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Thermochromism and Electrical Conductivity in Doped $SrTiO_3$

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Large reversible thermochromic changes in pure and transition-metal-doped $SrTiO_3$ were observed which depend markedly on impurity concentration, anealing temperature, and especially on the rapidity of the quench. The material also changes its electrical properties from insulator to semimetallic, and for moderately and heavily doped samples, from semiconductor to metalliclike behavior. The optical and electrical properties are stable. Two intrinsic optical-absorption bands and two bands previously found in photochromic studies which depend on the transition-metal impurity are observed. A partial energy-level scheme for $SrTiO_3$ is proposed.

I. INTRODUCTION

Photochromism (PC), the reversible change in color of a material under irradiation, has been observed in many organic and inorganic substances. Faughnan, Staebler, and Kiss have recently written a review of inorganic photochromic materials[1] in which they summarize current knowledge about these materials. Single-crystal $SrTiO_3$ doped with transition metals (TM) has had its PC behavior studied by optical-absorption and EPR techniques[2–5] and by applying dc electric fields.[6] Pure $SrTiO_3$, with a room-temperature band gap of 3.2 eV, is ordinarily transparent in the visible region when it contains stoichiometric amounts of oxygen. When doped with Fe or other TM impurities, a small amount of visible absorption occurs with a smearing out of the band edge. Faughnan *et al.*[1] found that when an Fe-doped sample was irradiated with light in the approximate range 2.9–3.2 eV, two broad visible absorption bands, centered at about 2.9 and 2.1 eV, appeared and decayed in less than a second at room temperature, but were thermally stable at 78 °K.

These and other studies have established that the transition-metal impurities enter the lattice on a Ti^{4+} site. For example, Fe^{3+} was observed by EPR in both cubic and axial sites. The axial sites are believed to be Ti^{4+} sites with a nearest-neighbor O^{2-} missing. The most logical explanation is that the oxygen vacancies are necessary to charge compensate the Fe^{3+}. The fact that equal numbers of axial and cubic sites were found in a moderate concentration, $SrTiO_3$: Fe, backs up this view. The correlation of the optical-absorption decay of these PC bands with the recovery of the EPR Fe^{3+} cubic-site signal indicates that these bands result from a charge transfer of an electron from an Fe^{3+} ion in a cubic site to some shallow trapping center. A suggested trap is the (Fe^{3+}-V_0) axial center, which carries a positive charge with respect to the lattice, and which disappears equally with the Fe^{3+} cubic sites in lightly doped samples. However, positive identification of the shallow trap responsible for the PC response has not been made. Another puzzling observation on the electrical behavior of doped $SrTiO_3$ was made by Blanc and Staebler in their electrocoloration studies.[6] The conductivities were found to be *not* proportional to the impurity content in clear $SrTiO_3$.

We have observed some interesting chromic behavior of pure and doped $SrTiO_3$ which is activated thermally and depends markedly on the impurity concentration, the annealing temperature, and especially the rapidity of the quench. This might be called thermochromism (TC) since it can be completely reversed by reheating and then cooling the sample slowly to room temperature. However, in contrast to photochromic response, the coloration and electrical response are stable at room temperature and above, perhaps to (300–400) °C. It had been assumed previously that to return pure or lightly doped $SrTiO_3$ from its colored conducting reduced state to its almost clear insulating oxidized state it was necessary to heat it in an oxygen atmosphere. Our observations are that this is not necessary. We have found that the annealing atmosphere may be reducing, oxidizing, or inert and that, when the crystal is cooled slowly to room temperature from any temperature above 850 °C (the "freezing-in" temperature for the diffusing of oxygen in $SrTiO_3$)[7] the pure and lightly doped crystals return to their almost clear insulating state. Heavily doped $SrTiO_3$ in its oxidized state is a brown insulating crystal with a narrowed bandgap of about 2.7–2.9 eV with a broad absorption band centered at 2.1–2.2 eV. These effects apparently come from the presence of Fe^{4+} in the lattice. When heavily doped crystals are slowly cooled to room temperature in a reducing or inert atmosphere, they are lightly colored and insulating similar to the lightly doped crystals. Yamada and Miller[8] have also observed that oxygen vacancies can be frozen in by rapidly quenching samples reduced in partial pressures of oxygen.

II. EXPERIMENTAL

A. Materials

Single crystals of pure and doped $SrTiO_3$ grown by National Lead Co. were used in this study. The percent impurity referred to are given in weight percent of oxide added to the crystal melt during growth. Mass-spectrographic analysis of similar samples[6] has shown the actual concentrations to be perhaps a factor of 5 lower than that quoted by the supplier, but the relative impurities retain significance.

Three of our samples, "pure" $SrTiO_3$, $SrTiO_3$: Nb (curves shown in Fig. 1), and $SrTiO_3$: 0.1-wt% Fe (curves in Fig. 3) were analyzed[9] and confirmed this ratio. The sample boules vary slightly throughout their bulk in impurity concentration and care was taken to use portions of the crystal where the photochromic color indicated more nearly uniform doping.

B. Heat Treatment

The crystals were first heated in oxygen at 900 °C to insure their stoichiometric insulating condition. The optical samples were cut and polished using 0.05-μ Al_2O_3 powder for the final finish. They were then subjected to the indicated sequence of 20-min reducing anneals in atmospheric pressure of H_2. The optimum annealing time was determined experimentally, as the colored region can be seen to penetrate into the bulk from the surface. One crystal, annealed for 20 min, was reduced by polishing to one half its thickness with the expected reduction in optical absorption, indicating that the absorption was a bulk effect extending uniformly through the crystal. The hydrogen gas was purified by passing it through a liquid-nitrogen trap and over a hot copper sponge to remove any trace oxygen. The crystals were annealed in a quartz tube which was removed from the oven and the crystals quickly cooled in the H_2-gas stream (≈ 70 sec to reach 300 °C). Between anneals, the optical absorption was measured in a Cary Model No. 14R spectrometer. In every case, the optical-absorption and electrical properties were stable and a function of both the maximum annealing temperature and the cooling rate. All samples returned to their original nonoxidized insulating condition when allowed to cool slowly in the oven to room temperature in the H_2 atmosphere. For a super-fast cool, the sample was placed on a Mo foil in the quartz tube which increased the conduction of heat from the crystal. The reducing atmosphere (H_2 or vacuum) is necessary to produce the thermochromic condition efficiently, but in several reducing or inert atmospheres the sample will return to its almost clear insulating condition when slow cooled in the oven to room temperature. In addition to H_2, we have used vacuum, air, oxygen, He, Ar, and N_2, with similar results. The only significant departure is the brown color acquired by heavily doped crystals in a slow oxygen anneal.

C. Optical

The optical absorption was measured in a Cary Model No. 14R spectrometer. All samples had essentially zero absorption in the visible region before the reducing anneals. Matching blanks of pure $SrTiO_3$ were placed in the reference path of the spectrometer to check the intrinsic absorption bands and to ensure that reflection losses were negligible. The thicknesses of the optical samples are given in the captions of Figs. 1–6.

D. Electrical

The thin (0.25 mm) optical samples were not suitable for measuring the resistivity, so rectangular samples (2.5×2.5×10 mm) were cut from the respective boules. Most common high-temperature metal contacts on reduced $SrTiO_3$ have been found to form rectifying junctions,[10] so a four-probe method was used to measure the resistivity of the bulk sample. Gold electrodes were evaporated on the ends for current leads and gold strips were evaporated on the side of the sample to form voltage probes. Stainless-steel contacts were used on the four electrodes.

The electrical measurements were thus made on larger volume samples, with correspondingly slower cooling rates, than the thinner optical-absorption samples. Consequently, since the quench times have influence, direct comparisons between the optical absorption at an indicated annealing temperature with the corresponding electrical response at the same annealing temperature are only approximately correct. Our purpose in measuring the conductivity is to demonstrate the good correlation between the optical-absorption spectra and the conducting state of the sample (i.e., insulating, semiconducting, or metalliclike).

E. Optical Results: Pure $SrTiO_3$ and $SrTiO_3$: Nb

The increased optical absorption in pure $SrTiO_3$ and $SrTiO_3$: Nb after 20-min anneals at the indicated temperatures in a pure-H_2 atmosphere is seen in Fig. 1. These samples, as well as the others in this study, were cooled as rapidly as possible in the H_2 atmosphere. The absorption spectra are virtually identical except that the 2.4-eV peak is always present in the Nb-doped crystal. This peak has previously been identified[11] as probably due to an interband transition of conduction electrons. It was speculated that it could be a transition from the normally empty Ti-3*d* band to a higher conduction band of mixed

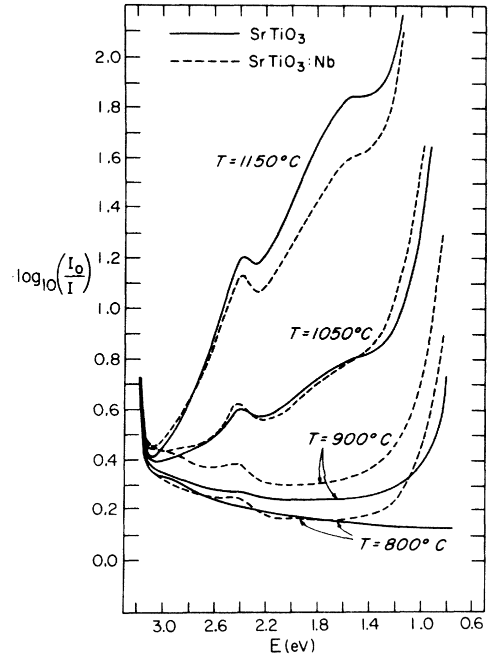

FIG. 1. Optical absorption vs wavelength for pure $SrTiO_3$ and $SrTiO_3$: Nb (5×10^{18}/cc) after 20-min anneals in H_2, at temperature indicated, with rapid quench. Sample thickness (pure, 0.0279 cm: Nb-doped 0.1235 cm).

Ti-4p and O-3p character. Yamada and Miller[8] have recently come to the same conclusion based on their results on $SrTiO_3$ reduced in a partial pressure of oxygen. However, recent band calculations by Mattheiss[12] [using augmented-plane-wave (APW) methods] indicates that the Ti-3d conduction band is split. He adjusts the t_{2g} band to the known absorption edge at 3.2 eV above the O-2p valence band and this is then below the ϵ_g band by about 1.3 eV. Likewise, the t_{2g} band itself is over 1 eV wide, and thus the fairly sharp 2.4-eV peak could hardly come from such a wide band. Wolfram, Kraut, and Morin[13] also predict a wide t_{2g} band with a logarithmic singularity of states present in the center of the band.

This 2.4-eV peak and the broad band at 1.6 eV are found in all activated samples (pure, Nb, Fe, and Ni doped) in this study in those cases where highly activated impurity centers have not overpowered these two fairly weak absorption peaks. The 2.4-eV peak has an oscillator strength, $f \approx 10^{-2}$, whereas the strong impurity peaks have oscillator strengths ranging from 0.1 to 1.

Baer[14] and others[8,15] have shown that the infrared Drude tail, which saturates around 0.8 eV in our highly reduced samples, comes from free-carrier absorption and depends directly on the concentration of free carriers.

These samples show a metalliclike behavior with the conductivity directly proportional to the infrared absorption. The annealing-quenching process obviously raises the Fermi level and changes the number of available charge carriers and/or trapping sites in the sample. However, since the entire process is carried out in the hydrogen atmosphere and the sample can be returned to the insulating nonabsorbing conditions by slow cooling in the same atmosphere, it would appear that the number of oxygen atoms is fixed although their location may change.

F. $SrTiO_3$: Fe

Our moderately doped $SrTiO_3$: Fe samples, (Fig. 2), show similar chromic behavior to the PC samples previously reported, but our peaks are sharper and exhibit long term stability whereas the PC peaks[2] decay in less than a second at room temperature. The Fe complexes which produce the 2.92- and 2.1-eV peaks are also thermally activated and can be destroyed by slow cooling as easily as the common centers at 2.4 and 1.6 eV. The 2.92-eV peak has been identified by Faughnan using EPR techniques as an absorption by an Fe^{4+} ion in a cubic site.

The heavily doped $SrTiO_3$: Fe absorption is seen in Figs. 3 and 4. These samples can be thermally transformed from the insulating state (1100°C anneal) to a semiconducting state [(1125–1150) °C anneal] and finally (above ≈ 1200 °C) to a metalliclike condition. The correlation of the optical absorption with the electrical resistivity is discussed

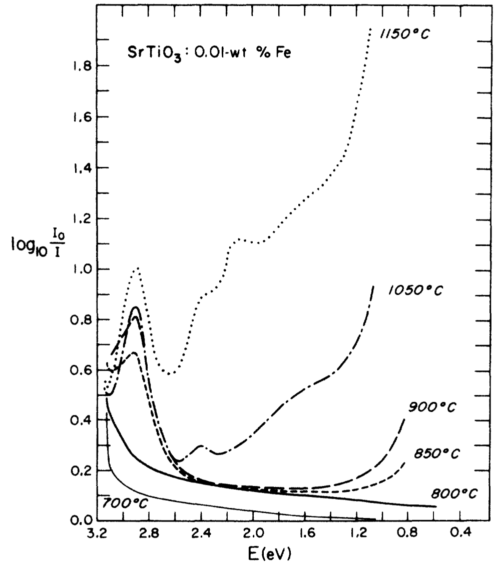

FIG. 2. Optical absorption vs wavelength for $SrTiO_3$: 0.01-wt% Fe after 20-min anneals in H_2, at temperature indicated, with rapid quench. Sample thickness (0.0456 cm).

below.

G. $SrTiO_3$: Ni

The TC absorption spectra of the Ni-doped crystals is seen in Figs. 5 and 6. The common peaks at 2.4 and 1.6 eV are even more sharply defined than in the iron-doped samples. The Ni associated absorption at circa 2.8 and 2.1 eV agrees generally with the PC absorption (circa 2.6 and 2.2 eV) reported in their earlier studies.[2] However, Fig. 6 shows a shift to higher energies as the activation level increases in the Ni doped sample. Our more heavily doped sample (Fig. 6) had the same concentration as the earlier PC sample and the positions of the impurity peaks in the two samples are essentially the same.

H. Electrical Response.

The relative resistivity versus temperature of the 0.1- and 0.4-wt%-Fe-doped samples is seen in Figs. 7 and 8. For the lower annealing activation temperatures the samples exhibit semiconducting behavior with activation energies determined from the slopes of the curves in the range 0.06–0.55 eV. Some of the curves show multiple slopes in the semiconducting phase with the changes occurring at about 435 and 513 °K in the 0.1% sample and at 416 and 488 °K in the 0.4% sample. These breaks in slope indicate activation of new trapping levels. They move to lower energy and eventually disappear as the annealing temperature

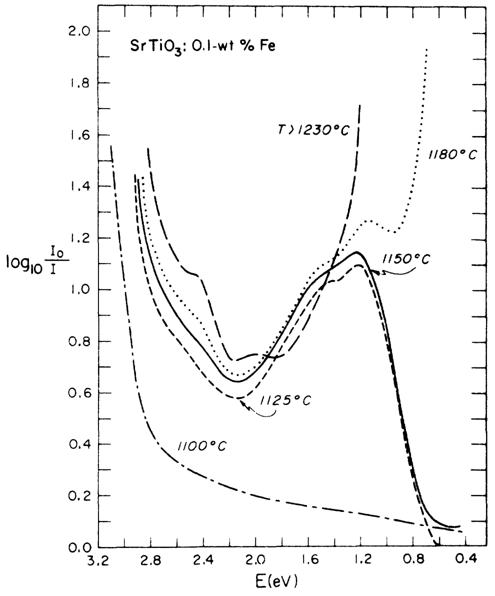

FIG. 3. Optical absorption vs wavelength for $SrTiO_3$: 0.1-wt% Fe after 20-min anneals in H_2, at temperatures indicated, with rapid quench. Sample thickness (0.0267 cm).

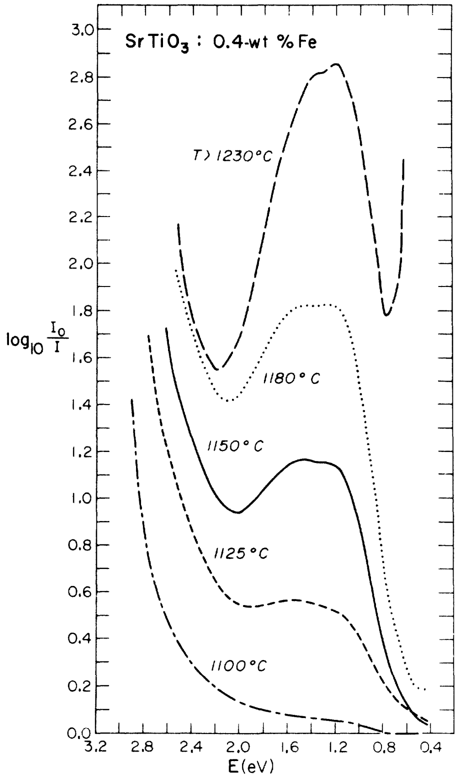

FIG. 4. Optical absorption vs wavelength for $SrTiO_3$: 0.4-wt% Fe after 20 min anneals in H_2, at temperatures indicated, with rapid quench. Sample thickness (0.0228 cm).

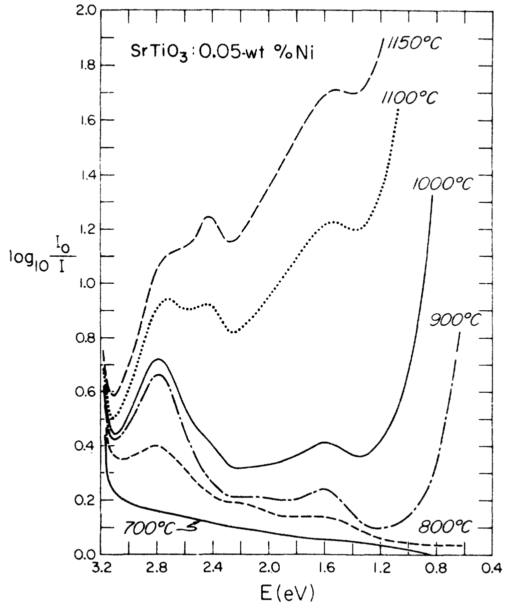

FIG. 5. Optical absorption vs wavelength for $SrTiO_3$: 0.05-wt% Ni after 20 min anneals in H_2, at temperatures indicated, with rapid quench. Sample thickness (0.0330 cm).

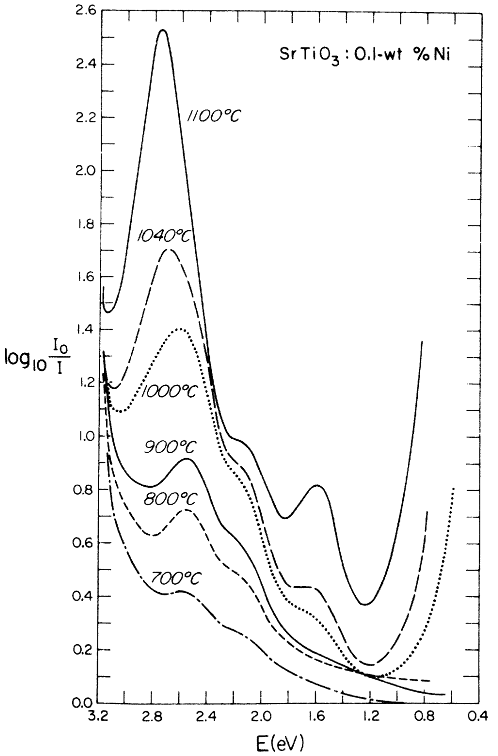

FIG. 6. Optical absorption vs wavelength for $SrTiO_3$: 0.1-wt% Ni after 20 min anneals in H_2, at temperatures indicated, with rapid quench. Sample thickness (0.0254 cm).

is raised, indicating a shift in the Fermi level. As the annealing temperature is raised to about 1100 °C the samples become metalliclike in their temperature response, corresponding to the expected behavior from the optical absorption, because the broad trap around 1.2–1.6 eV is filled and the free-electron infrared-absorption tail rises again. The number of traps obviously depends on the anneal-quench procedure also.

The electrical response of the undoped sample for two reduction states is shown in Fig. 7. The response for the higher annealing temperature resembles the metalliclike behavior of the Fe-doped samples as would be expected from the infrared optical-absorption curves. However for the slightly reduced sample the resistivity increases sharply at 420 °K indicating a rapid drop of mobility at that temperature. The higher temperatures reached in the conductivity measurements may actually be altering the characteristics of this sample.

III. Discussion

Detailed knowledge about the experimental band structure of $SrTiO_3$ is not available. However, our optical-absorption data show two kinds of peaks in the visible which may be distinguished by their dependence on the amount of doping. The location and size (after activation) of the 2.4- and 1.6-eV peaks are independent of the doping, and do not increase appreciably above the background as the activation of free carriers is increased. Hence they must be related to some transitions in the reduced lattice structure of the host crystal or to some common impurity. We might call these host-crystal peaks. The remaining peaks are obviously linked to the amount of controlled doping and the thermal activation of these impurity centers and could be designated impurity-doped peaks.

A. Host-Crystal Peaks

The 2.4-eV peak might be a band-to-band transition between normally empty Ti-3*d* and Ti-O mixed-*p*-type conduction bands as suggested earlier,[8,11] but more recent band calculations[12,13] than Kahn and Leyendecker's[16] make this unlikely. A second explanation of the 2.4-eV peak is to assume that oxygen vacancies in the reduced crystals form either a narrow impurity-type band or introduce several closely spaced overlapping levels

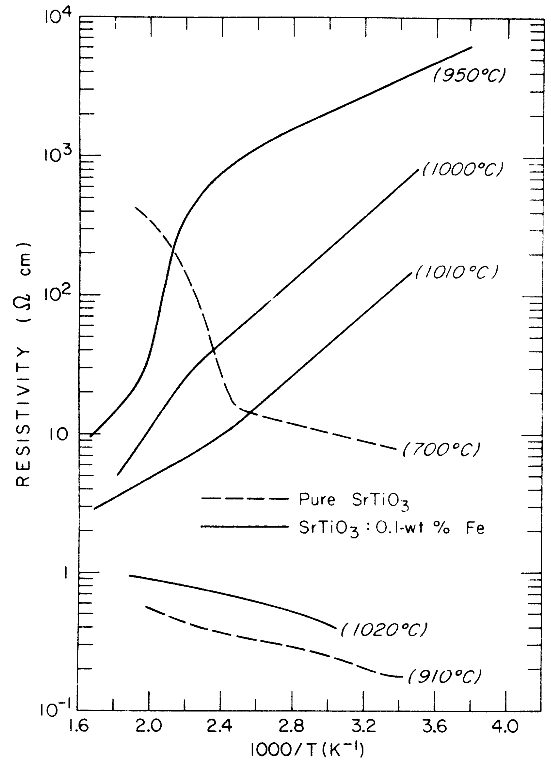

FIG. 7. Resistivity vs 1000/*T* for $SrTiO_3$ (dashed curves) and $SrTiO_3$: 0.1-wt% Fe (solid curves). The samples were annealed 20 min, in atmospheric H_2, at temperatures indicated with rapid quench.

in the band gap about 0.8 eV above the valence band. Then when these levels are thermally activated the 2.4-eV peak would be a transition from this impurity band to the empty Ti-3*d* conduction band. This proposed band is labeled *B* in Fig. 9. In the pure sample after limited activation these levels would be few. In the Nb-doped sample, whose activated absorption spectra closely resembles that of the pure material, the Nb^{5+} ion enters the lattice at a Ti^{4+} site and has donor impurity levels located just below the Ti-3*d* conduction band (level *D*, Fig. 9).[15] Thus in the Nb-doped samples these impurity bands as they are created, would be filled automatically and the size of the 2.4-eV peak would depend directly on the amount of the Nb impurity as observed.[11] The Nb^{5+} could also serve as an electron-hole trap and accomplish the same result. These electrons (or holes) could conduct and exhibit free-carrier absorption. Additional support for proposing this oxygen-vacancy band at about 0.8 eV above the valence band is that Morin *et al.*[17] have measured thermally stimulated conductivity in pure and Fe-doped $SrTiO_3$ and found a trap which dumps its charge at that energy. The broad band at 1.6 eV, which also appears to be tied to the host crystal, may be the level associated with two electrons trapped at an oxygen vacancy, or to a hole shared by the six oxygen atoms in the octahedral site. The latter is more likely in the Nb case since the oxygen vacancies are not required for charge compensation. A third possibility for the 2.4-eV absorption peak is a crystal-field transition, either allowed or unallowed, from an impurity indigent to all these samples. Cr^{3+} has such a transition[18] in a cubic octahedral field at ≈ 2.2 eV and Cr impurity has been measured in these samples (circa 1 ppm). However, the oscillator strength of this peak is too high ($\approx 10^{-2}$) for this explanation to be readily accepted as the source of this absorption.

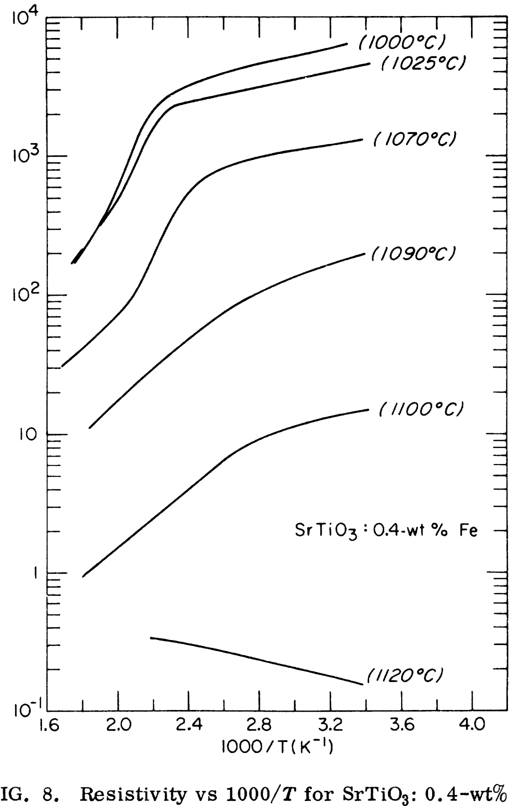

FIG. 8. Resistivity vs 1000/*T* for $SrTiO_3$: 0.4-wt% Fe. The sample was annealed 20 min, in atmospheric H_2, at temperature indicated with rapid quench.

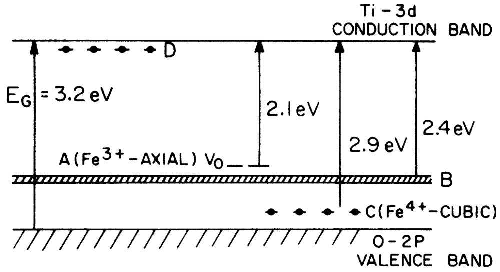

FIG. 9. Partial schematic energy level for $SrTiO_3$:Fe.

B. Impurity-Doped Peaks

The two absorption peaks at 2.9 eV and 2.1 eV in the Fe-doped samples are clearly connected with the iron impurity. At least three possibilities may be considered as the origin of these peaks. The first scheme to be suggested for the photochromic absorption reported earlier and the thermochromic response reported here, occurring at the same wavelengths, must incorporate the following experimental facts: (1)The PC absorption decays rapidly at room temperature while the TC absorption is stable. (2) The TC response involves the local distribution of oxygen vacancies since it can be frozen in by a rapid quench and yet anneals away if allowed to cool slowly in an oxygen-free atmosphere. (3) The EPR-PC studies have established that the absorption center is Fe^{4+} in a cubic site, and that the effect of the band-gap light is to remove an electron from Fe^{3+} in a cubic site which subsequently gets trapped. A model which incorporates these facts would place the energy of Fe^{4+} (cubic) just above the valence band (labeled *C*, Fig. 9) with the Fe^{3+} (axial labeled *A*) at a higher level. The Fe^{4+} cubic site could be either a donor or acceptor, but for discussion, we will regard it as a donor. The Fe^{3+} (axial) with an associated oxygen vacancy carries a net positive charge and will be regarded as an acceptor. These ion sites could exchange identity if the oxygen vacancies are mobile but are fixed in relative position if the vacancies cannot move.

We assume that the oxygen vacancies, which are highly mobile above 850 °C, are dispersed throughout the sample at high temperatures. If rapidly cooled, they are frozen in place leading to fairly large separations between those iron atoms located at cubic sites and those at axial sites. The thermal energy at (900–1200) °C (0.1–0.14 eV) is sufficient to ionize Fe^{3+} in a $SrTiO_3$ crystal and create Fe^{4+}. The TC optical absorption then involves a transition from the Fe^{4+} cubic site to the conduction band (2.9 eV) or to an excited state of the ion, and some of the electrons may be trapped in the oxygen vacancy at an Fe^{3+} (axial) separated from the Fe cubic site. This transition would produce Fe^{5+} (cubic), which is a valence state that has been observed in $SrTiO_3$.[3] The 2.1-eV peak associated with the Fe impurity could then be a transition from A to the Ti-3*d* band. We postulate that a slow quench would allow the vacancies to redistribute themselves, perhaps along dislocation lines, to produce clumping of Fe^{3+} (cubic and axial) sites relatively close to each other. Photochromic absorption then would come from the same transitions with an axial site located near the cubic site so that the electrons could hop back and reestablish the nonchromic Fe^{3+} state. If this mechanism is correct then the rapidly quenched crystals should show more permanent photochromism. We have observed additional coloration in our crystals, upon radiation, which did have a very long decay time. This location of the Fe sites near the valence band agrees with the model proposed by Lee *et al.*[15] and would account for the narrowing of the band gap as the impurity levels broaden into an overlapping impurity band due to increased activation and concentration (see Figs. 3 and 4).

While we cannot prove this to be the correct mechanism, it is a reasonable one which fits most of the observations. The thermal activation of the Fe^{4+} (cubic) centers and the dependence of the resulting electrical conductivity on the subsequent thermal treatment explains the observation[6] made earlier that the conductivity could not be correlated with the impurity concentration in $SrTiO_3$.

A second possibility is that these peaks could be crystal-field transitions of various ionized states of Fe. A double peak at ≈ 1.2 eV for the Fe $(H_2O)^{2+}$ ion is identified[18] as the transition ${}^5T_{2g} \rightarrow {}^5E_g$, split approximately 0.2 eV, due to a Jahn-Teller effect. This identification would agree quite well in wavelength position and splitting with the observed broad absorption band seen in Figs. 3 and 4. However, the measured iron impurity in our 0.1-wt% sample was 650 ppm which corresponds to a concentration of $10^{19}/\text{cm}^3$. If we assume that all the iron is in this valence state to calculate the oscillator strength we get $f = 0.4$ as the minimum value. The other peak at 2.9 eV has oscillator strengths of 0.1 and 0.8 in the 0.01% and 0.1% samples, respectively. These values are so large that it is difficult to believe they could be crystal-field transitions.

A third possible explanation for the high oscillator strength is that it could be due to a charge-transfer mechanism associated with the molecular-orbital interaction of the transition metal with the oxygen ligands. In addition to the enhanced crystal-field transitions there are excited states associated with the molecular complex of the metal and the surrounding oxygen atoms. Transitions of the type $t_{1u}(\sigma) \rightarrow t_{2g}^*$ have been identified by Kahn, *et al.*[19] in $EuFeO_3$ where the $t(\sigma)_{1u}$ level is predominately ligand in nature and the t_{2g}^* is predominately Fe^{3+} in nature. Also transitions like $t_{2g}^* \rightarrow t_{1u}^*$ are observed where an electron from the Fe^{3+} (3*d*) level goes to an orbital predominately Fe^{3+} (4*p*) in nature. The oscillator strengths for these transitions range from 0.05 to 0.5 for the energy range ~ 2.3 to → ~ 5.0 eV. We could expect similar behavior in $SrTiO_3$ from either the Ti ions or the TM impurities, or both, since the symmetry is essentially the same, i.e., TM in an octahedrally coordination oxygen environment.

There should be practical uses for using $SrTiO_3$ as a semiconductor material which can be doped with a fixed TM impurity and then have its electrical conductivity adjusted by the thermal treatment to any level falling between the available concentration limits. We have found the material to be completely recyclable and to return again to the same electrical conductivity after repeating the annealing temperature and quenching treatment.

The behavior of Fe- and Ni-doped $SrTiO_3$ are quite similar in their TC response, but differ slightly in their optical-absorption spectra, particularly in the electron-trap structure. We are studying the photoconductivity, magnetoresistance and Hall coefficient in $SrTiO_3$ doped with Fe and Ni impurities and hope to gain additional knowledge about the energy configuration of this interesting and complicated system.

IV. CONCLUSION

It is not possible from these measurements and the previous work on $SrTiO_3$ to choose unambiguously between the possible energy-level configurations discussed above. However, the strong oscillator strength of these absorption peaks is a cogent argument against crystal-field transitions as an explanation. Although we have a preference for the partial energy-level scheme proposed in Fig. 9, the case for it and the charge-transfer mechanism are about equally strong. Perhaps magnetoresistance and photoconductivity measurements will enable one to decide between these mechanisms and help establish the proposed existence of the oxygen-vacancy impurity band.

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