PHYSICAL REVIEW VOLUME 113, NUMBER 5 MARCH 1, 1959

Infrared Absorption of Reduced Rutile TiO_2 Single Crystals

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(Received May 7, 1958)

Rutile TiO_2 single crystal plates have been reduced in hydrogen at about 700°C for several minutes to make them semiconducting. The concentration of oxygen vacancies was controlled by variations of time and temperature. The infrared absorption of a series of plane parallel plates having electrical resistivities ranging from 3 to 0.01 ohm-m has been examined. It is postulated that the electrical conductivity arises from the ionization of either one or two trapped electrons from each oxygen vacancy.

In samples with electrical resistivity ($\perp$ to the c axis) greater than 0.04 ohm-m, the optical absorption at room temperature peaks at about 0.75 ev. For samples with electrical resistivity less than 0.03 ohm-m, the optical absorption shows a new maximum at 1.18 ev. The decrease of thermal activation energy with increasing oxygen vacancy concentration is expected to explain the "optical transition" from 0.75 to 1.18 ev. The ionization energies agree reasonably well with those calculated for a helium atom model of a doubly ionizable donor immersed in a dielectric medium $[K_e=n_o^2=(2.40)^2]$, namely 0.73 ev and 1.64 ev. A modification of this theory is also indicated which predicts the second ionization energy as 1.41 ev in better agreement with the experimental value of 1.18 ev.

INTRODUCTION

RUTILE (titanium dioxide) has many interesting dielectric and semiconducting properties. Tetragonal single crystals of high quality have been grown by the Verneuil technique—such crystals were used in this study. Only relatively impure colored rutile crystals are to be found naturally.[1,2]

The dielectric properties of the crystals are quite unusual. The dielectric constants are very high, 80 and 160 perpendicular and parallel to the c axis. The refractive index is also unusually high ($n_o \simeq 2.4$). The electrical resistivity of the pure insulating crystals is extremely high ($\sim 10^{20}$ ohm-m) at room temperature.

The intrinsic electrical conductivity, photoconductivity, and optical absorption were explored in an earlier work by the author.[3,4] Good evidence was found for an intrinsic energy gap of 3.05 ev from all three experimental techniques. Photoconductivity corresponding to this intrinsic process persisted down to at least liquid nitrogen temperatures.

When rutile crystals are "reduced" either by heating in vacuo or in hydrogen atmosphere, it is found that a blue coloration appears in the crystals which is accompanied by high electrical conductivity. Thus, by reduction, the insulating TiO_2 becomes semiconducting. It was found[3] that this blue color arose from the visible "tail" of an infrared absorption band peaking at about 0.75 ev.

Since the rutile crystal becomes semiconducting upon reduction, and it has been proved that this reduction is accompanied by a loss of oxygen from the crystal,[5–7] it seems reasonable to expect that a weight loss should occur upon reduction. The weight loss can be directly related to the number of oxygen vacancies. By Hall-effect measurements, the number of conduction electrons can also be determined. For heavily reduced samples with weight losses of the order of 0.01 to 0.1%, it was found[4] that the number of conduction electrons obtained from Hall coefficient measurements was approximately equal to twice the number of oxygen vacancies. Thus, it seems fairly conclusively established that an oxygen vacancy serves as a doubly ionizable donor in rutile.

It is expected, according to this model of an oxygen vacancy as a doubly charged positive center capable of trapping two electrons, that the ionization energy for the first electron will be that of a helium atom immersed in a dielectric medium; namely, $24.6/K_o^2$, where K_o is the optical dielectric constant. This ionization energy, for $K_o=n_o^2=(2.40)^2$, is 0.73 ev. This is in reasonable agreement with the observed peak in optical absorption in reduced rutile at about 0.75 ev.[3,4]

Moreover, if one electron is ionized from an oxygen vacancy, it should be possible to observe a second ionization energy of $54.4/K_o^2$, equal to 1.64 ev.

It would seem from the results of the weight loss experiment, that there must be a transition from singly ionized oxygen vacancies to doubly ionized oxygen vacancies, at room temperature, as the number of such oxygen vacancies is increased to large concentrations. This consideration is in harmony with another experimental observation, namely, the decrease of thermal ionization energy with an increase of oxygen vacancy concentration.[8,9] Such a decrease in ionization energy attributed to interaction of the individual donor centers when closely spaced is a well-known feature of the standard semiconductors.[10]

From these two experimental evidences, it should be expected that it will be possible to increase the number

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[1] T. Liebisch and H. Rubens, Sitzber. preuss. Akad. Wiss. Physik.-math. Kl. **8**, 211 (1921).

[2] A. Schröder, Z. Krist. **67**, 485 (1928).

[3] D. C. Cronemeyer and M. A. Gilleo, Phys. Rev. **82**, 975 (1951).

[4] D. C. Cronemeyer, Phys. Rev. **87**, 876 (1952).

[5] N. Nazu, Science Repts. Tôhoku Univ. **1**, 25, 510 (1936).

[6] P. Ehrlich, Z. Elektrochem. **45**, 362 (1939).

[7] M. D. Earle, Phys. Rev. **61**, 56 (1942).

[8] W. Meyer and H. Neldel, Physik. Z. **38**, 1014 (1937).

[9] W. Meyer, Z. Elektrochem. **60**, 11/12 (1944).

[10] G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).

of oxygen vacancies in the crystal to such a large concentration that one electron will be ionized from each oxygen vacancy. This partial ionization condition would then permit observation of the second ionization energy in the optical absorption spectrum of the semiconducting rutile.

This particular series of experiments which is described here relates to the absorption spectrum of reduced single cyrstals. The experiments were designed to test the hypotheses presented above, and in particular, as a search for the second optical ionization of an electron from an oxygen vacancy which was expected to lie at about 1.6 ev.

EXPERIMENTAL

Two single-crystal boules of rutile were obtained from the National Lead Company. These boules were oriented by the back-reflection Laue technique, so that plates with their faces perpendicular to the *c* axis of the crystal could be cut by diamond-sawing.

The accuracy of orientation was checked to be within a degree by means of convergent light patterns obtained with a polarizing microscope. The crystals, by virtue of locked-in strain, exhibited a slight biaxiality. Plates cut from the crystals were ground flat and parallel and polished on a wax lap.

Reduction of the crystals was accomplished in hydrogen at temperatures of the order of 600–800°C and times of several minutes.[11] Reduced samples were subsequently cooled in argon to prevent reoxidation. Times and temperatures were adjusted to give room-temperature resistivities varying from 3 to 0.01 ohm-m. Since these resistivities correspond to peak absorption coefficients of 10^2 to 10^5 m^{-1}, samples ranging in thickness from 5×10^{-3} to 5×10^{-5} m were required for the studies.

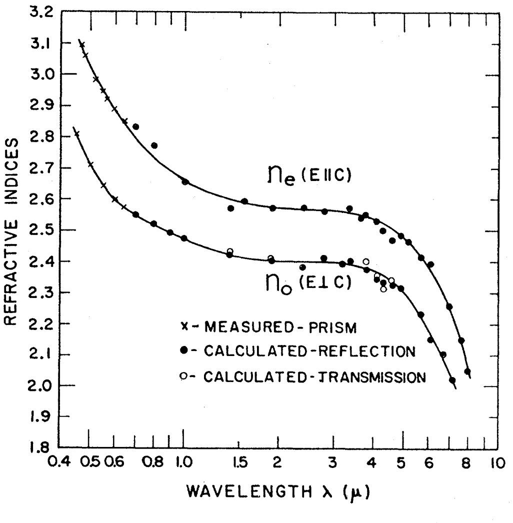

FIG. 1. Refractive indices n_o and n_e *versus* wavelength in microns for rutile TiO_2 single crystals.

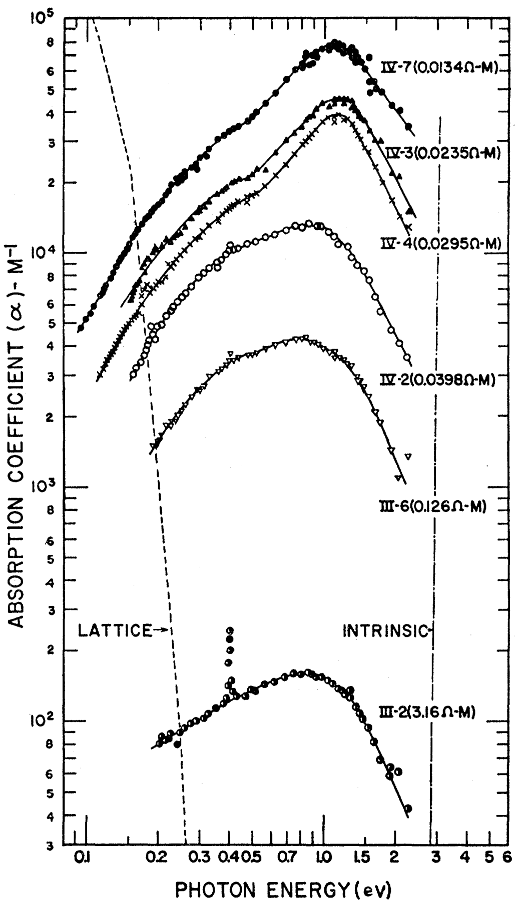

FIG. 2. Absorption coefficient α (m^{-1}) *versus* photon energy in electron volts for six samples of reduced rutile TiO_2 single-crystal material ranging in resistivity from 3.16 to 0.0134 ohm-meter. The lattice and intrinsic absorptions are indicated as dotted lines.

The reduced plates were cut into rectangular bars having edges along *a* axes of the crystal. All resistivity measurements refer to current flow perpendicular to the *c* axis of the crystals. The electrical resistivity measurements were made utilizing a potential traverse arrangement. A vibrating reed electrometer with a 10^{11}-ohm input resistor was utilized to measure potential differences.

The infrared transmission curves were obtained with a Perkin-Elmer, Model 112, single beam, double pass, recording spectrophotometer utilizing rock-salt optics. A tungsten lamp was used in place of the globar for optical measurements in the long-wavelength visible spectrum.

Optical transmission data were converted to absorption coefficient data by utilizing (1) the refractive index data, measured and compiled previously[4] (Fig. 1), and (2) a graphical representation of the function $\alpha(T,n)$ as defined by

$$T=(1-R)^2e^{-\alpha x}/(1-R^2e^{-2\alpha x}),$$

where $R=(1-n)^2/(1+n)^2$ and α is the absorption coefficient.

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[11] Reduced crystals have also been studied by R. G. Breckenridge and W. R. Hosler, Phys. Rev. **91**, 793 (1953).

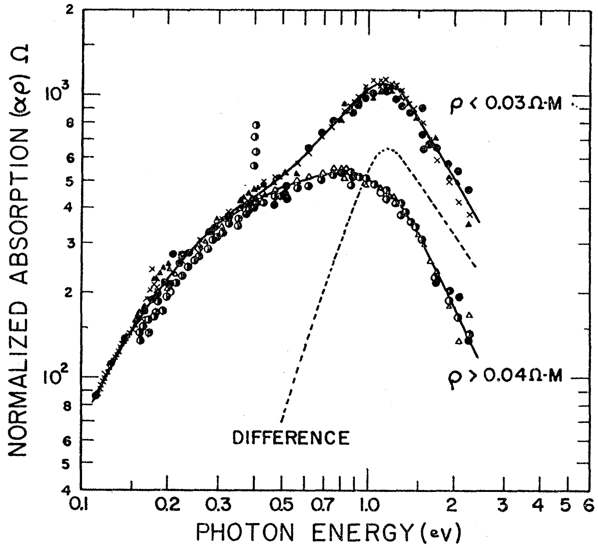

FIG. 3. The normalized absorption coefficient $\alpha\rho$ (ohms), equal to the absorption coefficient α (m^{-1}) times the sample resistivity ρ(ohm-m), *versus* the photon energy for the six reduced rutile samples of Fig. 2. The upper and lower branches corresponding to sample resistivities less than 0.03 ohm-m, and greater than 0.04 ohm-m, respectively, are clearly evident. The difference curve is shown as a dotted line.

Since the samples used in this study were all prepared so that the electric vector of the light beam was perpendicular to the c axis of the crystal ($\mathbf{E}\perp\mathbf{c}$), only the refractive index data for the ordinary ray, n_o, were required in the interpretation of transmission curves.

EXPERIMENTAL RESULTS

The set of absorption coefficient spectra for six different samples, ranging in resistivity from 3 to 0.01 ohm-m, are indicated (Fig. 2). The intrinsic optical absorption obtained from earlier work is indicated for reference purposes.[4]

Since the long-wavelength lattice absorption distorts the shape of the curves, and might confuse the interpretation, this lattice absorption has been subtracted off to obtain the set of characteristics (Fig. 2). It may be seen (Fig. 2, curves III-2, III-6, IV-2) that crystals having a room-temperature resistivity greater than 0.04 ohm-m, have an absorption coefficient spectrum consisting of a single broad maximum at about 0.75 ev. However, for crystals with a resistivity less than 0.03 ohm-m (Fig. 2, curves IV-4, IV-3, IV-7), composite curves having pronounced maxima at 1.1 ev are obtained. The transition occurs quite sharply apparently between 0.03 and 0.04 ohm-m. Since all of the absorption coefficient curves have the same shape at lower photon energies, and the absorption coefficient spectra regularly shift upwards with decreasing sample resistivity, the absorption coefficient curves were "normalized" by multiplying the absorption coefficient by the sample resistivity ($\alpha\rho$). Such a plot of $\alpha\rho$ is indicated (Fig. 3). It shows remarkably close coincidence of the experimental points for low photon energy ($h\nu<0.4$ ev), but a distinct separation into two branches for higher photon energies ($0.4<h\nu<3$ ev). The experimental points from curves III-2, III-3, IV-2, lie upon the lower branch, while points from curves IV-4, IV-3, IV-7 lie upon the upper branch. Since the two branches[12] do coincide for low photon energies, it is suggestive of two simultaneous processes occurring for the upper branch curve; therefore, the difference curve (upper-minus lower-branch), having a maximum $\alpha\rho$ product of 650 ohms at 1.18 ev is also indicated on the figure.

INTERPRETATION

Regardless of the motivation of the work as a search for the second ionization energy of an electron from an oxygen vacancy in rutile, we must consider whether the evidence will support the conclusion that the higher energy absorption peak found at 1.2 ev actually is this second ionization.

It should be pointed out in this connection that, in using the helium model for a calculation of the optical ionization energies, it is necessary to take an effective dielectric constant which is appropriate to the size of the orbit. This effective dielectric constant is usually intermediate between the static value and the optical value, as has been pointed out by Mott and Gurney.[13] If we let the symbols E_{d1} and E_{d2} designate respectively the ionization energies of the first and second electrons from an oxygen vacancy, and if we make the assumption that we should choose a dielectric constant value which

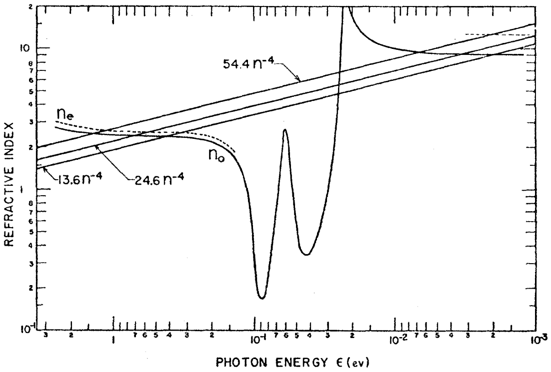

FIG. 4. The plot of refractive index *versus* photon energy (obtained by fitting reflectivity data by dispersion terms) is used to derive ionization energies of hydrogen-like and helium-like models for TiO_2 single crystals. The solutions are obtained for $E(n)=n(E)$, where $E=h\nu$, the photon energy.

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[12] It is interesting to note two features of the curves of Fig. 5: (1) The maximum $\alpha\rho$ product for the lower branch is 530 ohms, obtained for $h\nu\cong 0.75$ ev. The maximum $\alpha\rho$ product for the upper branch is about 1100 ohms obtained for $h\nu=1.15$ ev. The maximum $\alpha\rho$ products are very close to a factor of two in ratio. (2) The net energy abstracted by a single absorbing electron would be proportional to the area of the $\alpha\rho$ curve on the $h\nu$ plot. If we designate the area under the upper curve as A_u and the area under the lower curve as A_l, then, by graphical integration, $A_u/A_l=1580/783=2.02$.

[13] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1940), pp. 160, 161.

corresponds to the energy of the electron in its orbit, then we are able to obtain graphical solutions for E_{d1} and E_{d2} (Fig. 4) from the intersections of $n(\epsilon)$ with $E_{d1}(n)$ and $E_{d2}(n)$.

The $n(\epsilon)$ data are obtained by fitting the experimental reflection data[1] with two dispersion terms.[14] The functions $E_{d1}(n)$ and $E_{d2}(n)$ are for the helium atom model having ionization energies of 24.6 and 54.4 ev, respectively; thus $E_{d1}=24.6/n^4$, and $E_{d2}=54.4/n^4$. These solutions lead to theoretical values for E_{d1} and E_{d2} as detailed in Table I. The table indicates close apparent agreement between observed and calculated values of E_{d1} and fair agreement for E_{d2}.

However, we must discuss the mechanism by which an increase of oxygen vacancies at constant temperature gives first, optical ionization of the first electron, and then with larger oxygen vacancy concentration, optical ionization of both first and second levels.

The model of an oxygen vacancy which we have considered would lead to an energy diagram of the nature shown in Fig. 5. An arbitrary distribution is shown simply to illustrate the fact that the second ionization energy level E_{d2} does not exist until the first ionization energy level E_{d1} is empty. What we must ask for in detail is the Fermi level behavior as a function of oxygen vacancy concentration for this model.

If we consider the two ionization energies E_{d1} and E_{d2} to remain constant independent of the oxygen vacancy concentration, then we find as we first add a few oxygen vacancies to a pure crystal that the Fermi level shifts from mid-gap, its position for intrinsic conduction, upwards toward the conduction band. At first it lies between mid-gap and the second level, E_{d2}, so that both electrons are ionized from the oxygen vacancies, when only very few such vacancies are present. However, with any reasonable number of additions greater than, say, $10^{16}/m^3$, the Fermi level is just below the first ionization energy, E_{d1}, and only a small fraction of the electrons in E_{d1} levels are ionized; hence only a small fraction of E_{d2} levels appear and since the Fermi level lies above E_{d2}, these second levels are totally occupied. This situation persists with further addition of oxygen vacancies, except that the Fermi level moves a bit higher yet, slightly above E_{d1}, hence indicating smaller fractional ionization of E_{d1} levels, and E_{d2} levels therefore do not appear at all. Clearly then, if the ionization energies remain fixed, and there is no auxiliary process, this model cannot lead to the observed behavior of the optical absorption as a function of oxygen vacancy concentration.

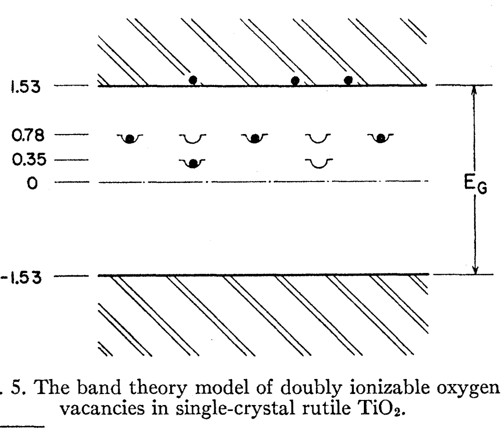

FIG. 5. The band theory model of doubly ionizable oxygen vacancies in single-crystal rutile TiO_2.

TABLE I. The theoretical and experimental values for the first and second ionization energies E_{d1} and E_{d2} for electrons ionized from an oxygen vacancy. The simplest helium model theory predicts ionization energies as given under $h\nu$(ev), ($n_o=2.40$); a more refined helium model treatment predicts the ionization energies listed in the column labeled $h\nu$ (ev) for $n(E)$. The experimentally determined values are noted in the last column denoted by $h\nu_{max}$(exp.).

	$h\nu$ (ev) ($n_o=2.40$)	$h\nu$ (ev) for $n(E)$	$h\nu_{max}$ (exp.)
E_{d1}	0.73	0.73	0.75
E_{d2}	1.64	1.41	1.18

However, we know from a number of pieces of evidence that at least insofar as thermal processes are concerned, semiconductors in general seem to show a decreasing ionization energy as a function of donor or acceptor concentration. For silicon[10] it is well known that for impurity concentrations above about $10^{22}/m^3$, the ionization energy decreases rapidly, falling to zero between 10^{24} and $10^{25}/m^3$.

If we say that the electrostatic potential V is given by $V=e/4\epsilon_0 K_e r$ and that $1/N_d^{\frac{1}{3}}=2r$, then $V=2.88\times10^{-9}N_d^{\frac{1}{3}}/K_e$; for $N_d=10^{24}/m^3$, this gives a value of V of 0.05 volt for $K_e=n_o^2=(2.40)^2=5.76$, and an appreciable effect would be noticed at about $N_d=10^{27}/m^3$ ($10^{21}/cm^3$). That the coefficient 2.88×10^{-9} from this very crude theory may be a bit lower than it should be is evident from the silicon work; that it should be nearly an order of magnitude low for TiO_2 is not obvious, but apparently this would be required to explain the effect. Actually, if $K_e=1$, then

$$E_c-E_{d1}=0.75-2.88\times10^{-9}N_d^{\frac{1}{3}}.$$

Values are given in Table II. The variation is pictured (Fig. 6).

We should also bear in mind that the degeneracy number for 25°C is $1.9\times10^{25}/m^3$.

It is indeed characteristic of the oxide semiconductors that the "thermal activation energy" is a function of the impurity concentration itself. The behavior has been termed "Meyer's rule," and may be illustrated by Meyer and Neldel's[8,9] work on TiO_2 ceramics. The variation of thermal activation energy begins at very low concentrations of impurities, however, which does not fit into the argument advanced by Pearson and Bardeen[10] and Shockley[15] to account for the silicon case.

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[14] D. C. Cronemeyer, Sc.D. thesis, Massachusetts Institute of Technology, 1951 (unpublished), pp. 115–120.

[15] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), pp. 227–229.

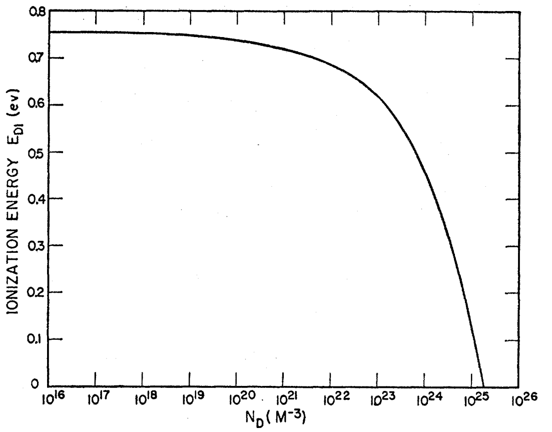

FIG. 6. The variation of ionization energy ($E_{d1}-E_c$) *vs* donor density N_D as calculated according to the interaction theory model for oxygen vacancies.

TABLE II. The variation of the first ionization energy of an electron from an oxygen vacancy as a function of the density of such vacancies, as calculated from the interaction model.

N_d (m^{-3})	(E_c-E_{d1}) volts
10^{17}	0.75
10^{18}	0.75
10^{19}	0.74
10^{20}	0.74
10^{21}	0.72
10^{22}	0.69
10^{23}	0.62
10^{24}	0.46
5×10^{24}	0.25
10^{25}	0.13
1.8×10^{25}	0.00

Experimentally, what is usually found for a wide variety of reduction or oxidation semiconductors[16] is that

$$\epsilon\sim-\ln\sigma \text{ and } \sigma=\sigma_{25^\circ\mathrm{C}}e^{-\epsilon/kT}.$$

A theory which predicts this sort of relationship is not presently known to the author. Regardless of the particular details of the interaction between the oxygen vacancies, we may use the "interaction theory" of Pearson and Bardeen[10] to indicate the effect of reduction of thermal activation energy with increased concentration of oxygen vacancies. With this addition to the Fermi level analysis discussed previously, it is now possible to see that the first donor levels will be largely depopulated at some large concentration where the number of oxygen vacancies is of the order of $10^{24}/\mathrm{m}^3$, and thus the optical absorption of electrons excited from the second donor level may be observed. Unfortunately, no great amount of evidence regarding the change in thermal activation energy with changing oxygen vacancy concentration is available for the crystals used in this study. It may be noted that the interaction behavior of oxygen vacancies would tend to lower the ionization energy E_{d2}, perhaps giving better agreement between the 1.18- and 1.41-ev experimental and theoretical values. The model described seems to be the best interpretation of the existing evidence at present.

ACKNOWLEDGMENT

I wish to thank Dr. W. C. Dunlap, Jr., for helpful advice and discussion with regard to this work.

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[16] W. Meyer, Z. Elektrochem. **50**, 274 (1944).