutile by the chemical vapor transport method (CVT).
   b.) Study of the dependence of the transport rate on diffusion and convection in the growth ampoule; i.e., variation of pressure, temperature and geometrical conditions.
   c.) Growth of macroscopic crystals by CVT onto seed plates, i.e., investigation of dependence of the growth morphology on the crystallographic seed orientation and the supersaturation nucleation conditions.
   d.) Evaluation of the crystallographic perfecton and chemical purity of the grown crystals with feedback into b.) and c.)
   e.) Successful completion of a.) - d.) above to be followed by work on growth of ultrapure rutile single crystals, i.e., preparation of ultrapure starting materials for the growth process, depending on the actual impurities found in crystals grown from commercially available chemicals.

During the first 17 months under this grant, problems a.) through c.) have been essentially solved, although more detailed work needs to be done towards a quantitative understanding of b.) for optimization of the growth rate. Crystal plates of 15 mm diameter and 1 mm thickness are being grown within 72 hours with crystallographically satisfactory quality. Furthermore, essential progress has been achieved in the understanding of various aspects of CVT growth. A detailed account of the results is given below.

2. Progress in Crystal Growth Program. The following subparagraphs are arranged in the same sequence as outline 1.:

a.) Growth technique and equipment.

The choice of the chemical vapor transport method (CVT), which had been used earlier for uncontrolled nucleated growth of small rutile crystals,[1] proved to be an excellent choice for this system. Whereas the experimental technique is characterized by great simplicity, this has not been found for the chemical mechanism of the specific transport reaction. Our results indicate that the reaction

$$TiO_2(s)+TeCl_4(g)\rightleftarrows TeO_2(g)+TiCl_4(g) \qquad (1)$$

as assumed by Niemyski and Piekarczyk(1) represents at best an overall equation for a series of more complex reactions (see b.) The possibility of in situ etching of the seedplates within the same sealed-off ampoule, prior to the growth procedure, proved to be an especially valuable feature. Subgrain nucleation, twinning, etc., due to perturbed seed surfaces from the mechanical shaping procedures can thus be completely avoided. The novel design for the two zone growth furnace also proved advantageous. Direct optical monitoring of the growth process by microscopic observation of the growth interface and its environment has allowed many valuable conclusions concerning the growth kinetics to be made. With a conventional furnace this would not have been possible. Though we had anticipated the necessity of temperatures above 1100°C for large transport rates, our experiments have shown that this is not the case. Thus, for routine growth, after optimizing the growth parameters, we can use Kanthal heating elements with long lifetime instead of the costly platinum-iridium arrangement originally planned for. Temperature constancy, heating geometry, and adaptability to small changes in the temperature profile required for further investigations (see c.) of the current simple setup are fully adequate for the growth of high quality crystals. However, greater flexibility can be achieved if the "production" of crystals according to the current state of the art can be separated from further investigations of the growth process by employing a second growth setup.

b. Diffusion, convection and transport reaction.

The growth rate for CVT according to a reaction such as (1) depends on the following parameters:

(1.) the reaction kinetics between transport agent and starting material (here supposedly $TeCl_4$ and TiO_2.)

(2.) the transport kinetics, i.e., transport of the reaction products TeO_2 and $TiCl_4$ towards the crystal as well as back transport of $TeCl_4$ to the starting material.

(3.) the surface kinetics on the growing interface, i.e., back reaction to TiO_2 and $TeCl_4$, and surface diffusion probably of TiO_2 molecules to attachment sites, including the nucleation kinetics if growth is onto "facets" (atomically smooth crystal faces, see c.).

Step 1 and the surface diffusion part of step 3 are strongly temperature dependent. In order to avoid problems of purity and ampoule stability, one would like to keep T for (1) as low as possible. On the other side the surface diffusion mechanism limits the choice of T for (3) towards lower values. We had anticipated a low temperature limit of ~900°C at the growth interface, since it has been generally agreed that anatase rather than rutile results from reaction temperatures below 850° - 900°C. However, we have established that this is not the case (see below) and we may adopt the lowest temperature consistent with satisfactory growth rates. If material transport is solely by diffusion, the transport rate will be limited by the concentration gradient, which in turn is fixed by the temperature difference between reaction zones and the ampoule geometry, and transport rates generally may be expected to be quite slow. Convection can increase the transport rate beyond the diffusion values. Therefore, we started with vertical geometries and several atmospheres ampoule pressure.

Because of the obvious importance of the actual temperature profile and the virtual impossibility of making meaningful calculations because of the many unknowns involved, a direct measurement of the temperature was crucial. A modified ampoule was constructed, with a room temperature O-ring seal and a small, movable Pt:Pt-Rh thermocouple. By allowing the reactants to form a "dynamic seal" near the hot zone, it was possible to closely duplicate actual CVT growth conditions, while monitoring the temperature profile.

Studies of the temperature distribution, in the vertical ampoule revealed;

(1) That the internal temperature distribution deviates drastically from that of the furnace- a fact which has in general been neglected so far in CVT.

(2) That the temperature in the vapor phase in front of the crystal for a given set of conditions fluctuated by ±35°C. The furnace at the same time was stable within the ±.5°C. In an ampoule of identical dimensions, in the same heating equipment, filled with inert gas to comparable pressure, deviations from the exterior temperature profile were negligable and fluctuations were below ±1°C.

From the observed nucleation density along the ampoule, it is clear that the actual transport reaction is more complex than equation (1). The temperature oscillations are apparently due to turbulent transport of reactants, which react exothermally in the gas phase before reaching the interface, probably involving intermediate chemical species. Reduction of the pressure, which should result in a transition from turbulent to the desired laminar convection, resulted in a drastic reduction of the transport rate. Thus, it was decided to work with horizontally oriented growth ampoules.

Further search for more suitable transport conditions revealed two further details:

(1.) The pressure dependence of the transport rate did not correspond to well established theoretical CVT models(2). Further literature study, however, revealed that $TeCl_4$ dissociates thermally to a high degree into $TeCl_2$ and Cl_2(3) at 900 - 1000°C- a fact totally neglected in Niemyski and Piekarczyk's work. This dissociation of $TeCl_4$, which should also depend on pressure, could qualitatively explain the unexpected pressure dependence of the transport rate, and gives further evidence for a more complex reaction mechanism than had been observed in (1). We hope to clarify this point by studies of the dissociation behavior of $TeCl_4$ at a later date.

Stimulated by this finding, we performed transport with Cl_2 only, and with varying ratios of $TeCl_4$ and Cl_2. The resulting transport rates indicate that the main transport agent is indeed a Te compound, and not Cl_2. Chlorine transport rates are about one order of magnitude less than with "$TeCl_4$", in contradiction to Niemyskis and Piecarczyk's theoretical predictions. Recalculation of the reaction kinetics for the Cl_2 and $TeCl_4$ case showed that their underlying calculations were erroneous by one order of magnitude for the chlorine transport- in good agreement with our experimental values.

(2) In many publications, it has been claimed that rutile can not be obtained at temperatures below 850°C, and that anatase is formed in reactions at lower temperatures. A careful literature survey, however, suggested that this limitation is strongly impurity dependent. X-ray studies of crystal grown at temperatures as low as 750°C showed no evidence of any phase other than rutile, and there are indica-

tions that this might be true for even lower temperatures. This was verified in growth and seedplates (homoepitaxial) as well as unseeded (heteroepitaxial) growth on the wall of the quartz container.

Further indications of more complex reaction kinetics were found during efforts to increase the reproducibility of the transport rate dependence on pressure. It appears very probable that traces of water introduced in the strongly hygroscopic $TeCl_4$, also play an essential role. Discussions with H. Schäfer the pioneer in CVT reactions$^{(2)}$, who had observed similar rate enhancement with minute concentrations of water, have lent credance to this interpretation. This aspect, however, was shelved for a more thorough investigation at a later date, since present transport rates are entirely adequate.

c.) Growth morphology and morphological stability.

Most crystal systems exhibit marked growth rate anisotropy which we can use advantageously to achieve stable growth configurations. Depending on the bonding characteristics of the molecules in the lattice, which varies with the crystallographic orientation of the face onto which growth occurs, two distinctly different crystallization mechanisms may underlie the growth process:

(1.) On "atomically smooth" surfaces, called facets, growth rates are nucleation limited. Relatively high degrees of supersaturation are required to achieve growth.

(2.) On "atomically rough" faces, nucleation is of no concern and growth proceeds at low supersaturations- which are experimentally difficult to control.

Only sparse and contradictory information was available concerning the growth morphology of rutile. Our initial runs with {001} seedplates and examination of the grown layers optically as well as with the scanning electron microscope, seemed to indicate that {111} faces form the most stable planes. This was then verified in a novel experiment in which a 1 cm rutile sphere was used as the seed in a growth run. The most stable faces developing from all possible orientations belong to the {111} family. Niemyski and Piekarczyk(1) had claimed that the best developed planes on their spontaneously nucleated platelets are {100}. Critical inspection of their photographs does not support this statement. Besides the practical consequences, this morphological question is especially interesting in the light of recent calculations(4) (based on a 100% heteropolar point charge model) which claims {110} as the most stable growth faces.

Consequently, {111} seedplates are being used for the growth experiments. Smooth growth (planar interface) can thus be achieved with drastically increased growth rates as compared to {001} seeds.

In addition to considerations relating to anisotropy of surface energy in connection with the optimal degree of supersaturation, morphological stability depends on the actual concentration and temperature profile at the interface. Since material transport close to the interface is necessarily diffusion limited, the growing crystal is surrounded by a depletion zone- a fact which has been taken into account for growth from the vapor phase only very recently(5). Stable (non-dendritic) growth is limited by "constitutional supersaturation" conditions(6). For evaporation-condensation type vapor growth, the range of stable growth can be theoretically extended to extremely high growth rates(5) if constitutional supersaturation is avoided by proper control of the temperature profile at the interface. Very recent experimental results seem to verify this concept. For CVT this aspect has been neglected so far. Some of our results, however, seem to indicate that, taking into account the different transport kinetics, this model is also valid for CVT. This would have important consequences for the optimization of the growth rate.

B. Dielectric Loss

In the proposal we noted that, although we had achieved a qualitative understanding of the phenomena, considerable work remained to be done on the details of the trapping mechanisms and on the identity of the migrating defects and impurities.

During this contract period the paper on the basic mechanisms active in dielectric loss in rutile type crystals has been accepted for publication in JAP. The understanding obtained in that work has enabled us to undertake the studies of trapping levels and defects mentioned above. It has also been invaluable in our attemps to make devices. These projects are discussed in C and G below.

C. Devices

In the proposal we stated that we planned to make and test FET devices and to devote increasing effort here as our knowledge of transport properties increased.

The first step in making such a device was the production of a sufficiently smooth surface. The surface must not only be free of damage but also smooth enough to eliminate variations in thickness and possible pin holes in the materials to be deposited - in particular SiO_2 insulating layers. This proved to be a substantial undertaking but was solved as described in the Semi Annual Report.

The next step was the production of an insulating SiO_2 layer on the smooth rutile surface. Various methods were tried before the present one was selected. This method consists in utilizing the reacion

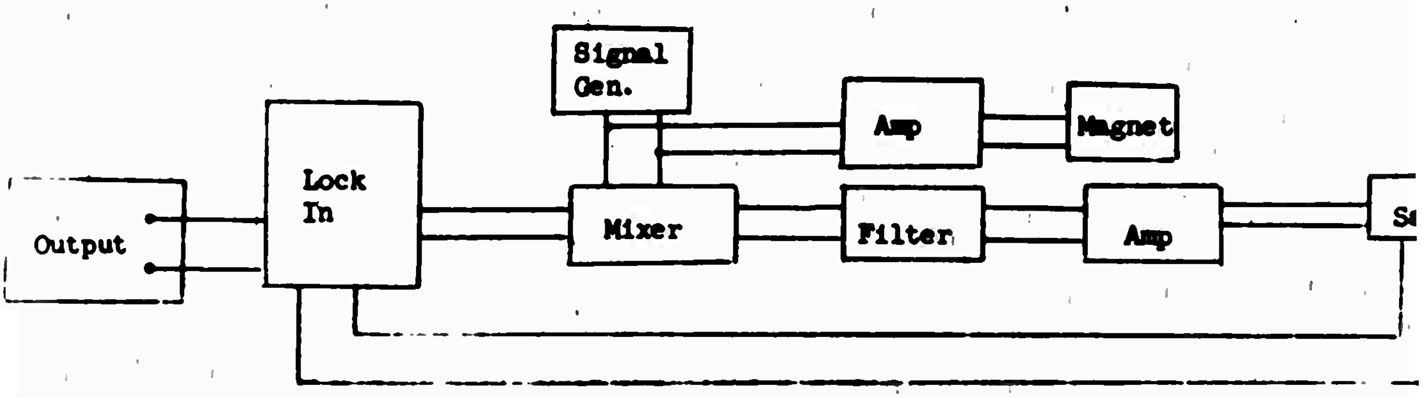
$$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$$

which takes place at about 375°C. The silane gas and the oxygen are sprayed through a fine tip onto the heated rutile surface where the reaction takes place resulting in a glass layer. The necessary control equipment, etc., has been installed and we have used this technique to fabricate our first FET devices. These are currently being tested, and while the results are quite encouraging, the data are too preliminary to merit discussion at present.

D. Hall Effect

In the proposal we noted that Hall Effect measurements were extremely important in understanding conduction mechanisms in rutile and hence that we were giving it a high priority. In particular, Hall measurements should permit a direct verification of P-type conductivity which has been suggested by dielectric loss measurements on Al doped material.

As discussed in the Semi-Annual Report, we decided on a method employing AC electric and magnetic fields. The signal is then picked up by a lock-in amplifier at the sum or difference frequency. The basic schematic was shown in the Semi-Annual Report and is repeated below:



The first problem encountered in this method was the magnet. Low power consumption dictated a ferrite care. Hence we investigated all commercially available ferrites at both 300°K and 77°K. Our results can be summarized as follows:

1. Ferrites with low loss at room temperature aren't too bad at nitrogen temperature.

2. Ferrites with significant loss at room temperature are terrible at nitrogen temperature.

3. The loss at nitrogen temperature is significantly higher (at least a factor of 5) than that at room temperature.

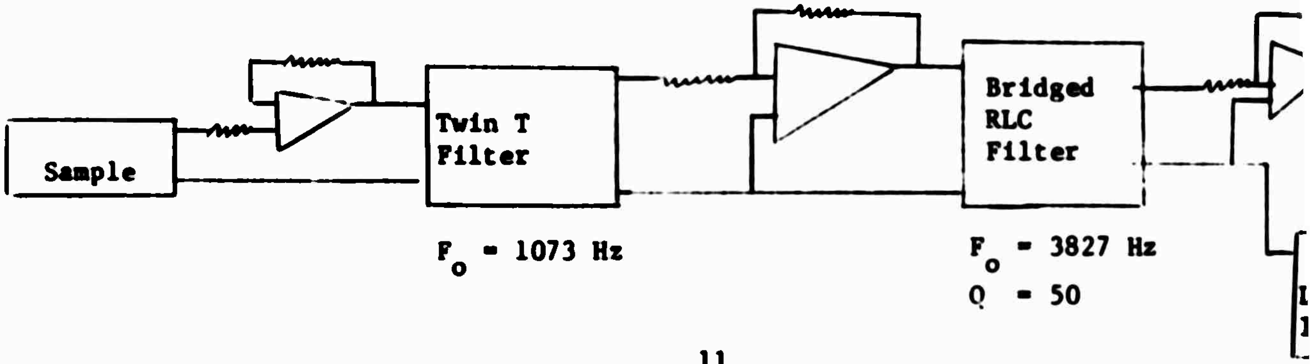
4. The peak magnetization increases as the temperature decreases.

The ferrite with the least loss at both 300°K and 77°K was Stackpole 24B. Its loss at 300°K was 60% smaller than the value published by Stackpole and at 77°K it was 8 times larger than at 300°K. (Even so its loss was low enough that it could be used, for example, in infrared magneto optic modulators in satelites.)

We then constructed a magnet of this material using two E cores. With it, fields of 1000 gauss at 1000 Hz are routinely achieved. The magnet is driven in a conventional manner using an HP oscillator and an Optimation amplifier.

The reference signal at the sum frequency is obtained by mixing the two signals in a multiplier and then using a twin T active band reject filter to eliminate the difference frequency.

Signal detection has been more difficult than we anticipated due to non-linear elements mixing the stray pickups from the AC electric and magnetic fields to produce a sum frequency which appeared as a spurious Hall Voltage. This problem has been solved by the circuit shown below:



This circuit has an input impedence of 10^{11}ohms, an overall gain of 100 at 5000 Hz and an effective rejection of 1000 at the electric and magnetic field frequencies.

The apparatus has been tested and we have measured the Hall coefficient on lightly reduced crystals ($\rho \sim 10^3\,\Omega$cm), with results in good agreement with measurements by others groups on lower resistivity material. Present equipment is probably adequate for measurements on crystals with resistivity up to 10^5 - 10^6 Ωcm. The limitation at present is due to relatively high lead capacitance; redesign of the sample holder and magnet assembly will extend our capabilities to resistivities of 10^7 - 10^8 Ωcm. Should it become necessary we are considering a pulse system similar to that used by Smith at Sandia and Hodny at Oxford. This system works only on high resistance samples and hence they are complimentary methods. It is not yet clear whether this second method will be needed.

E. Radiation Damage

In the proposal we indicated that radiation damage studies could be most efficiently done after better sample material and certain device configurations became available. Good progress has been made in both these areas but no radiation damage measurements have yet been undertaken.

F. Theory and Data Analysis

In the proposal we stressed the importance of rigid band calculations as a starting point for understanding the polaron nature of the carriers in rutile.

The calculation of the band structure is proceeding although the final results are not yet available. The calculations are being done using a modified APW technique, with "starting functions" based on known results for titanium and oxygen. An iteration process is used to insure self-consistency. The resulting wave functions can then be used to calculate experimentally observable quantities such as band gap, etc. Work has progressed to the point of getting a first estimate of the band gap as 3.9 volts. This is a very encouraging start.

We have also commenced some work on a phenomenological model for the polaron effects.

G. Optical Absorption Spectoscopy

In the proposal, we noted the importance of several experiments we proposed to do to elucidate the polaron nature of the carriers in rutile: (1) Temperature dependence of the 1.5 μ conduction electron absorption peak, (2) Study of doped material in the region below 100 cm^{-1}. (3) Study of spectra associated with electron trapping levels.

Good progress has been made on both items 1 and 3 as well as several related areas, as discussed below. Item 2 must await completion of a Fourier transform spectrometer, which is being built under the direction of Dr. Richard Brandt of our group. (The total cost of this instrument, which is being funded by the Physics Department, is expected to be ~ \$35,000.) All of the major components are on order, design work is nearly completed and some of the preliminary construction is under way. We hope to begin using the system in about six months.

1. Conduction electron absorption: The near IR absorption associated with free carriers discussed in previous reports has been studied in more detail in the temperature range from 80 to 300°K. As previously pointed out, this absorption peak cannot be explained on the basis of simple "free carrier" behavior (Drude theory) and the details of the absorption spectrum and its temperature dependence contain substantial information bearing on the polaron character of charge carriers in this material. It appears that a modified small polaron theory will at least qualitatively account for the spectrum, but more data, particularly at lower temperatures, is needed before a detailed comparison with theory can be made. Polaron theory is still in a fairly early stage of development, and detailed experimental data on a system such as rutile should serve as a useful guide to further development of the theory. In any event, detailed, reliable data is clearly needed, and the next step is to extend measurements to liquid helium temperatures.

Data accumulated during the past six months requires some revision of previously published curves. The absorption spectra at room temperature and 80°K are shown in Figs. 1 and 2, for $\vec{E} \perp$ C-axis. These curves reveal considerably more detail than was previously obtained, and several sources of error in previous data have been eliminated. In particular, the absorption at short wavelengths is considerably lower than was previously thought. This error was due to absorption by electrons in deep traps and was eliminated by taking the difference spectrum for two carefully matched crystals with Fermi levels differing only slightly. A small temperature shift is now evident --

the absorption peak shifts by ~ ten percent between 300°K and 80°K. Also, a slight periodicity on the low energy side of the spectrum is evident, particularly at 80°K (see arrows in Fig. 1.) This periodicity corresponds to the energy of the strongest coupling longitudinal phonon in rutile, in qualitative agreement with small polaron theory.

A more extensive study of the relationship between the magnitude of the OH stretching absorption and the free carrier absorption at room temperature as a function of H^+ concentration has been carried out, using the differential absorption technique described above. These measurements have verified our previous conclusions, particularly that the magnitude of these two absorptions are strictly proportional over a wide range of concentrations, after taking account of electron trapping levels, and enabled us to establish the relative absorption strengths much more precisely. In fact, it appears that these measurements can be made with sufficient accuracy to enable us to obtain quantitative data on trapping level density. The temperature dependence of the free carrier absorption in a particular crystal should then yield detailed information on thermal trapping energies for comparison with optical excitation energies discussed below.

2. OH^- stretching vibration: We have measured the temperature dependence of this absorption line from 10°K to 300°K. The line shifts linearly with temperature down to 100°K, where the shift "saturates." Very similar behavior was also found in $SrTiO_3$, except that a phase transition at 105°K makes the spectrum more complex in this material.[7] By comparing the results for TiO_2 with the results for $SrTiO_3$ and with the results from Cr^{3+} luminescence in $SrTiO_3$[8], we have been able to develop a microscopic model describing the peculiar temperature dependence for all of these spectra.

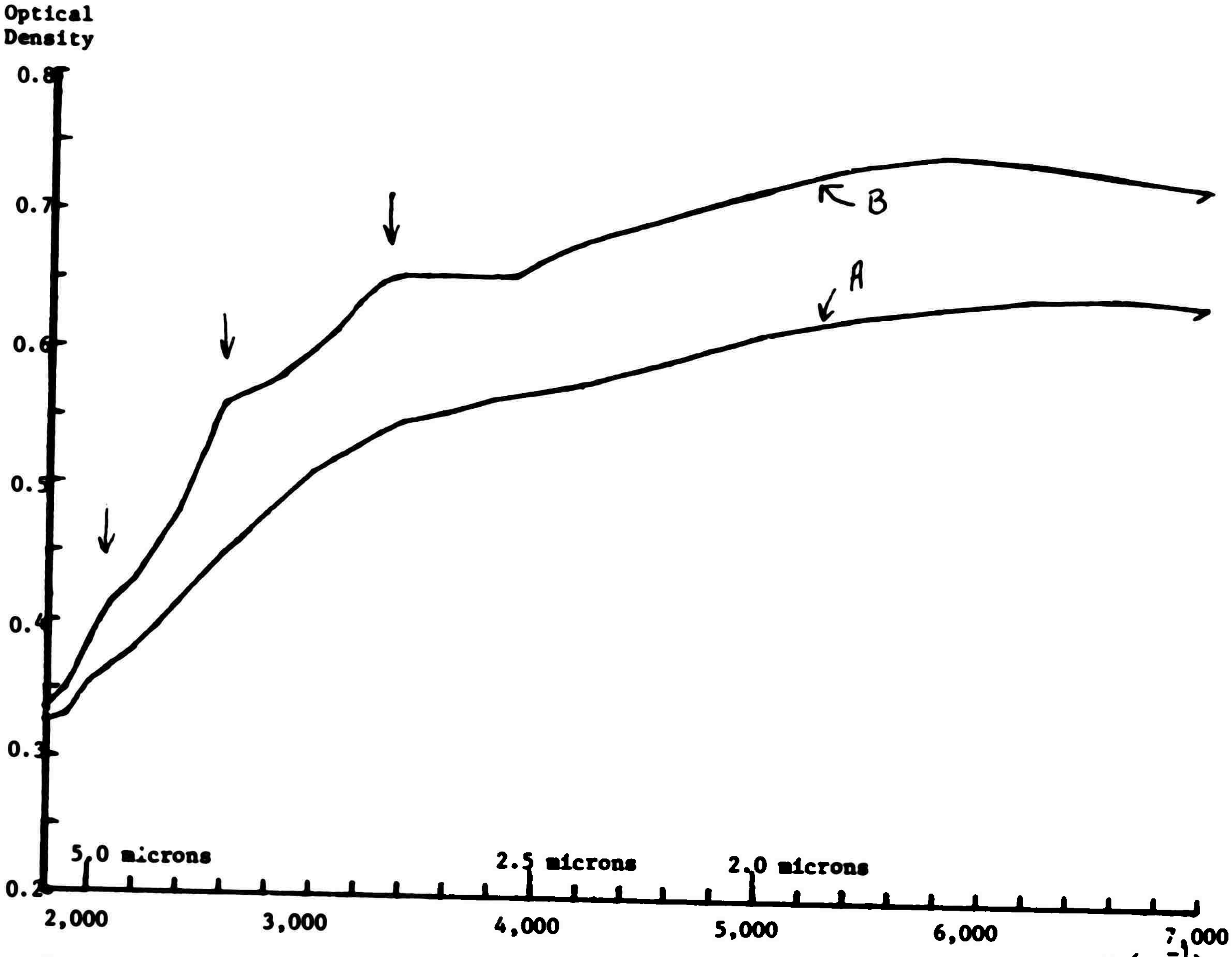


Fig. 1: Optical density for conduction electrons at (A) 300°K and (B) 80°K. Arrows indicate possible phonon sidebands.

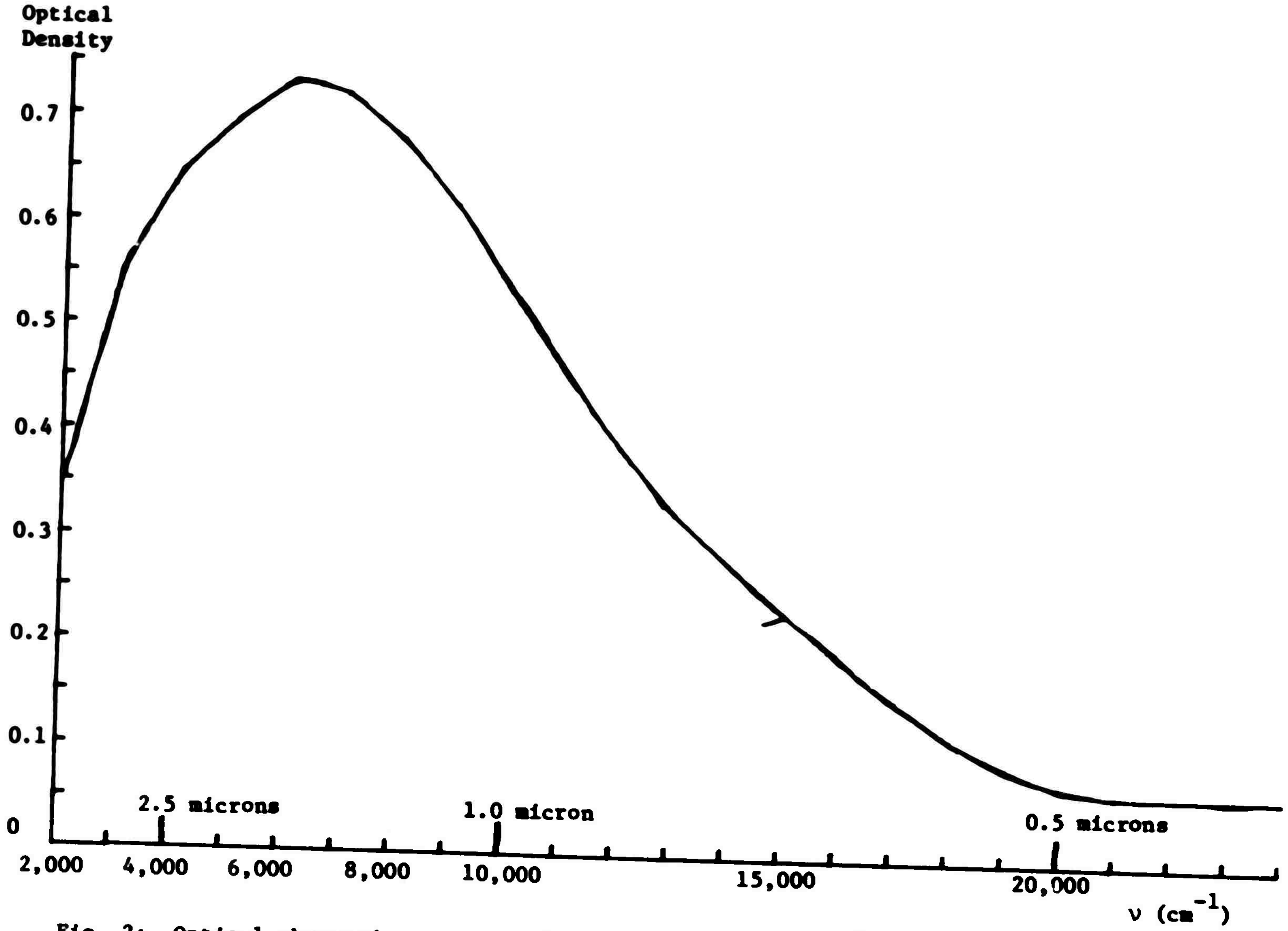


Fig. 2: Optical absorption spectrum for free carriers at 300°K, E ⊥ C (See also Fig. 1)

The OH^- stretching vibration and Cr^{3+} luminescence both appear to be microscopic probes of local lattice distortion with sensitivities rivaling X-ray diffraction. Note, however, that X-ray diffraction measures only average bulk distortion; thus this technique provides considerably more detailed information.

A brief summary of part of this work is contained in the following abstract of a paper to be presented at the San Francisco meeting of the APS. A detailed description of the work will be submitted for publication shortly.

> "Effects of Temperature and Phase Transitions on the OH^- Stretching Vibration in $SrTiO_3$ and TiO_2. J. W. Shaner (introduced by W. D. Seward), W. D. Seward, Univ. of Utah -- The OH^- stretching vibration near 3500 cm^{-1} in $SrTiO_3$ was measured from 10° to 300°K. The line above the 105° phase transition has a width less than 1.5 cm^{-1} and shifts linearly by -.08 $cm^{-1}/^{\circ}K$. Below 105° the line splits into a triplet, as was recently reported. Two lines shift linearly with translation, δ, of the O^{2-} ions and are due to OH^- dipoles with a component along δ. The third line shifts like δ^2. The frequency shifts with nearest neighbor distance are +140 $cm^{-1}/Å$ for $OH^- -Sr^{2+}$ bonds and -2200 $cm^{-1}/Å$ for OH - O bonds, in agreement with OH^- systematics in other materials. These assignments are qualitatively consistent with the electric field splittings observed. The OH^- stretch in rutile shows the same temperature dependence except for the splitting. Either rutile has an as of yet unobserved zone boundary soft mode like $SrTiO_3$, or the shift of the OH^- stretch has a more complex origin.

3. Absorption spectra associated with electron trapping states.

Detailed data has been accumulated on absorption spectra associated with a variety of substitutional cation impurities, including Mo, W, V, Nb, and Ta, and some preliminary data on Ni, Cr and Al. Differential spectra (to eliminate spurious absorptions) were taken on matched crystals as a function of Fermi level (controlled by low temperature H doping), temperature, and polarization (discussed in "4" below). Preliminary measurements of oscillator strengths were obtained by monitoring the OH absorption peak. A number of interesting and rather surprising effects have been observed, which promise to cast further light on the polaron problem in rutile. This work should be far enough along to justify a first publication during the next six months.

a. Mo and W. Strongly oxidized Mo-doped (.05 mole percent) crystals exhibit a strong, broad absorption band, peaking at .66 μ. (See Fig. 3). In the visible, this absorption band strongly resembles the free carrier absorption and had previously been erroneously identified with conduction electrons. Progressive raising of the Fermi level, E_F, by H doping apparently causes the peak to shift to longer wavelengths, until it saturates at ~ .93 μ. At this point the free carrier absorption band begins to appear (in Fig. 3, a small free carrier absorption has been subtracted from Curve II to yield the Mo absorption indicated by Curve III.) In the oxidized state, the H^+ concentration in the crystal is negligible. The H^+ concentration required to saturate the Mo-associated absorption at .93 μ corresponds within experimental error to the known Mo concentration. The most reasonable interpretation of these data would seem to be the following: In the oxidized state, the Mo has a valence of +4. The absorption peak at .66 μ corresponds to the energy required to remove the fifth electron from Mo to the conduction band (presumably in a time short compared to the lattice relaxation time, so

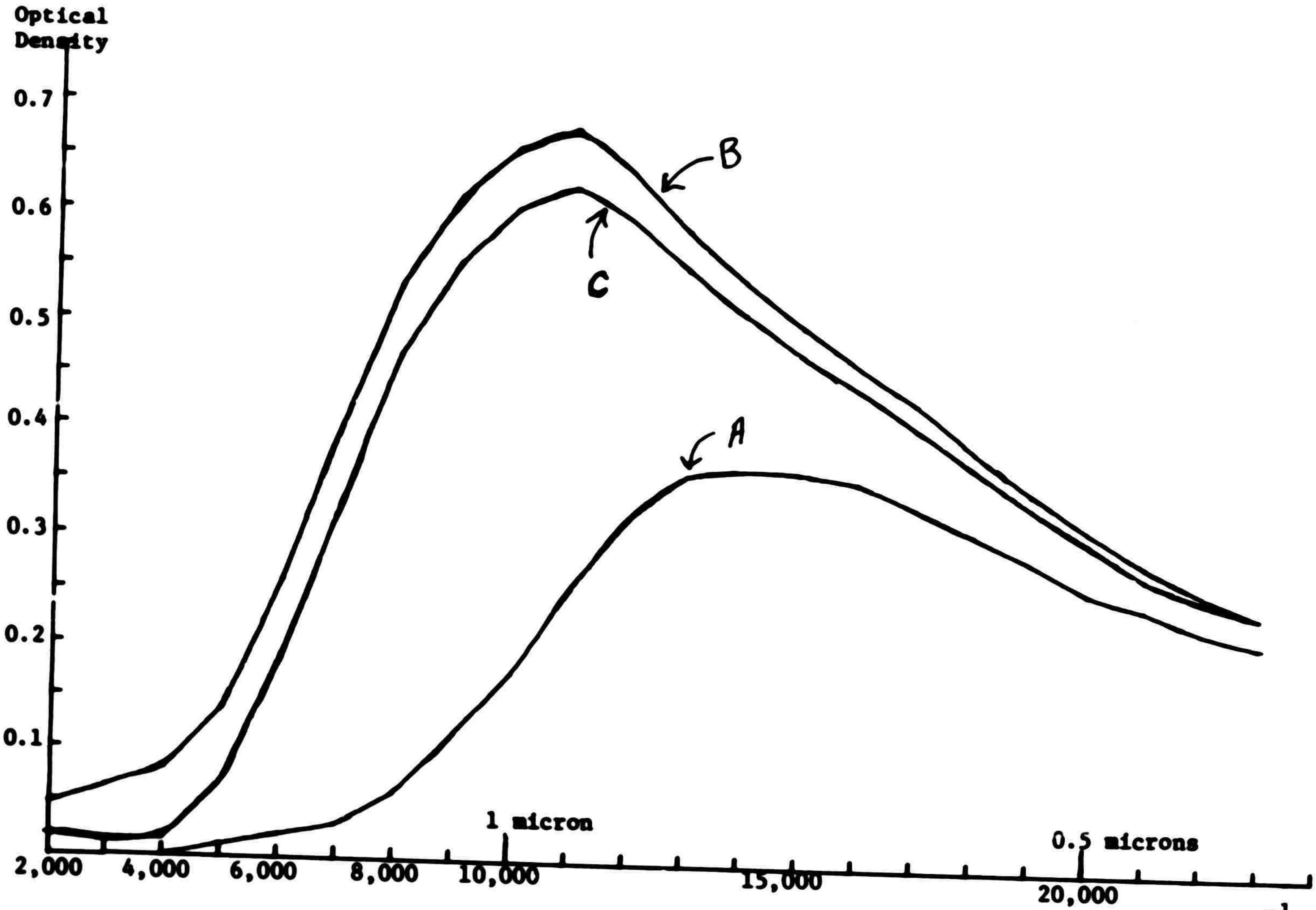


Fig. 3: Optical density (E $\perp$ C) of Mo doped specimen in (A) oxidized state and (B) reduced state. (C) results after subtraction of free carrier contribution.

excitation is from a "relaxed" Mo^{4+} state to an excited (i.e., "rigid band") state of the conduction band.) The apparent shift of the absorption peak as E_F is raised, is due to the superposition of an overlapping absorption associated with Mo^{3+}, located at about <u>1.1</u> μ, thus requiring that Mo^{4+} can bind an additional electron at a level below the bottom of the conduction band. This interpretation is consistent with dielectric loss measurements on these crystals, which indicate a trapping level, associated with Mo, not more than 0.4eV below the conduction band. This observation is particularly interesting, since the dielectric loss measurements yield thermal trapping energies (i.e., energy difference between two "relaxed" states), while the optical absorption includes lattice polarization energy. More detailed understanding of the optical properties of polarons are needed to draw quantitative conclusions, but the availability of these measured parameters should be quite helpful. These observations nicely illustrate the importance of the interplay between a variety of different experimental techniques, applied to the same crystals, which we have felt was a strong point in our program. It should be noted, however, that there appears to be some disagreement between our assignment of valence states of the Mo and that indicated by EPR measurements. These measurements were made by another group on less pure crystals, however, and the discrepancy may be due to deep lying traps in their crystals. Re-examination of these EPR results by our group is planned in the near future.

W-doped material has not been examined in the same detail as the Mo-doped crystals, but appears to be very similar, except that the two absorption peaks appear to be shifted by ~ 30%, to longer wavelengths.

In both of these cases there appears to be some phonon side-band structure in the peaks, similar to that found on the free-carrier band described above, but only preliminary data are available.

b. V. V seems to represent a quite different type of behavior than that observed for W and Mo. Strongly oxidized V-doped crystals have a spectrum similar to undoped material except that the band edge appears to have shifted to longer wavelengths. This spectrum is superficially similar to that exhibited by Fe doped crystals under some circumstances; this spectrum has been interpreted by other groups as actually representing a shift in the band gap, but it appears more likely that both represent an absorption band which happens to peak at a wavelength less than 4000 Å, as will be discussed below. As the V-doped crystals are doped with a successively higher concentration of H, the short wavelength absorption near the band edge decreases and an absorption peak appears ~ .55 μ (see Fig. 4); the strength of this absorption is proportional to H^+ concentration, and it saturates when the H^+ concentration is approximately equal to that of the V. At this point, the absorption near .4 μ is indistinguishable from that of a "pure" crystal. We tentatively interpret this behavior as an absorption band centered below .4 μ due to excitation of an electron from the valence band to a trapping level associated with V^{4+} substitutional, and an excitation (absorption peaking at .55 μ) from V^{3+} to the conduction band. It is interesting to note that the sum of these two excitation energies should be roughly equal to the band gap if no lattice polarization effects were involved. Instead, the energies are ~ 3.5eV and 2.3eV, totaling ~ 5.8eV, compared to a gap energy of ~ 3.2eV. Thus, if this interpretation is correct, we are forced to conclude that the polarization energies in this system are very large -- probably too large to be explained on the basis of present polaron theories. This is, of course, not terribly surprising -- present theories cannot be applied to TiO_2 with any real confidence. The assignment of valence states to the V is also rather uncertain at present and should be compared to EPR data.

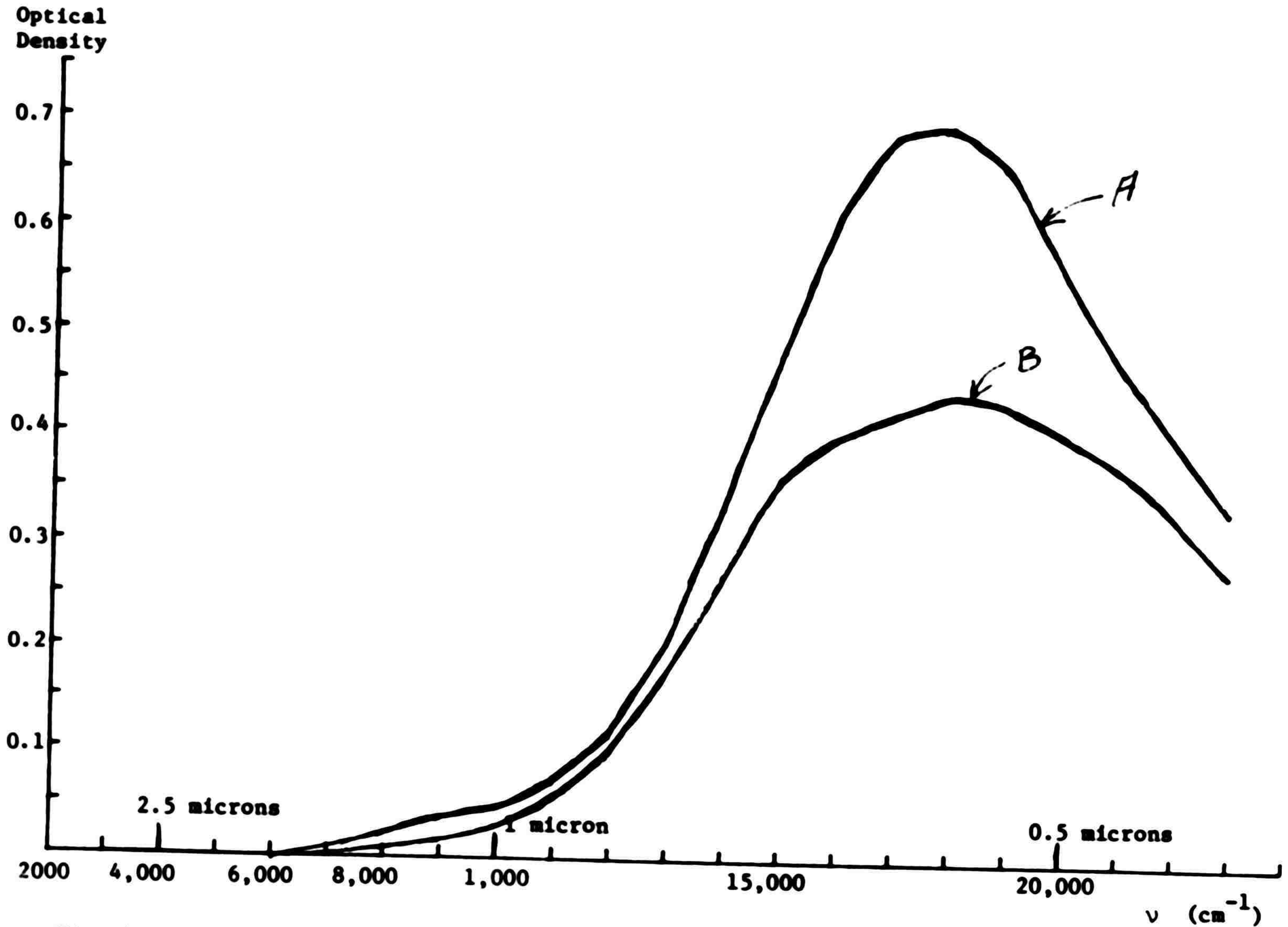


Fig. 4: Optical density of partially reduced V-doped crystal, for (A) E || C and (B) E ⊥ C.

c. Ta and Nb. We have so far found no evidence for trapping levels associated with these impurities, although we have not yet made measurements below 80°K. These crystals are always in a "reduced" state, even after strong oxidation, with a conduction electron density close to the concentration of the Ta or Nb. Our present data are consistent with a 5+ valance state for both of these dopants. Work is continuing on these impurities.

d. Other dopants. Preliminary indications are that Ni, Cr and Al all have absorption bands centered below 0.4 μ, but the behavior is complex and needs further study.

4. Anisotropy of absorption spectra. The polarization dependence of the various absorption spectra was not discussed above, since all appear to have similar characteristics and may be treated together (except for the OH absorption band which is 100% anisotropic, due to the orientation of the OH dipole in the basal plane, as discussed in previous reports.) The data discussed above and presented in Figs. 1 through 4, was taken with the electric field vector ⊥ to the C-axis of the crystal (except in Fig. 4, where the || orientation is also shown.) The anisotropy data for free carriers, the .66 μ Mo band and the .55 μ V band are presented in Fig. 5, in terms of the "anisotropy parameter". While it is not surprising to find anisotropic absorption in a tetragonal crystal, the details of the spectra are very puzzling, and we have no explanation for the data at present. Of particular importance is the fact that in all three cases the anisotropy peaks at the same wavelength as the absorption does. It is obvious that the explanation does not lie in the anisotropy of dielectric function of the material; an adequate explanation will probably be possible only after good band structure calculations are available.

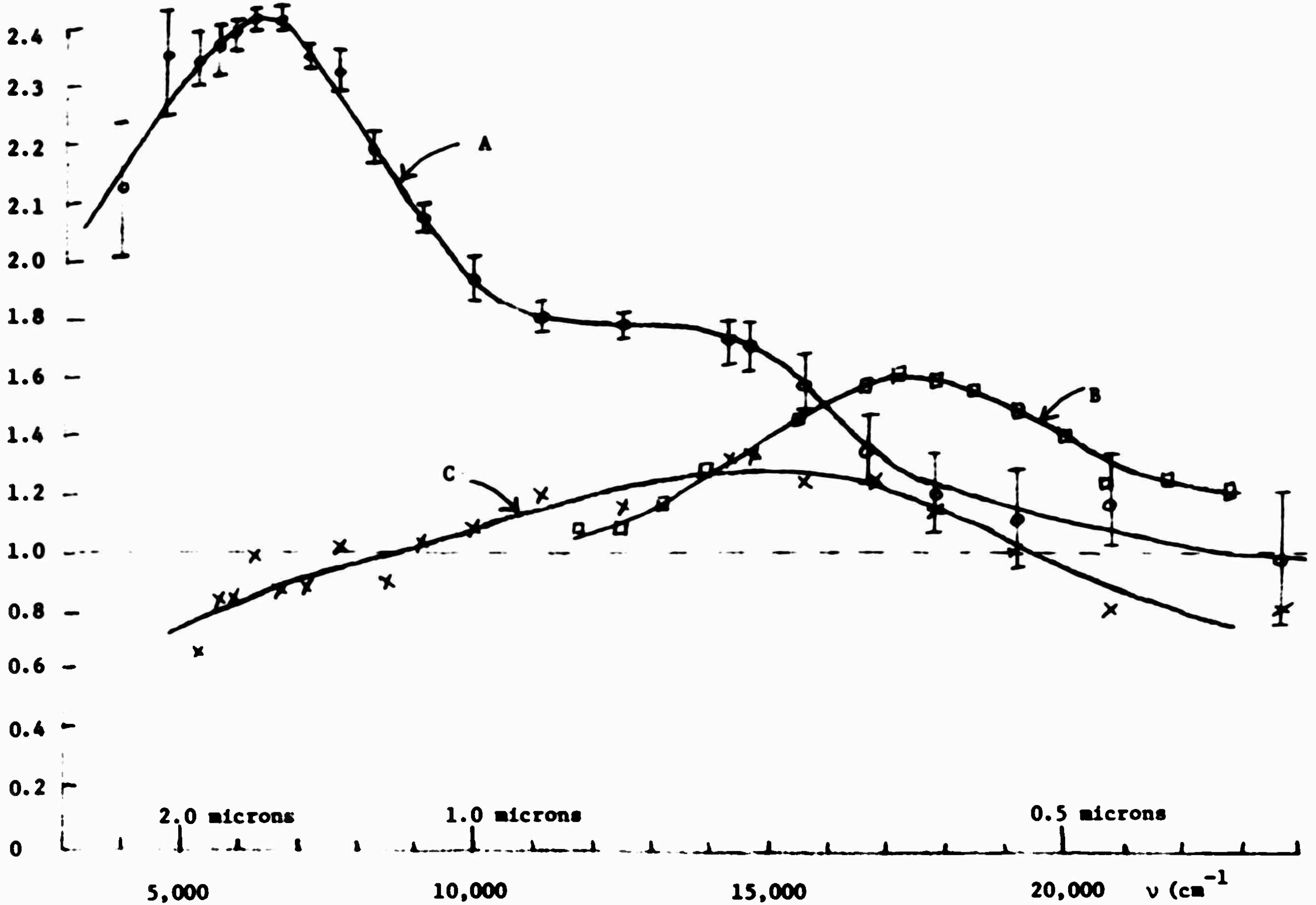


Fig. 5: Anisotropy factory (ratio of absorption coefficients for E || C and E ⊥ C for (A) free carrier absorption band, (B) V absorption band in partially reduced material and (c) Mo absorption band in oxidized material.

It is clear that the wealth of optical information which can be readily obtained, will go far in explaining the electron properties of this system, when the data can be fully correlated with such other measurements as dielectric loss and EPR.

H. Photoconductivity and Photoemission

In the proposal, we noted the importance of these areas and the extreme complexity of photoconductivity. Due to that complexity, we were unsure how much effort would be devoted to it.

Preliminary photoconductivity measurements early in the contract period indicated that the complexity of the photo response of this system was so great that meaningful interpretation would be prohibitively difficult at this stage of development. Since the information we had hoped to obtain using this technique can be obtained in other ways, it was decided to drop these measurements from the program, at least for the time being.

The photoemission study proved unnecessary due to recent work elsewhere which has measured the work function of rutile and found a value of 7.0 ± 0.5 eV in excellent agreement with the predictions of our model.

I. Review Paper

In the proposal we stated an expected completion date of summer, 1971. We have not quite met that goal. The review paper has proceeded more slowly than expected because of the several experiments which are suggested each time we start on a new section. (See, for example, the section on OH^- stretching vibration.) We have, however, essentially completed all sections except for the electrical transport properties section, the crystal growth and sample preparation section, and the sections summarizing the effects of defects. Our present goal for completion of the review paper is winter, 1971-72.

J. Ultrasonic Attenuation

In the proposal we considered the possibility of doing work in this area and concluded that it would have to await results of other work. To date it has not appeared profitable to devote effort here.

In addition to the areas above, covered in the proposal, we have devoted substantial effort to sample preparation as discussed in the Semi-Annual Report.

Progress on several other problems has also been possible, as a result of Dr. William Ohlsen joining the group. In addition to his expertise in magnetic resonance work, Dr. Ohlsen brings several years experience in research on TiO_2 and has strengthened the group in a badly needed area. His services will be particularly useful when we begin evaluating the results of our crystal growth efforts, and in our study of electron trapping levels. His efforts during the past few months have been mainly devoted to a careful study of the long-standing problem of "vacuum reduction" of rutile and the question of the relative importance of Ti interstitials and O vacancies in reduced material. We have been convinced for some time that the so-called vacuum-reduction of rutile is, in fact, caused by sloppy vacuum technique and that TiO_2 is not significantly reduced in a clean vacuum, at least up to temperatures of ~ 1000°C. However, papers continue to appear in the literature, reporting various measurements on "vacuum reduced" rutile, and it was obviously important to establish, if possible, exactly what the reduction mechanism is, and whether or not real vacuum reduction can occur. The first part of this study consisted of heating a rutile crystal in a sealed system, consisting of a quartz tube attached to a Ti sublimation pump. The system contained no O-ring seals or other sources of contamination (other than the quartz tube, which continued to outgas even after heating to ~ 1000°C). The whole system was baked to 350°C and carefully evacuated, through a constricted quartz tube, which was then sealed. Total gas pressure was monitored with the sublimation pump, and was maintained at a level below 10^{-8} Torr except when outgassing from the quartz caused a temporary rise as the temperature was increased. The degree of reduction was periodically monitored by measurement of the free carrier absorption peak of the rutile without opening the system. The results of this work will be reported in detail in a forthcoming paper. Briefly, we observed a very slight reduction at ~ 700°C (less than 1% of the reduction usually reported to occur at such temperatures), which was doubtless due to H_2O outgassed from the quartz, then no further measurable reduction after many hours of heating at successively higher temperatures, until a temperature of ~ 1200°C was reached. Above this temperature, rather strong reduction occurred, and we are now studying this crystal in more detail. There are indications that the reduction was caused by defects other than Ti interstitials, but this work is still progressing. In any event, it is now clear that no significant reduction occurs below 1000°C in a clean system.

The problem remains as to the nature of the reduction process which has been so frequently observed in "dirty" vacuum systems. The most obvious candidate for the reducing agent is hydrocarbons from O-rings and pump oil. The presence of carbon in the vacuum system suggests the possibility of carbon interstitials behaving as a donor impurity. While we view this as a rather unlikely possibility, it is of sufficient importance in the interpretation of other experiments, that it seemed essential to rule out the possibility. For this reason, an experiment is underway, in which we are reducing a crystal in $C^{13}O$, and will look for an EPR signal attributable to a C^{13} interstitial.

EPR studies of several substitutional impurities, including examination of lifetimes of excited states using photo-EPR techniques (for which equipment has been built) are also in progress.

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