PHYSICAL REVIEW B VOLUME 10, NUMBER 5 1 SEPTEMBER 1974

Reinterpretation of the "Ti^{3+} interstitial" electron-spin-resonance spectrum in rutile*

L. N. Shen, O. W. Johnson, W. D. Ohlsen, and John W. DeFord
Department of Physics, University of Utah, Salt Lake City, Utah 84112

(Received 27 March 1974)

A variety of rutile samples were heat treated in atmospheres of H_2, H_2O, and O_2 according to prescriptions which theoretically and experimentally either favor or suppress H interstitial formation. The H concentration and conduction-electron concentrations in the samples were monitored optically. The "*A*" spectrum, which has been universally accepted as being due to Ti^{3+} interstitials, is found instead to be associated with H.

INTRODUCTION

Over a decade ago Chester[1] studied an ESR spectrum in hydrogen-reduced rutile which he labeled "*A*". He cautiously proposed four possible models for the center responsible for this spectrum. One of these models, that of the Ti^{3+} interstitial, was accepted by other workers and widely quoted.[2,3] The alternative models of Chester, including that of an unknown center involving hydrogen, were not so much eliminated as ignored.

Kingsbury, Ohlsen, and Johnson[4] reinvestigated the "*A*" center. Lattice potential calculations based on a point-ion model showed that the *g*-tensor axes of the "*A*" spectrum were consistent with the face- and edge-centered interstitial site, $(\frac{1}{2}, 0, 0)$. The fact that a weak "*A*" spectrum could be produced by treatment with degassed Li and Na seemed to argue against a hydrogen center and supported a Ti^{3+} interstitial model for the "*A*" center. It was assumed the Li or Na donated an electron which was trapped at the Ti^{4+} interstitials which were present as impurity compensators. Unfortunately, these experiments were performed before it was understood that extreme care must be taken to overcome the high affinity rutile has for hydrogen and before the thermodynamics of the system $TiO_2 + H_2O + O_2 + H_2$ were understood.[5]

In this paper we report the results of ESR experiments performed on samples treated according to the prescriptions of Ref. 5. The findings are that the "*A*" spectrum is found only in conjunction with interstitial hydrogen and not in samples treated in a manner favorable to the formation of Ti interstitials.

THERMODYNAMICS

The "*A*" spectrum is only observed near liquid-helium temperature. The diminution of the signal from this center as the temperature is raised appears to be due to thermal ionization of the center rather than due to a shortened spin-lattice relaxation time.[1] If the "*A*" center spectrum were due to Ti^{3+} interstitials, then at normal sample-preparation temperatures the change state of the Ti interstitials would be 4+. DeFord and Johnson[5] assume Ti^{4+} interstitials to be the dominant defect in nonstoichiometric rutile. They point out that other defects could easily be considered by the same methods.

DeFord and Johnson consider two particularly interesting sample treatment conditions. In these cases the thermodynamic equations are considerably simplified. The first case is that for which $P_{H_2} \gg P_{H_2O}, P_{O_2}$ where the *P*'s are partial pressures. In this case the ratio of the concentration of H^+ interstitials to Ti^{4+} interstitials, $N_{\langle H^+\rangle}/N_{\langle Ti^{4+}\rangle}$, is equal to

$$[(P_{H_2O})^2/(P_{H_2})^{3/2}]\, e^{3\mu_e/kT} R_1(T) . \tag{1}$$

μ_e is the Fermi energy and $R(T)$ is a function of the temperature containing such unknowns as the binding energies of the Ti^{4+} interstitial and H^+ interstitial. The rather surprising result is that the pressure dependences are such that heating in dry hydrogen favors Ti^{4+}-interstitial formation in comparison to the incorporation of H^+ interstitials.

In the second simple case of interest $P_{H_2O} \sim P_{O_2} \gg P_{H_2}$. In this case, Eq. (1) may be rewritten in an equivalent form which is somewhat easier to interpret;

$$N_{\langle H^+\rangle}/N_{\langle Ti^{4+}\rangle} = (P_{O_2})^{3/4}(P_{H_2O})^{1/2} \times e^{3\mu_e/kT} R_2(T) . \tag{2}$$

Thus high O_2 and H_2O pressures favor H^+ interstitials.

Due to the unknown factors in $R(T)$ it is impossible to theoretically predict whether conditions can be easily obtained which make either defect dominant over the other. Experimentally, however, Johnson *et al.*[6] find the limit of solely H^+ and the limit of very little H^+ can be obtained. These authors measure ir OH absorption and monitor weight changes as a function of sample treatment. Besides confirming the behavior suggested by Eqs. (1) and (2), they find that the conditions $P_{H_2O} \gg P_{O_2} \sim P_{H_2}$ can result in hydrogen interstitials and a Fermi energy near the conduction band. This latter result is important for the experiments reported in this paper.

The clear hydrogen signature of the infrared absorption was particularly useful in the work of Ref. 6. The "*A*" center spin resonance similarly has been thought to be a specific indication of Ti interstitials. The experimental part of this work was an attempt to use this ESR probe to confirm the Ti-interstitial behavior predicted by the thermodynamic theory, referred to above. However, since the experiments point instead to the "*A*" spectrum being due to H and not to Ti, it is necessary to return to the thermodynamic theory and consider other possibilities besides the Ti^{4+} interstitials whose existence is no longer certain. Other charge states of Ti result in the same pressure dependences but differ in the $R(T)$ and Fermi-energy factor. For example, where $N_{\langle H^+ \rangle}/N_{\langle Ti^{4+} \rangle}$ contains the factor $e^{3\mu_e/kT}$, the case $N_{\langle H^+ \rangle}/N_{\langle Ti^{3+} \rangle}$ would have the factor $e^{2\mu_e/kT}$. Qualitatively, however, the partial-pressure conditions favoring H^+ over Ti^{3+} would be unchanged from those of the case H^+ over Ti^{4+}.

For oxygen vacancies the ratio $N_{\langle H^+ \rangle}/N_{V_O}$ turns out in the case $P_{H_2O} \sim P_{O_2} \gg P_{H_2}$ to be proportional to $[P_{H_2O}{}^{1/2}\, P_{O_2}{}^{1/4}]\, e^{\mu_e/kT}$. For comparison to Ref. 5, the complete expression is given in the Appendix. Again different charge states of the oxygen vacancy result in changes in the exponential terms but not in the pressure dependences. As with Ti interstitials, it can be seen that this case of $P_{H_2O} \sim P_{O_2} \gg P_{H_2}$ favors H interstitials over the competing defect, although not so strongly.

EXPERIMENTAL

The experimental results are qualitative since it is very difficult to make quantitative ESR measurements of defect concentrations in samples of high dielectric constant and variable loss. Samples of nominally pure rutile as well as samples doped with W, Al, and Sn were studied. Measurements on any given sample were done in pairs. For one set of measurements, the sample was heat treated in a very dry-hydrogen atmosphere. This treatment introduced donor defects but no hydrogen. For the second set of measurements, the sample was doped to the same Fermi energy as resulted from the dry-hydrogen treatment. The dopant in this case was either H or D from H_2O or D_2O heat treatment or Li. For each run, the ESR spectrum at 4 °K, the OH or OD infrared absorption, and the 1.5-μm conduction-electron peak were monitored.

The "*A*" spectrum was seen if, and only if, there were present both H or D and conduction electrons as measured at room temperature. These conditions could be obtained in all the types of samples studied. At high enough concentrations ($\sim 10^{19}/cm^3$), the "*A*" spectrum was replaced by the "*B*" spectrum as observed by Chester.[1]

A typical treatment leading to the "*A*" spectrum would be 800 °C for 10 h in an atmosphere of <1-Torr O_2 or H_2 and 18 Torr of H_2O. As already mentioned, this set of partial pressures does not correspond to one of the simple cases discussed in the previous section, but is known both theoretically and experimentally to strongly favor H over intrinsic defects. The oxygen pressure must be this low to achieve a Fermi energy high enough to populate shallow donors at low temperatures. During treatment the atmosphere is maintained in equilibrium with water at room temperature by means of convection currents. A special multiply connected sample tube with an external heater is used to establish these convection currents.

The same sample tube is used in the treatment to exclude H. In this case the convection currents continuously circulate the gas through a liquid-nitrogen-cooled charcoal trap to remove H_2O and O_2. The exact pressures and temperatures used for the various samples are not significant, since the conditions required to achieve the appropriate state depend strongly on accidental impurities as well as the dominant dopant and hence vary considerably from sample to sample. The important point is that the two types of treatment used were known to strongly favor either H^+ or lattice defects, to the virtual exclusion of one or the other, and that variation of the pressures and heat-treating temperature could be used to achieve the same room-temperature Fermi level with either H^+ or lattice defects.

CONCLUSIONS

It is concluded that the "*A*" spectrum arises not from Ti^{3+} interstitials, but from interstitial H in rutile. The electron is weakly bound as already known from the thermal ionization observations. The electron must be very little associated with the H since no sign of resolved hyperfine structure is seen.

The free-hydrogen hyperfine splitting (hfs) is 508 G and the "*A*" lines are about 1 G wide. Far too little information is available to make a reasonable model for the center; yet, smallness of the hyperfine interaction deserves at least a rough consistency check. We assumed the paramagnetic-electron wave function is a symmetric linear combination of 3*d* orbitals on the six nearest Ti^{4+} ions. The Ti^{3+} 3*d* wave function of Clementi[7] was used. A contact hfs of 0.16 G was calculated. The role of oxygen-ion polarization is by no means obvious. The large Ti-O and O-H overlaps would suggest a large contribution to the hfs, but the symmetric location of the Ti ions around the oxygen may significantly reduce this contribution.

The weak "*A*" spectrum seen by Kingsbury *et al.*[4] in Li- and Na-treated samples must have resulted from hydrogen contamination. The source of the hydrogen was most likely water adsorbed onto the sample tube walls.

Many articles on defects in nonstoichiometric rutile which assume the "*A*" spectrum arises from Ti^{3+} interstitials must be reexamined. For example, Bogomolov and Sochava[8] conclude a defect they studied in partially reduced rutile must be an oxygen vacancy since the defect has a different ESR signature than the "known" Ti^{3+} interstitials.

The site multiplicity and *g*-tensor orientation for the "*A*" center are consistent with the $(\frac{1}{2}, 0, 0)$ interstitial site as mentioned in the Introduction. There are other experiments consistent with H in this position. The site is consistent with the pure-OH-stretch infrared data.[9] In addition to the pure-OH-stretch line, there are satellite lines arising from association with impurities. Since the satellite shifts are small, it may be concluded that the H occupies basically the same lattice position in the associated and unassociated conditions. The case of $Fe^{3+} \cdot H$ has been studied through the perturbation of the Fe^{3+} ESR spectrum, with the conclusion that the hydrogen occupies sites of the type $(\frac{1}{2}, 0, 0)$ relative to an iron at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.[10]

More direct measurements of the role of H in the structure of the "*A*" center are being attempted through electron nuclear double resonance and optical experiments.

The center (or centers) which results from treatment in dry hydrogen has not yet been identified.

ACKNOWLEDGMENT

Helium gas was provided by a departmental grant from the Office of Naval Research.

APPENDIX

The complete expression for $N_{\langle H^+ \rangle}/N_{V_O}$ for the case $P_{H_2O} \sim P_{O_2} \gg P_{H_2}$ is

$$N_{\langle H^+ \rangle}/N_{V_0} = (\gamma/\alpha) P_{H_2O}{}^{1/2} P_{O_2}{}^{1/4} e^{\mu_e/kT} \times \exp[(E_{\langle H^+ \rangle} + \tfrac{1}{2} E_{TiO_2} - \tfrac{1}{2} \gamma_{TiO_2} - \tfrac{1}{2} \gamma_{H_2O} - \tfrac{1}{4} \gamma_{O_2})/kT],$$

where γ is the volume per V_O site; α the volume per $\langle H^+ \rangle$ site; $E_{\langle H^+ \rangle} = -E_R - E_P$, E_R is the ionization energy of the hydrogen atom; E_P the energy required to insert a bare proton into the rutile lattice; $-E_{TiO_2}$ the energy of the ground state of the TiO_2 molecule in the crystal relative to the isolated Ti and O atoms;

$$\gamma_{TiO_2} = -\int_0^T dT' \int_0^{T'} [C_V(T'')/T''] \, dT'';$$

where $C_V(T)$ is the specific heat per molecule of TiO_2;

$$\gamma_{H_2O} = kT \ln\left[6.649 \times 10^4 (1 + 3.921 \times 10^{-9}) \times T^{5/2} \exp\left(\frac{1.101 \times 10^5}{T}\right) T^4\right];$$

and

$$\gamma_{O_2} = kT \ln\left[2.795 \times 10^6 (1 + 3.843 \times 10^{-4} T) \times \exp\left(\frac{5.898 \times 10^4}{T}\right) T^{7/2}\right].$$

In the above definitions all temperatures are in °K and all other quantities are in cgs units.

---

*Work supported by Advanced Research Projects Agency Grant No. DAHC-15-73-G2 Amendment No. 1.

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

[2] H. J. Gerritsen, in *Paramagnetic Resonance*, edited by W. Low (Academic, New York, 1963), Vol. I, p. 3.

[3] W. Low and E. L. Offenbacher, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1965), Vol. 17, p. 135.

[4] P. I. Kingsbury, Jr., W. D. Ohlsen, and O. W. Johnson, Phys. Rev. 175, 1091 (1968).

[5] J. W. DeFord and O. W. Johnson, J. Appl. Phys. 44, 3001 (1973).

[6] O. W. Johnson, J. DeFord, and J. W. Shaner, J. Appl. Phys. 44, 3008 (1973).

[7] E. Clementi, IBM J. Res. Dev. 9, 2 (1965).

[8] V. N. Bogomolov and L. S. Sochava, Sov. Phys.—Solid State 9, 2647 (1968) [Fiz. Tverd. Tela 9, 3355 (1967)].

[9] O. W. Johnson, W. D. Ohlsen, and P. I. Kingsbury, Jr., Phys. Rev. 175, 1102 (1968).

[10] W. D. Ohlsen and O. W. Johnson, Bull. Am. Phys. Soc. 18, 467 (1973); and P. Anderson, E. L. Kollberg, and A. Jelenski, Phys. Rev. B 8, 4956 (1973).