Photoelectronic Processes in Rutile

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From a wide variety of experiments which include photoconductivity and photoluminescence excitation spectra, thermoluminescence, thermally stimulated current, electroreflectance spectra, kinetic response of photoconductivity, and optical and thermal bleaching of traps, a large number of defect energy levels were detected. A consistent interpretation of all of the data, combined with a knowledge of expected crystal field splittings, leads to the assignment of specific levels and observed transitions to Ti^{3+} interstitial ions. This center is also responsible for the luminescence emission at 0.85 μ. At least eight shallow-trap levels (<1 eV) were detected, and the possible assignment of one of these levels to oxygen vacancies is discussed. The thermal ionization energies of these traps, determined from the initial rise of the thermoluminescence glow, are in good agreement with those determined from Fermi-level analysis of the thermally stimulated current curves. The optical ionization energies of some of these levels were found to be 2.5 times their thermal ionization energies from the results of experiments utilizing modified optical bleaching techniques. The intensity of structures in photoconductivity excitation spectra depends on the electron population of the traps. A structure at 3.2 eV (0.39 μ) in photoluminescence excitation spectra (seen also in photocurrent excitation spectra when the traps are populated) is believed to be related to the onset of direct optical transitions.

I. INTRODUCTION

RUTILE has a wide range of interesting physical properties, many of which are associated with impurities and defects in its structure.[1,2] The oxidized crystal is an insulator, while the reduced crystal is an n-type semiconductor. The nature of the donor center is still in dispute. Recently, we reported on the presence of a number of defect states in oxidized and slightly reduced material, detected by thermally stimulated current and luminescence measurements.[3] The present paper includes a more detailed account of that work along with additional results obtained from photocurrent response spectra and photoluminescence excitation spectra.

This paper presents primarily the results of our findings regarding the existence of a large number of different defect energy levels in rutile. The defect levels are classified according to the measured values of their ionization energies. Those levels having thermal ionization energies less than 1 eV are called "shallow levels." They were detected primarily by thermoluminescence (TL) and thermally stimulated current (TSC) measurements. Their thermal ionization energies were determined by two different techniques (decayed TL and quasi-Fermi-level analysis of TSC), and good agreement was obtained for most levels. The optical ionization energies of three of these levels were deduced from the results of TL bleaching experiments. The ratio of optical to thermal ionization energy was the same for all three, but this value is different from the ratio of static to high-frequency dielectric constant predicted by elementary theory.[4,5] Those levels having optical ioniza-

tion energies greater than 1.5 eV are called "deep levels." They were detected primarily by optical excitation spectra (photoconductivity, photoluminescence, and excitation of TL and TSC). Because the values of some of these ionization energies correspond closely to the expected values of optical transitions within the Ti^{3+} ion in interstitial sites having nearly octahedral coordination,[6] a tentative assignment of observed energy levels to this specific defect has been made. The possible assignment of one of the shallow-trap levels to an oxygen vacancy is also discussed. The existence of these defects in rutile has been ascertained by recent electron paramagnetic resonance (EPR) studies.[7-10] The optical ionization energy of the luminescence center also has been deduced from the results of these measurements, and it appears to be identical to the ground-state level assigned to the Ti^{3+} interstitial ion.

In addition to documenting the large number of defect energy levels in rutile, the dependence of the photocurrent on the electron population of the shallow traps is presented. The magnitude of the photocurrent response is much greater when the shallow traps are filled than when they are initially empty, for both extrinsic excitation (wavelengths longer than the band edge at 0.41 μ) and intrinsic excitation (wavelengths shorter than the band edge). Under the proper experimental conditions, the effect of filling the shallow traps can be observed in the kinetic response of the photocurrent during a sustained excitation. In addition to this effect, the spectral distribution of photocurrent

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[7] P. F. Chester, J. Appl. Phys. **32**, 2233 (1961).

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response with respect to intrinsic excitation was found to depend on the occupancy of the shallow traps. A peak in the response spectrum at about $0.39\,\mu$ appeared only when the shallow traps were occupied. The onset of direct optical transitions in rutile occurs at $0.39\,\mu$, and the band edge at $0.41\,\mu$ is due to indirect transitions.[11,12] A well-defined peak at $0.39\,\mu$ also was found in photoluminescence excitation spectra, but this did not seem to be related to the occupancy of the shallow traps.

II. EXPERIMENTAL RESULTS AND DISCUSSION

The commercially obtained crystals used in this study were described previously.[3] These were not intentionally doped, but semiquantitative spectrographic analyses indicated the following concentrations of impurities (in parts per million): Si, 3; Fe, 3; Cu, 1; Mg, 1; Ag, 0.3; plus a trace of boron in the Linde crystals, and a trace of calcium in the National Lead crystals. Measurements were made primarily on crystals having two different degrees of oxidation, unless specified otherwise. As-cut crystals were slightly reduced, exhibiting a dark resistivity at room temperature on the order of $10^7\,\Omega$ cm. Fully oxidized crystals were obtained by baking in air or oxygen at some temperature in the range 850–1000°C for 3 or 4 days; their resistivity was too high to measure with the experimental arrangement used in this study ($\rho > 10^{13}$ ohm cm at room temperature). The basic experimental arrangement for the current and luminescence measurements has been described elsewhere.[3]

A. Thermoluminescence and Thermally Stimulated Currents

TL and TSC measurements in rutile, as well as its luminescence emission spectrum, were reported previously.[3] The present studies are related to the earlier work, and so the results pertinent to the present studies are summarized in brief. The photoluminescence emission spectrum due to excitation by 3650 Å light consists of a well-defined peak at $0.85\,\mu$ and an indication of a secondary peak at about $0.82\,\mu$. Both the TSC and the TL were measured simultaneously. Typical results are shown in Fig. 1. In general, eight distinct peaks can be identified in both the TSC and the TL between -190 and $+100$°C, although not all are equally prominent for all experimental conditions. There is a one-to-one correspondence between the TSC and the TL peaks, although the peak positions and relative magnitudes are not identical [Figs. 1(a) and 1(b)].

The observed luminescence is tentatively attributed to recombination radiation upon capture of an electron from the conduction band by a luminescence center. We speculate that upon uv irradiation holes become trapped in these luminescence centers, thus activating

the sites for subsequent electron capture. Since a TL peak can be observed for each TSC peak, release of an electron to the conduction band must be involved for each of the observed peaks; this suggests that all of the observed structures are due to electron traps. The origin of these trapping levels, whether they correspond to residual impurities or other defects in the rutile lattice, is not known. The origin of the luminescence center will be discussed later.

B. Thermal Ionization Energies (Shallow Traps)

The thermal ionization energies of the eight trapping levels seen in Fig. 1 were calculated by two independent techniques: (a) Fermi-level analysis of the TSC (after Bube),[13] and (b) analysis of the kinetics of the initial rise of the TL-glow peaks. By Fermi-level analysis, the ionization energy is computed from the sample conductivity at the peak of the TSC curve, assuming that a quasi-Fermi level exists at the level of the trap which gives rise to the peak when the temperature reaches that at which the peak occurs. For this analysis to be valid, retrapping must dominate over competing recombination processes. For these calculations, the density-of-states effective mass was assumed to be 20 times the free-electron mass,[2,14] and the variation of electron mobility with temperature, as re-

TABLE I. Ionization energies of shallow traps.

Peak No.	Approx. temp. of peak (°C)	Thermal ionization energy (eV)		Fermi-level analysis of TSC	Optical ionization energy (eV)	Ratio Opt./Therm.
		Initial rise of TL — Individual measurements	Average			
1	-180		...	0.27		
2	-170	0.28 0.30	0.29	0.28		
3a	-150	0.33 0.33 0.33	0.33	0.32		
3b	?	0.40 0.38	0.39	...		
4	-105	0.47 0.48 0.49	0.48	0.48	1.18 (1.05 μ)	2.5
5	-75	0.56 0.57	0.56	0.56	1.40 (0.88 μ)	2.5
6a	-40	0.59 0.60	0.60	...		
6b	-30	0.66		0.62	1.55 (0.80 μ)	2.4–2.5
7	$+25$		...	0.76		
8	$+40$	0.54 0.55 0.57 0.40 0.52	0.51	0.87		

[11] F. Arntz and Y. Yacoby, Phys. Rev. Letters **17**, 857 (1966).
[12] A. Frova, P. J. Boddy, and Y. S. Chen, Phys. Rev. **157**, 700 (1967).
[13] R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York, 1960), pp. 285–299.
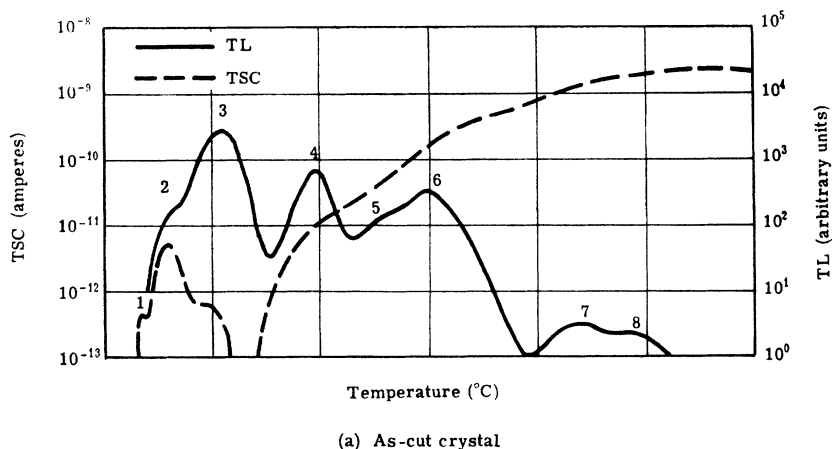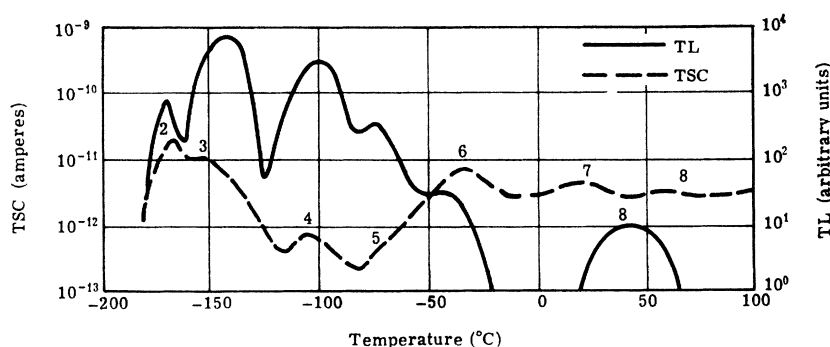[14] M. Itakura, N. Niizeki, H. Toyoda, and H. Iwasaki, J. Appl. Phys. (Japan) **6**, 311 (1967).

FIG. 1. TSC and TL curves for rutile, obtained simultaneously: (a) As-cut crystal; (b) same crystal after further oxidation. Heating rate: ~0.5°C/sec (Ref. 3). Peak No. 1, which is not evident in the TL curve shown, was observed at slower heating rates.

(a) As-cut crystal

(b) Same crystal after further oxidation

ported by Breckenridge and Hosler and others,[5,15,16] was taken into account. The results are given in Table I. The initial rise of a TL-glow peak was found to vary exponentially with the reciprocal absolute temperature. The activation energy thus obtained is taken to be the thermal ionization energy of the trap giving rise to that peak. There is theoretical justification for this provided certain conditions are met, such as the probability of the luminescent transition being directly dependent only on the free-carrier concentration.[17,18] To perform the experiment, a particular peak was selected, and all lower-temperature peaks were removed by thermal cleaning, i.e., heating the sample to a temperature just below that of the peak of interest, and recooling. Several curves were usually obtained for each peak, each curve differing in the temperature to which the thermal cleaning was carried out. All such curves should yield the same activation energy if the peak truly represents a single-trap level. The results are shown in Table I along with the results obtained from the Fermi-level analysis. Except for the higher-tempera-

ture peak (No. 8), good agreement was found between the results of these two techniques. In addition, the initial-rise technique gives evidence that peak Nos. 3 and 6 are actually both doublets, not normally resolved. Each gave two distinctly different activation energies as the thermal cleaning temperature was gradually increased. Peak No. 6a was subsequently resolved as a separate peak at about −40°C after thermal cleaning to −75°C.

C. Optical Ionization Energies (Shallow Traps)

The optical ionization energies of defect centers are often greater than the thermal ionization energies of the same defect centers. This is particularly true in lattices where ionic bonding is significant, and comes about because of the Franck-Condon principle and the change in lattice polarization in the vicinity of the defect.[4] The optical ionization energies of three of the observed trapping levels (Nos. 4, 5, and 6b) were determined by a technique involving optical bleaching of the TL peaks. To detect bleaching effects, all of the shallow traps were filled first by exposure to 0.365 μ light at liquid-nitrogen temperature. Then the sample was heated to a temperature below that of the peak of interest and recooled to liquid-nitrogen temperature. This thermal cleaning process removed all lower-temperature peaks from the

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[16] J. H. Becker and W. R. Hosler, Phys. Rev. **137**, A1872 (1965).
[17] R. R. Haering and E. N. Adams, Phys. Rev. **117**, 451 (1960).
[18] G. F. J. Garlick and A. F. Gibson, Proc. Phys. Soc. (London) **60**, 574 (1948).

G H O S H ,   W A K I M ,   A N D   A D D I S S

TL curve that would be obtained upon reheating the sample at this point. However, before reheating the sample, it was exposed to light of one of a series of suitable wavelengths between 0.7 and 2.0 μ. If this infrared (ir) irradiation had been effective in bleaching the peak of interest, one would expect its intensity to be reduced in the resulting TL curve. Although we believe that we have seen this effect, optical bleaching of TL peaks in this material appears to be extremely inefficient, suggesting a very high probability for retrapping. Therefore, measurement of the decrease in height of a TL peak due to ir irradiation is a very insensitive means for detecting quenching, because it involves the detection of small differences between two large quantities. However, some of the electrons excited from the trap by ir light are retrapped by the shallower traps which had previously been thermally cleaned. Thus, a much more sensitive measure of bleaching is obtained from the growth of the lower-temperature TL peaks following the ir irradiation. The optical ionization energy of the trap was equated to the particular wavelength giving rise to the maximum bleaching effect, and was found by repeating the procedure outlined above for each of the series of ir wavelengths such that the total exposure was the same in each case (constant energy). The results of this procedure for thermal cleaning, up to (but not including) peak No. 6b, are shown in Fig. 2. The heights of TL-peak Nos. 3–5, 6b, and 8 are plotted versus the wavelength of the ir light exposure. Following the above discussion, bleaching is detected by an increase in peak height of Nos. 3–5, which were thermally cleaned, and by a decrease in peak height of Nos. 6b and 8, which were not thermally cleaned. Of course, the peak which is actually bleached must be one of those not thermally cleaned. In Fig. 2, a weak minimum at about 0.8 μ appears in peak No. 6b, suggesting that 0.8 μ is the
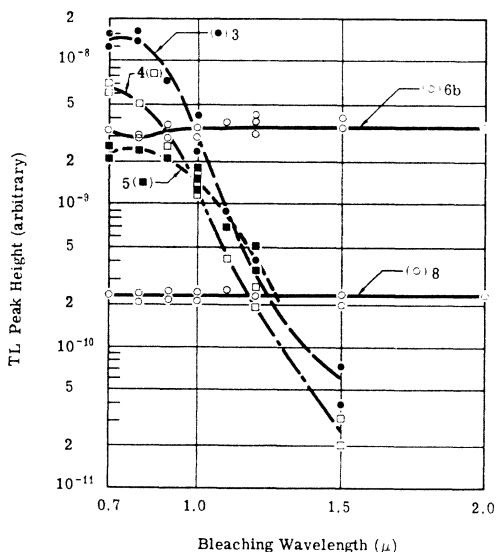

FIG. 2. Optical bleaching effects on TL-peak heights and thermal cleaning up to peak No. 6b. Labels indicate specific TL peaks by number.

optimum wavelength to bleach that peak. Although the magnitude of this dip is well within the normal scatter in the data, we believe it is real, because in every experiment done so far, including measurements at different exposure levels, the value at 0.8 μ was always found to be slightly lower than that at 0.7 μ. The evidence for bleaching is clearer in the growth of peak Nos. 3–5. Peak Nos. 3 and 5 appear to reach a maximum at about 0.8 μ, corresponding to the slight dip in peak No. 6b. Peak No. 4 also becomes large, but does not clearly show a maximum at this same wavelength. The results are complicated by the fact that emptying traps deeper than the one under study can occur at shorter wavelengths, and this can contribute to the filling of the levels under observation. Also, wavelengths around
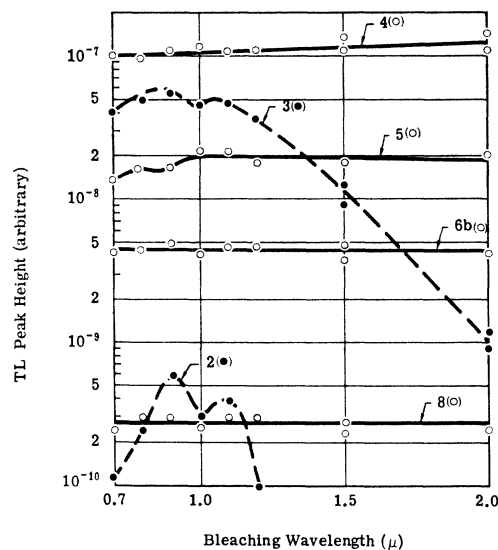

FIG. 3. Optical bleaching effects on TL-peak heights and thermal cleaning up to peak No. 4. Labels indicate specific TL peaks by number.

0.8 μ can contribute directly to filling the shallow traps (see later).

The results for thermal bleaching up to peak No. 4 are shown in Fig. 3. No distinct minimum can be detected in the intensity of peak No. 4, but an indication of a minimum at about 0.9 μ is evident for the next-higher peak (No. 5). However, two maxima at about 0.9 and 1.05 μ are exhibited in the growth of peaks Nos. 2 and 3, and these are attributed to the bleaching of peaks Nos. 5 and 4, respectively. The scatter in the data for a few of the points that were repeated is shown. The scatter in the rest of the data is possibly of the same magnitude. Taking this into consideration, the two maxima in these two curves may not be as well defined as shown. Nevertheless, we believe the results still indicate two overlapping peaks. Because of the complications mentioned, it is difficult to place confidence in the ionization energy obtained from the results of a single set of measurements. However, confidence in the values obtained is greatly increased

when the results of several sets of measurements can be interpreted self-consistently, as is the case here. The optical ionization energies thus obtained for three trapping levels (Nos. 4, 5, and 6b) are given in Table I. Note that the ratio of optical to thermal ionization energy is very close to 2.5 for each of these three trapping levels. If we allow for a reasonable error in choosing the wavelengths corresponding to the optimum bleaching effects, these three ratios still will be within 20% of 2.5. In the photoconductivity excitation spectra of a reduced crystal to be described later, structures are observed around 0.9 and 1.1 μ. These values agree with the optical ionization energies determined for peak Nos. 5 and 4.

D. Deep Levels

The existence of even deeper levels than those reported above can be deduced from the results of different types of measurements on uv-irradiated rutile. These include spectral response of photoconductivity and
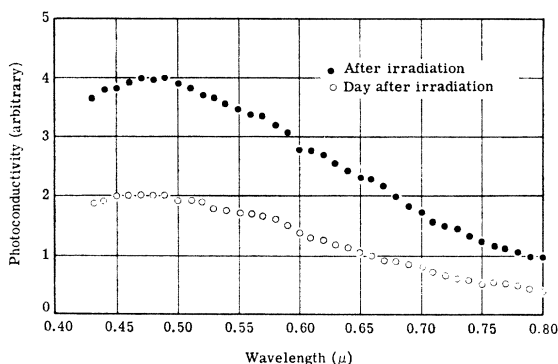
FIG. 4. Photoconductivity excitation spectra of uv-irradiated crystals (ac photocurrent due to incident light chopped at 13 cps).

photoluminescence excitation spectra. The photoconductivity spectral response shows a broad-band increase in sensitivity to visible light after uv exposure (Fig. 4) or after reducing the as-cut crystal (Fig. 5). There are many weak structures in the spectral response curves which are difficult to distinguish from the background. However, some maxima appear fairly consistently at certain specific wavelengths, indicating a series of deep-lying discrete levels. Although the peaks cannot be identified with any degree of confidence from a single curve, the examination of a wide variety of such data has led to a consensus regarding the energy levels of the discrete deep-lying levels which are present in rutile. Their optical ionization energies correspond approximately to the following wavelengths: 0.420, 0.450, 0.490, 0.535, and 0.630 μ. Some of these levels were also detected in photoluminescence excitation spectra (Fig. 6). In addition, less well-documented data indicate that possible levels also exist at longer wavelengths. Most of
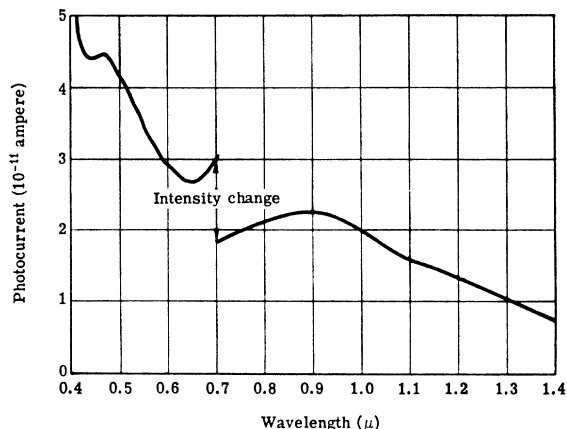
FIG. 5. Photoconductivity spectra of reduced crystal at −194°C. Crystal heated at 900°C in one atmosphere of CO_2 for over 50 h (resistivity = 7600 Ω cm). The break in the spectrum is because of two different excitation intensities which were used; 22.5 V across sample.

these same levels were observed in neutron-irradiated samples by Townsend, Kan, and Levy.[19]

The redistribution of electrons among the various trapping levels upon exposure to light can be detected by several means. The redistribution of electrons in the shallow traps due to ir light was described earlier in connection with the determination of the optical ionization energies of these shallow traps. In addition, the shallow traps seen in TSC and TL can be filled by optically exciting electrons to the conduction band from the deep levels as well as from the valence band. If all eight traps seen in Fig. 1 are emptied thermally, the same peaks in the TSC and the TL can be regenerated by visible-light excitation in place of the usual uv excitation. Based on the fact that one observes photoconductivity with visible or uv light and that both
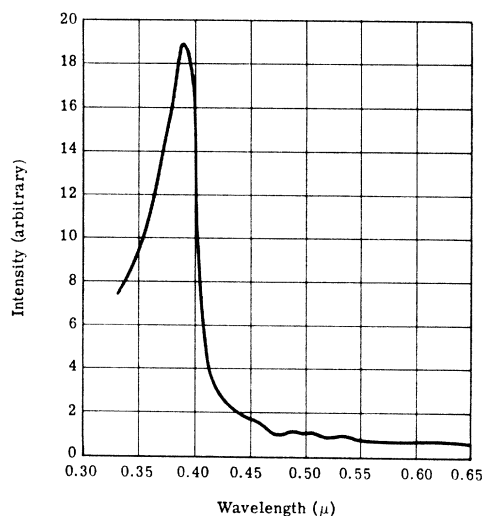
FIG. 6. Photoluminescence excitation spectrum. Rutile single crystal at liquid-nitrogen temperature.

[19] P. D. Townsend, H. K. A. Kan, and P. W. Levy, Proc. Brit. Ceram. Soc. 1, 71 (1964).
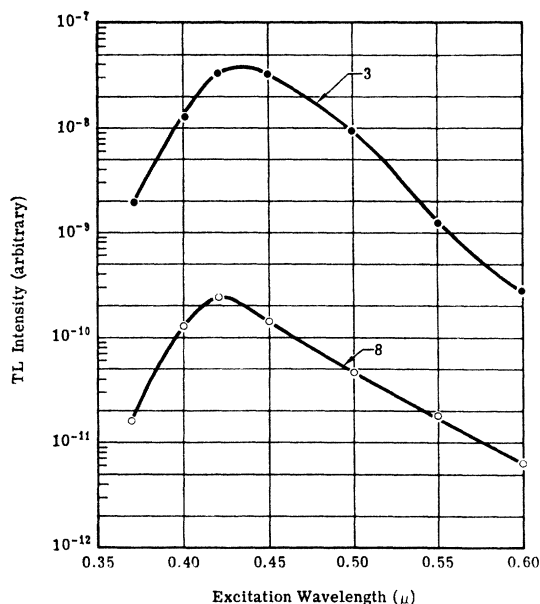
Fig. 7. TL excitation spectra of rutile.
Heights of peaks Nos. 3 and 8.

TSC and TL peaks are observed on warming the crystal, we conclude that the filling and emptying of traps take place via the conduction band. However, these results do not completely rule out the possibility that higher excited states or metastable states associated with the deeper levels exist. TL excitation spectra for two of the TL peaks (Nos. 3 and 8) are shown in Fig. 7. Note that both spectra peak at about 0.42 μ, which is just slightly above the rutile band edge at 0.41 μ. Similar results were found in TSC excitation spectra which also exhibited an auxiliary peak at about 0.8 μ, indicating another deep level. Light of wavelength greater than 0.7 μ does not generate any of the TL structures, although the TSC structures continue to be generated by wavelengths up to about 0.9 μ. This must mean that light of wavelength between 0.7 and 0.9 μ populates the shallow levels with electrons excited from deeper levels, but does not activate the luminescence center by exciting its electrons. Wavelengths below 0.6 μ must excite electrons from the luminescence center because TL is observed along with TSC in that case. Therefore, the optical ionization energy of the luminescence center must correspond to some wavelength between 0.6 and 0.7 μ. Conceivably, it might correspond to the 0.63-μ level reported earlier. Note that this energy is greater than that of the luminescence emission at 0.85 μ. This is another consequence of the Franck-Condon principle and the polarizability of the lattice ions surrounding the defect.

E. Effect of Shallow-Trap Population on Photocurrent Response

The redistribution of electrons among the various trapping levels also changes the photocurrent response

characteristics in both the visible spectral region (extrinsic response) and in the uv region (intrinsic response). Most of the photocurrent measurements were made on the highly oxidized samples, because differences between the trap-filled and trap-empty cases were more distinct for these samples. Also, the measurements were made using very low-intensity light in most cases, so that the shallow-trap population was not changed appreciably during the photocurrent measurement. The magnitude of the extrinsic photocurrent at liquid-nitrogen temperature was found to be strongly dependent on the population of the shallow traps. The photocurrent was greatest when the shallow traps were fully populated. The dependence of the photocurrent on the population of each trap individually was determined by observing the magnitude of the photocurrent due to 0.50-μ light after each of the shallow traps was emptied in succession. This was accomplished by thermal cleaning to successively higher temperatures, such that each time the next deeper trap was emptied. The results are shown in Fig. 8. Note that the photocurrent decreased by successive steps as each trap was emptied successively. The largest incremental decrease followed the emptying of trap No. 3.

The population of the shallow traps also affected the intrinsic photocurrent response. Figure 9 shows the spectral response of the photocurrent after the shallow traps have been emptied and after they have been filled. When the shallow traps were empty, the response peaked at about 0.41 μ. This behavior is attributed to excitation from a defect level at about 0.42 μ (at room temperature the peak appears between 0.415 and 0.425 μ for these highly oxidized crystals) plus band-gap excita-
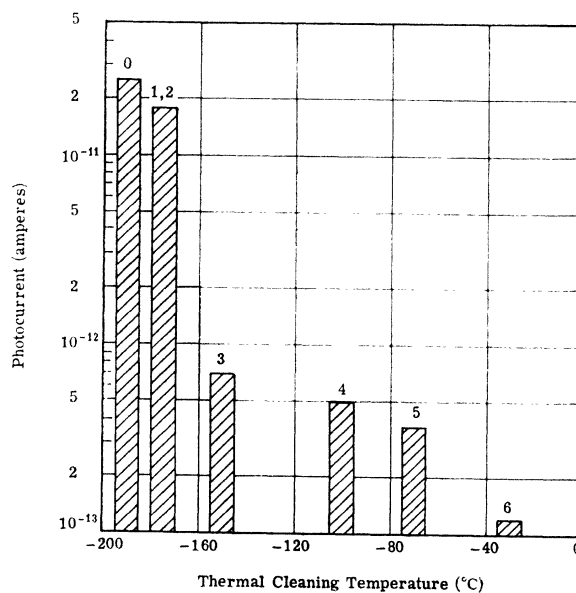

Fig. 8. Photocurrent response after successively emptying shallow traps (by thermal cleaning to indicated temperature). Labels indicate by number the specific traps emptied. Response to 0.50-μ light at liquid-nitrogen temperature. Oxidized sample; 23 V across sample.

tion beginning at 0.41 μ, followed by decreased response at the shorter wavelengths which are absorbed closer to the surface due to surface recombination effects. However, after the shallow traps were populated, a much bigger response, peaking at about 0.38 μ, was observed. This peak was fairly broad, as shown, and the wavelength of its maximum point varied between 0.375 and 0.39 μ depending on experimental conditions (e.g., sample used, temperature, and population of shallow traps). This peak is nearly coincident with a critical point in the energy-band structure of rutile, as determined from optical studies of band structure (such as electroreflectance spectra—Fig. 10). The appearance of structure of this type in the photocurrent response spectra was unexpected, because all light entering the crystal in this wavelength region is absorbed independent of wavelength (i.e., all wavelengths shorter than about 0.405 μ), and the amount of light entering the crystal (determined from the variation of reflectivity with wavelength[20]) does not vary with wavelength by an amount sufficient to account for the structure.[21,22]

As shown, the photoresponse peak at 0.38 μ appeared only after the shallow traps were populated. The disappearance of the 0.41-μ peak after filling the shallow traps is attributed to overlapping by the long wavelength tail of the strong 0.38-μ peak rather than to quenching of the 0.41-μ peak. Both peaks can be seen together if the 0.38-μ response is reduced by partially emptying the shallow traps. At room temperature, the 0.38-μ peak was always absent in oxidized samples, because the traps are automatically depopulated at that temperature. However, both the 0.38- and 0.42-μ peaks were detected at room temperature in slightly

Fig. 10. Electroreflectance spectra of rutile [1.6 V_{dc}; 7 V_{ac} (rms)]. Electrolytic technique. $E \perp c$ and $E \| c$ means light polarized perpendicular and parallel to c axis.

reduced samples (e.g., as-cut crystals), as shown in Fig. 11. The peak is slightly shifted towards shorter wavelengths in this case. The higher conductivity means a higher Fermi level, which in turn means that the shallow traps are more highly populated at thermal equilibrium. Therefore, all of these results are consistent: A peak in the photocurrent response at about 0.38 μ appears only under conditions such that the shallow traps are populated sufficiently with electrons.

A very strong well-defined peak at about 0.39 μ also appeared in the photoluminescence excitation spectrum (Fig. 6). In some crystals, this peak was slightly shifted towards longer wavelengths. Although photoluminescence excitation spectra have not been investigated under as wide a variety of conditions as the photocurrent response spectra, the peak at 0.39 μ appears to be present independent of the population of shallow traps, unlike the peak at 0.38 μ in the photocurrent spectral response.

The increased photocurrent observed after the traps are filled must be attributed to either an increased mobility or an increased lifetime of the photogenerated free carriers. Although we have not measured mobilities, we are very reluctant to attribute any appreciable part of this effect to a mobility change, because we cannot conceive of a reasonable model to account for the very large mobility changes that would be required to account for over 2 orders of magnitude change in the photocurrent. Therefore, we believe the effect must be attributed primarily to an increase in lifetime when the traps are filled.

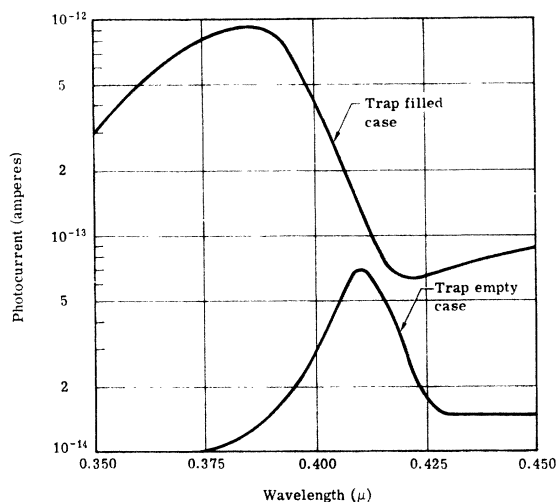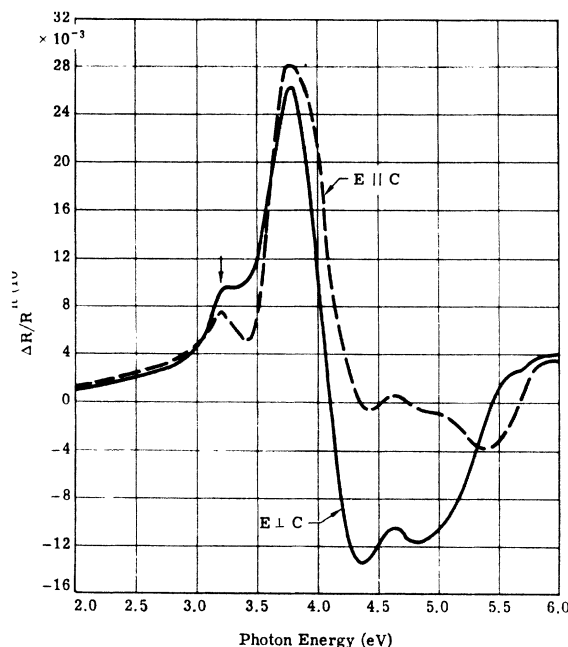There are at least two mechanisms which can con-

Fig. 9. Spectral response of photoconductivity (intrinsic region). Trap-empty case and trap-filled cases. Oxidized sample at liquid-nitrogen temperature; 23 V across sample.

[20] M. Cardona and G. Harbeke, Phys. Rev. 137, A1467 (1965).
[21] H. B. DeVore, Phys. Rev. 102, 86 (1956).
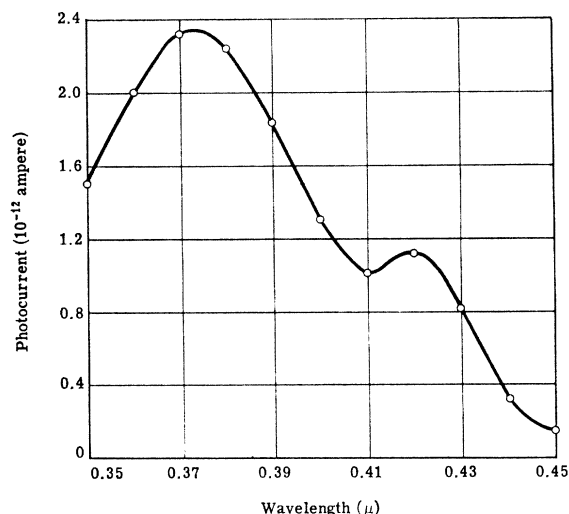[22] A. M. Goodman, J. Appl. Phys. 30, 144 (1959).

FIG. 11. Spectral response of photoconductivity for an as-cut crystal at room temperature; 23 V across sample.

tribute to a dependence of lifetime on trap population. One involves the competition between recombination centers and traps for the photoexcited carriers. If the trapping probability is extremely high, as indicated by the optical bleaching experiments described above, then the trap-empty lifetime will be very short due to the dominance of the trapping processes. When the traps are filled, trapping no longer plays a role, and the longer lifetime determined by the recombination processes dominates. This mechanism was described by Böer and Vogel[23] to account for photocurrent growth characteristics in CdS and is also discussed by Bube.[13] Under appropriate experimental conditions, we have observed similar photocurrent growth kinetics in rutile.[24]

It is possible that the mechanism described above is entirely responsible for the increased lifetime due to trap filling. Order of magnitude calculations of the total number of photons absorbed when the photocurrent first reaches the high value corresponding to the trap-filled case give reasonable values of total trap density, assuming each absorbed photon fills one trap. This is not a critical test, however, because reasonable values of trap density cover several orders of magnitude. Experimental results of our studies of the relations between photoconductivity and photoluminescence[25] first suggested to us the possibility that Auger recombination occurs when the shallow traps are filled, thereby increasing the effective lifetime of photogenerated carriers. Although we have not been able to definitely establish that this process occurs, we believe it is worth considering as a possible contributing factor. As we visualize this process, an electron dropping into a recombination center from the conduction band may lose its energy by exciting a trapped electron to the conduction band via an Auger-type interaction, as

illustrated in Fig. 12(a). Since the luminescence emission band overlaps with the absorption band of some of the traps, as determined from the TL-bleaching experiments described earlier, energy transfer between these two centers is possible when the traps are populated. Other recombination centers which do not give rise to luminescence may also contribute to this process. An Auger process very similar to this type has been considered for GaP by Tsang, Dean, and Landsberg.[26] Alternatively, we can conceive of a two-step process involving more conventional Auger recombination concepts, followed by impact ionization of the shallow traps, which accomplishes the same result [Fig. 12(b)]. If either of these Auger processes occur, they would contribute to the observed increase in free-carrier lifetime when the shallow traps become populated.

In addition to the general increase in the photocurrent throughout the spectral region when the traps were filled, a pronounced change in the photocurrent spectral response in the intrinsic absorption region near the band edge was noted. In particular, the appearance of a peak in the spectral response at about 0.38 μ only when the traps were filled cannot be explained solely by mechanisms which give rise to a general increase in lifetime. In an attempt to gain a better understanding of the appearance of this peak, we have been led to consider the electronic energy-band structure of rutile and the possible influence it might have on the experimental results.

The band structure of rutile is believed to be very similar to that of strontium titanate.[27,28] Other than optical measurements, most experimental evidence suggests that the lowest conduction band in $SrTiO_3$ consists of a set of minima located at the Brillouin-zone edge in the $\langle 100 \rangle$ direction.[29,30] This conclusion also has
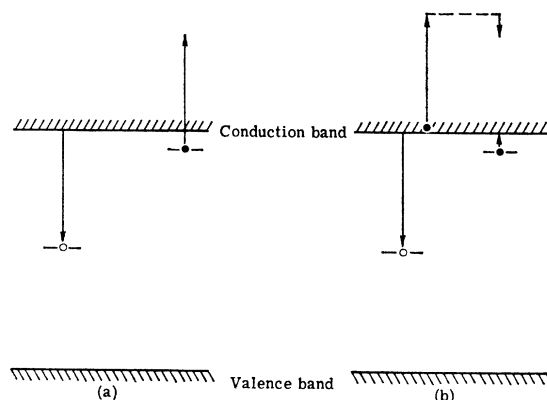

FIG. 12. Proposed Auger processes in rutile. (a) Direct excitation of trapped electron; (b) two-step process: conventional Auger recombination followed by impact ionization of the shallow traps.

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been supported by Kahn and Leyendecker's theoretical calculations.[27] Reflectance spectra of rutile do not reveal any structures at the band edge.[20] However, electro-absorption measurements by Arntz and Yacoby[11] indicate that the band edge at 3.03 eV (0.409 μ) is due to indirect transitions. Electroreflectance measurements indicate that the onset of direct optical transitions could possibly occur somewhere between 3.2 and 3.5 eV.[12] Electroreflectance spectra from (110) and (001) crystal faces[12] also show a structure at about 3.0 eV which has been attributed to the indirect transitions, in agreement with Arntz and Yacoby. Spectra from the (100) face do not show the 3.0-eV structure, but do exhibit a structure at about 3.2 eV (0.387 μ) such as shown in the spectrum we have obtained (Fig. 10). We believe these results favor the conclusion that the band edge in rutile at 3.0 eV is due to indirect transitions and that the onset of direct optical transitions occurs at about 3.2 eV or slightly higher energy. Therefore, the appearance of the 0.38-μ peak in the photocurrent spectral response when the shallow traps are filled may be related to the onset of direct optical transitions.

We have not carried out an investigation of this phenomenon sufficient enough to determine the specific mechanism of interaction between the direct optical excitations and the trapped electrons, leading to the appearance of the peak at 0.38 μ. We can only speculate about the factors which may be involved. In many semiconductors, a peak in the photocurrent spectral response is observed at the band edge when the surface and volume recombination rates are appreciably different. This phenomenon has been adequately described by DeVore.[21] The peak appears primarily because more carriers are excited at the band edge, where a large fraction of the incident light is absorbed in the material; but at shorter wavelengths, where most of the light is absorbed very close to the surface due to the very rapid increase in the absorption coefficient, a larger fraction of the excited carriers recombine faster via the surface, resulting in a decrease of the photocurrent. This mechanism cannot be applied directly to account for either the trap-empty or the trap-filled case, because in both cases the observed peak is displaced from the band edge at 0.41 μ.[31] The 0.42-μ peak is at lower energy than the band gap and, as already stated, is attributed to a defect level. We believe that the response due to the onset of indirect transitions at the band edge is masked by this structure. The 0.38-μ peak is at higher energy than the band gap, where the onset of direct optical transitions occurs. However, the same principles invoked by DeVore, along with the increased lifetime due to trap filling, are among the factors which probably contribute to the appearance of this peak. Another factor which should be considered is the possibility that the traps

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[31] In more perfect crystals grown from a flux, a peak is observed at the band edge (0.41 μ) (Ref. 24), as predicted by a straightforward application of DeVore's theory. These crystals do not exhibit any of the defect structures reported here.
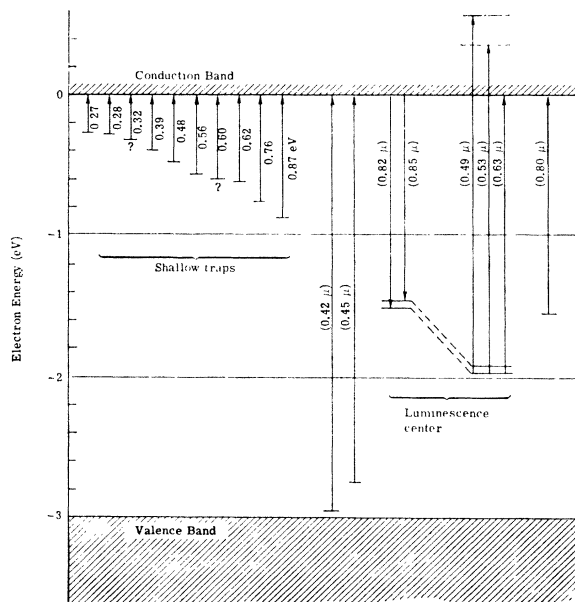

FIG. 13. Sketch of the proposed energy-level diagram of defect states in rutile. Question marks indicate traps detected only by initial rise of TL. The luminescence center is tentatively identified as a Ti^{3+} ion.

are not distributed uniformly throughout the bulk of the sample; this would give rise to a variation of trap-filled lifetime with depth, which could contribute to the appearance of this peak if the Auger processes described earlier contribute to the increased lifetime. We would expect the effective lifetime due to the Auger processes to increase with the density of filled traps because the probability of energy transfer to a trapped electron increases with the concentration of trapped electrons. The trap-filled lifetime obtained from the loss of competition for the excited electrons by the shallow traps will be independent of the trap density, because the same recombination-lifetime limit is reached when the traps become filled.

F. Model of Defect States in Rutile

From the results of all of these experiments, an energy-level diagram of the defect states in rutile crystals is proposed (Fig. 13). The shallow traps are placed according to their thermal rather than their optical ionization energies, because greater confidence is placed in the thermal values which were obtained from more straightforward experiments than those from which the optical values were obtained. The deeper levels are placed according to their optical ionization energies, because these were observed directly, and no thermal ionization of these levels has been observed. Although no correlations between the specific-defect energy levels identified above and specific defects in the rutile lattice were obtained from this study, we can speculate about the specific levels which may be associated with Ti^{3+} interstitial ions and with oxygen vacancies.

One of the levels (labeled "Luminescence Center") is tentatively assigned to Ti^{3+} ions in octahedral coordination. If such a defect were present in rutile, e.g., an interstitial Ti^{3+} ion, its energy level would be split (~ 2.5 eV, corresponding to 0.50 μ) by the octahedral crystal field.[6] The upper ^2E_g level of Ti^{3+} in many materials is found to be split by the Jahn-Teller effect, and the lower (ground-state, $^2T_{2g}$) level might also be slightly split due to distortions from true octahedral symmetry or spin-orbit effects. The $^2T_{2g}$-^2E_g transitions are expected to be weak, because the oscillator strength is about 10^{-4}. The approximate energy values of the first two splittings mentioned are known from data obtained from the same center in other materials.[6] Fitting together these values with the optical excitation energies found in rutile places the ground-state level within the forbidden band and the two higher levels above the conduction-band edge, as shown in Fig. 13. In this scheme, three of the observed optical excitations are actually from the same initial state to different excited states. No experimental results which are inconsistent with this interpretation have been found. A splitting of the ground-state level by 0.05 eV is postulated mainly to account for the doublet structure seen in the luminescence emission spectrum; this splitting might also account for the doublet structure near 0.50 μ seen in the luminescence excitation spectrum (Fig. 6). The splitting is about the same order of magnitude expected for the spin-orbit interaction.[27]

Although electron paramagnetic resonance (EPR) spectra of Ti^{3+} ions have been reported only for highly reduced crystals,[9,10] we believe that Ti^{3+} ions are present in both oxidized and reduced crystals, the concentration being higher in the reduced material. The number of Ti^{3+} ions in oxidized crystals is possibly too small to be detected by EPR. The band structures of $SrTiO_3$ and $BaTiO_3$ are very similar to that of rutile,[27,28] and the optical spectra associated with Ti^{3+} ions in octahedral coordination is expected to be weak and around 0.50 μ in these materials too. In reduced $SrTiO_3$, a weak absorption band is observed at 0.515 μ,[32] while in $BaTiO_3$, the bands are at 0.48 and 0.64 μ.[33,34] The 0.515-μ band in $SrTiO_3$ has been attributed to Ti^{3+} ions by some[35] and to oxygen vacancies by others.[32] In $BaTiO_3$, some attribute only the 0.64-μ and not the 0.48-μ band to an oxygen vacancy,[34] while others attribute both bands to such a center.[33] The experimental data on $BaTiO_3$ does not provide sufficient information to precisely identify these levels. However, Dvorak's theoretical calculation[34] identifies only the 0.64-μ band to be due to an electron trapped at an oxygen vacancy. Thus, the 0.48-μ band in $BaTiO_3$ could still be due to Ti^{3+}.

The EPR spectra associated with interstitial Ti^{3+} ions have been observed in reduced rutile crystals at temperatures below 8°K,[7,10] but this does not mean that Ti^{3+} is not present at higher temperatures. There are many reasons why EPR signals cannot be detected at higher temperatures. In neutron- and γ-irradiated crystals, EPR signals due to interstitial Ti^{3+} ions have been observed at 78°K.[9] The reason for the difference in thermal stability of EPR signals associated with the Ti^{3+} ions formed under different conditions is not known at present. There are other experiments which indirectly indicate the presence of interstitial Ti^{3+} ions at higher temperatures.[36] Attempts to determine the optical absorption bands in the visible in reduced rutile have failed because of the large absorption associated with the charge carriers giving rise to the blue color of the sample.[37] Bogomolov et al.[38] attribute this absorption to light interaction with small-radius polarons.

One of the levels identified in this study is possibly due to electrons trapped at oxygen vacancies. In neutron-irradiated and reduced crystals, such a center has been observed by EPR measurements.[8,9] In highly reduced crystals, Cronemeyer[39] observed a structure at 1.05 μ at room temperature, which he attributed to an electron trapped at an oxygen vacancy. We have observed a structure around 1.1 μ in the photoconductivity excitation spectrum of a reduced crystal. It so happens that the optical ionization energy of trap No. 4 also appears to be about 1.18 eV (1.05 μ). At very low temperatures (10–20°K), Bogomolov et al.[38] found a peak in the optical absorption spectrum of a reduced crystal at about 1.08 μ, which they assign to a donor center. At higher temperatures, a peak at 1.51 μ appeared, and the 1.08-μ structure was no longer seen. Thus, three different studies (including the present one) report optical structures around 1.05 μ. On the basis of our present work, it is not possible to precisely identify the center or centers associated with the 1.05-μ level.

Only defect levels for which a reasonable amount of experimental evidence exists have been included in the proposed energy-level diagram. Additional levels also might be present, but sufficient evidence of their existence was not obtained in this study.

ACKNOWLEDGMENTS

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