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Photochromism in Ni-doped $SrTiO_3$

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Electron-paramagnetic-resonance conversion-rate measurements combined with optical-absorption data in Ni-doped $SrTiO_3$ have been carried out. From these experiments in oxidized and reduced crystals, assignment of the photochromic bands in the visible could be made and the trapping mechanism identified. The (B) band at 525 nm is due to donor transfer of cubic Ni^{3+} to become Ni^{4+}. The free electrons created are trapped at Ni^{3+}-V_O centers which convert to Ni^{3+}-$V_O + e$. Acceptor charge transfer at near-band-gap energy $\lambda < 500$ nm generates Ni^{3+}-$V_O + 2e$ centers from the latter. The holes liberated are trapped at cubic Ni^{2+} sites which convert back to Ni^{3+}. The D_2 band at 575 nm is a Ni^{3+}-$V_O + 2e$ donor band which changes this center back to the Ni^{3+}-$V_O + e$ state. The optical transfer rates measured for the creation and quenching of the Ni^{3+}-$V_O + 2e$ center verify the above-described mechanism.

I. INTRODUCTION

When $SrTiO_3$ is lightly doped with transition-metal ions it may show photochromic coloration changes. Faughnan and Kiss[1,2] have discussed the photochromic behavior of $SrTiO_3$ doped with various ions: Fe, Ni, Co, Cr, and V. EPR measurements showed these impurities to have different valencies in the optical darkened and transparent states. Furthermore, it was concluded that charge-transfer processes were responsible for the change of state of the crystal as well as for the optical density in the darkened state.

The specific charge-transfer process responsible for the coloration in the Fe-doped $SrTiO_3$ was shown by Blazey *et al.*[3] to be that between the oxygen valence band and Fe^{4+}. This was achieved by correlating the photochromic absorption bands with the wavelength dependence of the creation and quenching of Fe^{3+} and Fe^{5+} detected by EPR. Schirmer *et al.*[4] have shown that the axial centers Fe^{4+}-V_O, where V_O is an oxygen vacancy, undergo the same type of acceptor charge transfer.

Here we report EPR and optical measurements on $SrTiO_3$ doped with nickel. The results differ from those in the iron-doped system and it appears that in this case some of the charge-transfer processes involved in the photochromic switching are between the nickel centers and the conduction band.

The nickel centers usually seen with EPR in $SrTiO_3$ have been described by Müller *et al.*[5] as Ni^{2+} or Ni^{3+} substitutional on a cubic Ti^{4+} site and the axial centers Ni^{3+}-V_O. A further center induced by optical irradiation was identified as Ni^{3+}-$V_O + 2e$, where the oxygen-vacancy–Ni^{3+} complex has captured two electrons. The intermediate center Ni^{3+}-$V_O + e$ with one additional electron is unobservable with EPR but its existence has been predicted by Müller *et al.*[5]

Optical-absorption spectra of Ni-doped oxides, where the nickel is octahedrally coordinated as in $SrTiO_3$, have been reported for MgO,[6] and Al_2O_3.[7,8] The transitions observed are interpreted as *d-d* internal transitions of the substitutional Ni^{2+} and Ni^{3+} ions. The photoinduced absorption bands of $SrTiO_3$:Ni occur at different energies. Faughnan and Kiss[2] correlated the principal photochromic bands with cubic Ni^{3+} and Ni^{3+}-$V_O + 2e$ centers. Their high oscillator strength, ~0.1, suggests charge-transfer processes are responsible for these absorptions rather than internal *d-d* transitions.

II. EXPERIMENT

The crystals investigated were all obtained from the N. L. Industries Inc. with the following nominal dopant concentrations: crystal J,[5] 0.15-wt% NiO; crystal M, 0.20-wt% NiO; and crystal C, co-doped with 0.04-wt% Al and 0.01-wt% NiO. A crystal R, cut from boule M, was annealed for 6 h in a reducing atmosphere at 1000°C.

All EPR spectra were taken at K band at 77 K. The creation and quenching curves of certain nickel centers were obtained by shining light from a 450-W xenon arc filtered by interference filters with a 9-Å bandwidth through a quartz light pipe onto the crystal in the EPR cavity. Most of the measurements were made on crystal J, since its response to optical irradiation was approximately exponential as expected from simple decay-rate equations. The photosensitive concentration N of all Ni centers studied depended on the illumination time t as

$$N(t) = N(\infty) + \text{const}\, e^{-kt} .$$

The rate constants k for different wavelengths were normalized for 2×10^{15} quanta/sec incident on the light pipe. When the photoinduced quenching or creation of a center takes place by a direct charge-transfer transition, the rate constant should be proportional to the transition probability. It is thus related to the optical-absorption coefficient of the transition divided by the energy.

Optical-absorption spectra were measured with a Beckman Acta M VII spectrophotometer while the crystal was mounted in a CTI Spectrim cryocooler at 77 or 24 K. Spectra were taken before and after irradiation with light from a 250-W Hg arc filtered through the same interference filters used to obtain the EPR quenching and creation rates. The photoinduced changes are reversible and the original condition of the crystals was attained by irradiating with infrared $\lambda > 715$ nm or warming the sample up to room temperature.

Crystals *J* and *M* showed EPR spectra of Ni^{2+}, Ni^{3+}, Ni^{3+}-V_O, and Fe^{3+} when cooled in the dark; most of the nickel being in the cubic Ni^{2+} state. In contrast to these as-grown samples, the reduced crystal *R* contained cubic Ni^{2+} but no cubic Ni^{3+}. The axial Ni^{3+}-V_O spectrum was very weak and Ni^{3+}-$V_O + 2e$ already present before irradiation. The co-doped crystal *C* when cooled in the dark showed the Ni^{3+}-V_O spectrum but neither cubic Ni^{3+} nor Ni^{2+}. Iron is always present in these crystals to a lesser extent by at least a factor of 10, but in the co-doped crystal its concentration was comparable to the nickel concentration and observable as Fe^{3+} and Fe^{5+}.[9]

The optical absorption spectra of these crystals are shown in Fig. 1. Before irradiation, crystal *R* shows a smeared-out absorption edge which obeys Urbach's rule down to about 470 nm. It is transparent for longer wavelengths. Both crystals *J* and *M* show a strong band near 525 nm observed by Faughnan[1] to be associated with the presence of cubic Ni^{3+} and labeled *B* by him. Not shown in the figure is the spectrum of crystal *C*, co-doped with Ni and Al, which contained a substantial amount of iron impurities. The optical spectrum of this crystal cooled in the dark was determined primarily by this iron concentration causing a broad charge-transfer band[3] below the band gap.

Illumination of the *J* and *M* crystals with light of wavelength ~ 500 nm bleaches band *B* but leaves a sloping background so that absorption in this region is not reduced to zero. Under the same treatment, the EPR spectra show that both the cubic Ni^{3+} and the axial Ni^{3+}-V_O centers are quenched. In fact, an equal number of both these centers disappears for irradiation in the wavelength range $460 \lesssim \lambda \lesssim 780$ nm. The quenching-rate constants for the cubic Ni^{3+} and axial Ni^{3+}-V_O centers were measured and are compared in Fig. 2. Also shown in Fig. 2 is the absorption coefficient divided by the energy of the bleachable part

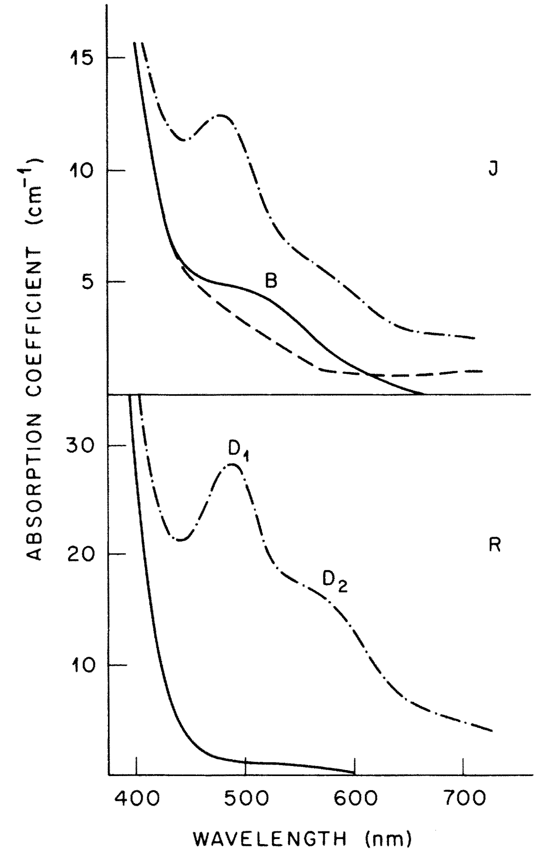

FIG. 1. Optical absorption spectra of $SrTiO_3$:Ni crystals at 77 K, *J* and *R* (*M* reduced). Solid lines: cooled in the dark. Dashed lines: irradiated with 500-nm radiation. Dash-dot lines: irradiated with 400-nm radiation.

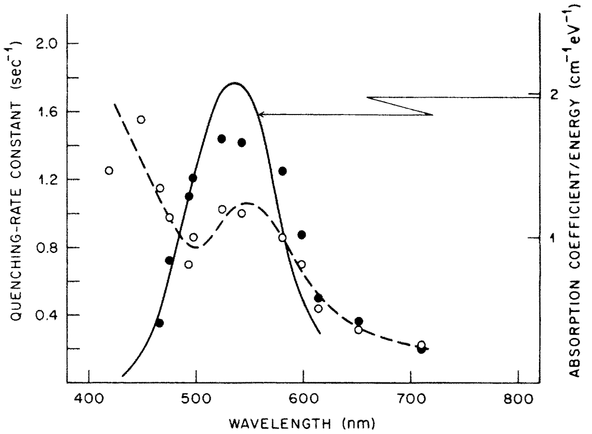

FIG. 2. Comparison of Ni^{3+} quenching-rate constant (solid circle), and Ni^{3+}-V_O quenching-rate constant (open circle) with 525-nm optical-absorption band *B* in crystal *J*.

of band B. It is seen to agree with the quenching of cubic Ni^{3+} but not with the quenching of the axial Ni^{3+}-V_O centers which are still quenched with shorter wavelength irradiation.

Irradiation with wavelengths shorter than the B band has a decreasing quenching effect on the cubic Ni^{3+} which is even enhanced between 450 and 370 nm, while the Ni^{3+}-V_O centers are still quenched. In this region where the Ni^{3+} is enhanced instead of quenched, the axial Ni^{3+}-V_O+2e centers appear. The threshold for their creation is near 480 nm and their final concentration is at least four times larger than the quenched Ni^{3+}-V_O. This implies that another charge state of the same Ni-V_O center exists which is unobservable by EPR and already present in the crystal prior to irradiation, namely, Ni^{3+}-V_O+e.[5]

The light-generated Ni^{3+}-V_O+2e centers are thermally stable at 77 K and the absorption spectrum associated with these centers shown in Fig. 1 exhibits two peaks at 480 nm (D_1) and 575 nm (D_2).[1] These centers can be optically quenched by irradiation with light of longer wavelength than that required for their formation according to

$$N(t)=N(\infty,\lambda)+[N(0)-N(\infty,\lambda)]e^{-k(\lambda)t}.$$

The wavelength dependence of the creation and quenching-rate constants as well as the final concentration $N(\infty,\lambda)$ are shown in Fig. 3. In the wavelength region where both creation and quenching could be measured, the final concentration was the same for both processes. Quenching of the Ni^{3+}-V_O+2e centers occurs by irradiation into band D_2 but not D_1.

As already stated, irradiating crystal J with light of ~ 400 nm increased the Ni^{3+} concentration, whereas the Ni^{3+}-V_O centers were still quenched. These uv-generated Ni^{3+} centers may also be quenched by irradiation. The wavelength dependence of the quenching-rate constant of these uv-generated Ni^{3+} centers is much broader with a maximum at longer wavelength than for the Ni^{3+} centers present when the crystal is cooled in the dark.

The EPR creation and quenching-rate experiments described so far were performed on crystal J. The reduced crystal R when cooled in the dark showed cubic Ni^{2+} but no cubic Ni^{3+} in its EPR spectrum. This is consistent with the optical spectrum where band B which is associated with Ni^{3+} is absent (see Fig. 1).

Irradiation with 370–450-nm wavelength light produces a large Ni^{3+}-V_O+2e EPR signal in crystal R. This again is accompanied with the creation of cubic Ni^{3+} at the expense of Ni^{2+}. The quenching-rate constant of these uv-created Ni^{3+} centers is shown in Fig. 4 as a function of the wavelength.

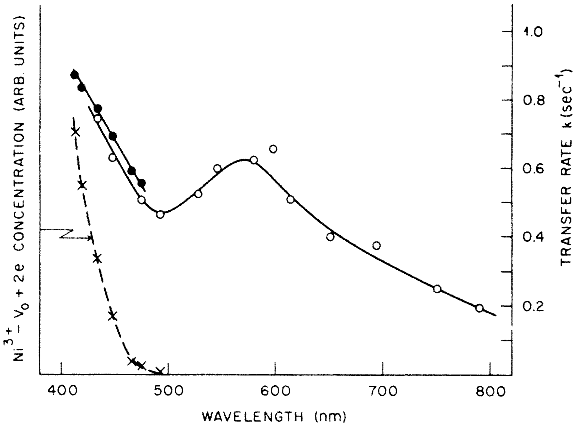

FIG. 3. Creation (solid circle) and quenching (open circle) rate constants of Ni^{3+}-V_O+2e centers induced by uv irradiation of $SrTiO_3$:Ni crystal J. The wavelength dependence of the concentration of uv-induced centers is also shown (crosses).

Here the trend just described for crystal J is stronger. The Ni^{3+} quenching band no longer agrees with the B band but is very similar to the quenching curve of the Ni^{3+}-V_O+2e centers also shown in Fig. 4 for comparison.

Besides the charge-transfer bands described so far, some weak and narrow lines, characteristic for internal d-d transitions, were observed. In crystals J, M, and R, lines at 723.5 nm, 731.2 nm, 1.123 μm, and 1.147 μm were found to be insensitive to optical irradiation. By comparison with the spectra of MgO:Ni^{2+},[6] and in accordance with the EPR results, these two doublets

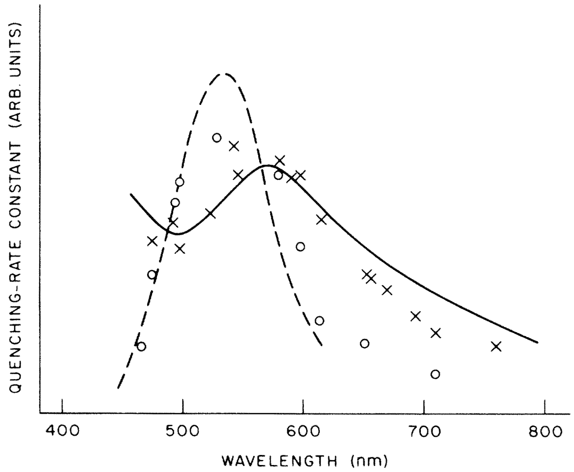

FIG. 4. Comparison of quenching of normal (open circle) and uv-induced (crosses) cubic Ni^{3+} centers. The quenching rate of Ni^{3+}-V_O+2e centers, solid line and the optical-absorption band B, dashed lines, are also shown.

are ascribed to the ${}^3A_2 \rightarrow {}^3T_1(F)$ and ${}^3A_2 \rightarrow {}^3T_2(F)$ transitions of cubic Ni^{2+}, respectively.

Another weak doublet around 464 nm, and a much stronger group of lines around 2.4 μm were observed in crystals J, M, and R when cooled in the dark. These lines could be enhanced by a factor of 4 by irradiation with visible or ir light in crystal M. Subsequent irradiation with uv or visible light did not change their intensity by more than 20%. Quenching of the factor of 4 could only be achieved by warming the crystal up to room temperature but the 20% change was quenchable with ir. This behavior is different from what has been observed with EPR, and thus implies the centers causing the 464-nm and 2.4-μm lines to be different from all Ni centers observed with EPR.

Cubic Ni^{4+} is not expected to show strong crystal-field or charge-transfer transitions at 2.4 μm. However, as Dischler and Räuber[10] have shown, the presence of an oxygen vacancy may drastically change the level scheme of transition metal ions, and selectively enhance the intensity of certain transitions.

III. DISCUSSION

One of the major problems in investigations of this kind is to distinguish the direct charge-transfer processes where a center is quenched or created by the addition or subtraction of an electron by optical excitation from the indirect processes which occur due to centers trapping the remnants of the direct process. Each of the conversion processes observed will now be discussed in more detail.

A. Ni^{3+} donor transfer

The close correspondence between the EPR quenching-rate constants of Ni^{3+} and the optical absorption band B which is necessarily a direct process, suggests that this band is caused by a charge-transfer process involving Ni^{3+}. This is in agreement with the findings of Faughnan.[1] There are two direct processes whereby Ni^{3+} can be quenched. An electron may be excited from the valence band onto the Ni^{3+} center converting it to Ni^{2+} and the hole being subsequently trapped at another center. The other possibility is that the Ni^{3+} is photoionized to Ni^{4+} and an electron freed into the conduction band where it may diffuse through the crystal until trapped at another defect.

Experimentally, no hole centers were formed during the B-band quenching. Furthermore, an obvious electron trap was quenched by the same amount with the same wavelength dependence as Ni^{3+}, namely, Ni^{3+}-V_O. Therefore, we conclude that the optical band B shown in Figs. 1 and 2 represents a donor charge-transfer process between the Ni^{3+} and the conduction band; the liberated electron being subsequently trapped at Ni^{3+}-V_O centers. This is shown schematically on the left side of Fig. 5. The Ni^{4+} and Ni^{3+}-V_O+e centers formed are both, unfortunately, unobservable with EPR.

Since the conduction band consists mainly of Ti^{3+} d-wave functions, the donor charge transfer responsible for the B band may be thought of as an intervalence transfer between metal ions. This type of charge transfer could easily explain the high oscillator strength of the transition, ~0.1.[11]

B. Ni^{3+}-V_O +e acceptor charge transfer

Figure 2 shows that at shorter wavelengths beyond the B band the Ni^{3+}-V_O centers are quenched by another process. In this same wavelength region Ni^{3+}-V_O+2e centers are formed. Since the number of Ni^{3+}-V_O+2e centers created was much greater than the number of Ni^{3+}-V_O centers quenched, the experimental creation-rate curve of Ni^{3+}-V_O+2e shown in Fig. 3 represents the conversion of the intermediate state Ni^{3+}-V_O+e into Ni^{3+}-V_O+2e rather than the two-step process of Ni^{3+}-V_O into Ni^{3+}-V_O+2e. In view of the appearance of axial Ni^{3+} centers with additional electrons, quenching of the Ni^{3+}-V_O centers in the short-wavelength region is thought to be due to an acceptor charge transfer of an electron from the valence band to the Ni^{3+}-V_O centers. The Ni^{3+}-V_O+e centers thus formed will be subsequently photoreduced further to form Ni^{3+}-V_O+2e centers.

We now consider the creation process of the Ni^{3+}-V_O+2e centers. In crystal J the creation of these centers is accompanied by the enhancement of cubic Ni^{3+} at the expense of Ni^{2+}. The formation of the same center in the codoped crystal

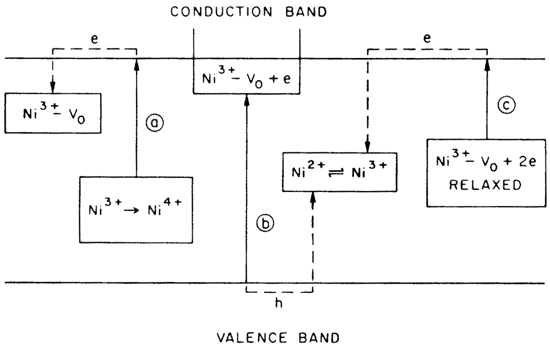

FIG. 5. Schematic representation of (a) Ni^{3+} donor charge transfer, (b) Ni^{3+}-V_O+e acceptor, and (c) Ni^{3+}-V_O $+2e$ donor-transfer primary processes. Dashed lines: secondary electron or hole-trapping processes.

C is accompanied by the creation of the hole center I1 at 4.2 K.[3] Since the same Ni^{3+}-V_O+2e center may be induced in two different crystals accompanied by the appearance of two different centers, it is concluded that the creation of the Ni^{3+}-V_O+2e itself is due to a direct process. Furthermore, since this direct process puts additional electrons onto the axial nickel centers, it is an acceptor charge-transfer process from the valence band to the Ni^{3+}-V_O+e centers. The accompanying enhancement of Ni^{3+} in crystal J and the formation of I1 in crystal C are then due to hole trapping (see Fig. 5).

It will be shown in Sec. III E that the transition probability of the acceptor charge-transfer process producing Ni^{3+}-V_O+2e has the same wavelength dependence as the impurity-induced Urbach tail of the absorption edge of crystal R in Fig. 1. Thus the same charge-transfer absorption process is thought to contribute to this Urbach behavior. Since no maximum is observed in the creation curve, a most probable value of the charge-transfer energy is not determined, but a lower limit of at least 3.0 eV may be used.

C. Ni^{3+}-V_O+2e donor charge transfer

As Fig. 3 shows, the Ni^{3+}-V_O+2e centers are best quenched by 575-nm radiation. Since this quenching occurs in all the crystals studied, it is believed to be due to a direct charge-transfer process. The most probable direct process is where an electron is liberated and the centers return to Ni^{3+}-V_O+e. Conversion all the way back to Ni^{3+}-V_O is excluded as the Ni^{3+}-V_O EPR signal does not increase while the Ni^{3+}-V_O+2e is quenched. Thus the quenching band shown in Fig. 3 is assigned to a donor charge transfer of electrons from the Ni^{3+}-V_O+2e centers to the conduction band. This is shown on the right-hand side of Fig. 5.

D. Secondary electron trapping

Part of the Ni^{3+} quenching shown in Fig. 4 is also clearly related to the Ni^{3+}-V_O+2e quenching. When crystal J is cooled in the dark it contains approximately equal numbers of Ni^{3+} and Ni^{3+}-V_O. In this case the quenching of Ni^{3+} fits the B band and is caused by a donor charge transfer [Fig. 5(a)] with subsequent electron trapping by the Ni^{3+}-V_O. Irradiation with uv enhances the Ni^{3+} by hole trapping at Ni^{2+} while Ni^{3+}-V_O is quenched and Ni^{3+}-V_O+2e created. Thus the balance between electron donors and traps is disturbed. However, visible light still quenches the Ni^{3+}. Since no new electron traps have been created by the uv irradiation, the Ni^{3+} itself most probably acts as an electron trap during the bleaching process. In crystal J, where the B and D optical bands are of comparable strength, the Ni^{3+} can trap electrons released by both other Ni^{3+} centers as well as the Ni^{3+}-V_O+2e centers. This process explains why after uv irradiation the Ni^{3+} quenching curve is rather like a superposition of the B band and the Ni^{3+}-V_O+2e quenching band. In crystal R, where uv irradiation produces many more Ni^{3+}-V_O+2e centers than Ni^{3+}, quenching of the Ni^{3+} is no longer similar to the B band at all, but corresponds nicely to the quenching band of Ni^{3+}-V_O+2e as shown in Fig. 4. These results demonstrate that Ni^{3+} may trap electrons moving in the conduction band but with a smaller capture cross-section than Ni^{3+}-V_O, which agrees with the fact that the latter is two times more positively charged with respect to the lattice than Ni^{3+}. The observation that Ni^{3+} is an electron trap rather than a hole trap is further evidence that the Ni^{3+} and Ni^{3+}-V_O quenching does not occur through an acceptor charge transfer to the Ni^{3+}-V_O centers with subsequent hole capture by the Ni^{3+}.

E. Transfer rates between Ni^{3+}-V_O+2e and Ni^{3+}-V_O+e

We have shown that Ni^{3+}-V_O+e is converted to Ni^{3+}-V_O+2e by an acceptor charge transfer. This second electron is ionized by a donor charge transfer most efficiently with 575-nm irradiation, returning the center to the Ni^{3+}-V_O+e state. The change in the Ni^{3+}-V_O concentration is small and may be neglected in this connection. We may thus concentrate on the two former centers which will be converted by light into each other with rate constants K_{12} and K_{21}. The system of two coupled rate equations yields, for the concentration,

$$N_2=[Ni^{3+}\text{-}V_O+2e]\,,$$

$$N_2(t)=N_2(\infty)+[N_2(0)-N_2(\infty)]\exp[-(K_{12}+K_{21})t]\,,$$

$$N_2(\infty)=[K_{12}/(K_{12}+K_{21})]N\,,$$

where N, the total concentration of Ni-V_O in all charge states, remains constant. The result of Fig. 3 agrees with these formulas. Especially for irradiation around 470 nm, where experimentally N_2 can be both quenched or enhanced, the equilibrium concentration $N_2(\infty)$ shown in Fig. 3 is found to be independent of the illumination history of the crystal. In the same wavelength region, creation and quenching constants were found to be equal. In fact, in both cases the sum of the rate constants of the acceptor and donor charge transfers $K_{12}+K_{21}$ was measured.

For $\lambda > 500$ nm, $N_2(\infty)$ was found to be zero. This implies $K_{12}=0$ and the transfer rate shown in Fig. 3 is K_{21}, i.e., that of the donor charge transfer. For $\lambda < 500$ nm, both K_{12} and K_{21} are $\neq 0$. The wavelength dependence of the acceptor charge-transfer rate K_{12} may be obtained by multiplying the experimental transfer rate, $K_{12}+K_{21}$, with the equilibrium concentration $N_2(\infty)$. This leads to the wavelength dependence of K_{12} which follows the impurity-induced Urbach-type absorption.

In order to excite an electron from the valence band via the Ni^{3+}-V_O+e center to the conduction band, two quanta of at least 410 and 580 nm are required, i.e , a total energy of 5.2 eV which is 2 eV more than the band gap. This excess energy is similar to the difference of 1.8 eV found between optically and thermally determined acceptor charge-transfer energies of Fe^{5+}, Fe^{4+}, and Fe^{4+}-V_O in $\mathrm{SrTiO_3}$.[3,4,12] It may be caused by Franck-Condon shifts due to lattice distortions accompanying the charge-transfer processes and by acceptor charge transfer starting from oxygen states lying below the top of the valence band.

IV. SUMMARY

By correlating EPR quenching and creation experiments and optical-absorption spectroscopy, the microscopic origin of the photochromic absorptions in $\mathrm{SrTiO_3}$:Ni has been elucidated.

The band (B) at 520 nm, characteristic for Ni^{3+}, is caused by a donor charge transfer which converts this ion to Ni^{4+}, the electrons liberated being subsequently trapped at Ni^{3+} or, more efficiently, at Ni^{3+}-V_O centers. Acceptor-type charge transfer converting Ni^{3+}-V_O+e into Ni^{3+}-V_O+2e contributes to the smeared-out absorption edge found in reduced samples of $\mathrm{SrTiO_3}$:Ni. The holes liberated are trapped at Ni^{3+} centers which become Ni^{2+}. A donor charge transfer converts Ni^{3+}-V_O+2e back into Ni^{3+}-V_O+e and is responsible for the 575-nm band (D_2) associated with Ni^{3+}-V_O+2e. The strong band D_1 at 480 nm although due to the presence of Ni^{3+}-V_O+2e was not found to be correlated with a quenching of that center. This band is thus most probably caused by an excitation of Ni^{3+}-V_O+2e into an unstable configuration or charge state which relaxes back into the initial state before the carriers liberated can move away.

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[1] B. W. Faughnan, Phys. Rev. B 4, 3623 (1971).

[2] B. W. Faughnan and Z. J. Kiss, Phys. Rev. Lett. 21, 1331 (1968).

[3] K. W. Blazey, O. F. Schirmer, W. Berlinger, and K. A. Müller, Solid State Commun. 16, 589 (1975).

[4] O. F. Schirmer, W. Berlinger, and K. A. Müller, Solid State Commun. 16, 1289 (1975).

[5] K. A. Müller, W. Berlinger, and R. S. Rubins, Phys. Rev. 186, 361 (1969).

[6] J. E. Ralph and M. G. Townsend, J. Phys. C 3, 8 (1970).

[7] D. S. McClure, J. Chem. Phys. 36, 2757 (1962).

[8] R. Müller and Hs. H. Günthard, J. Chem. Phys. 44, 365 (1966).

[9] K. A. Müller, Th. von Waldkirch, W. Berlinger, and B. W. Faughnan, Solid State Commun. 9, 1097 (1971).

[10] B. Dischler and A. Räuber, Solid State Commun. 17, 953 (1975).

[11] N. S. Hush, Prog. Inorg. Chem. 8, 391 (1967).

[12] F. J. Morin and J. R. Oliver, Phys. Rev. B 8, 5847 (1973).