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Phys. Rev. **136**, A1633 (1964)]. This cannot cause the observed large increase in the relaxation rate between the two Ce^{3+} doublets because the EQQ operator $O_2{}^m(i)O_2{}^{-m}(j)$ gives only an energy-conserving cross-relaxation process. Also, the rapid disappearance of χ' for $H=0$ and high ω and low T shows that magnetic dipole interactions are unimportant for relaxation within the Ce^{3+} ground doublet compared with the observed Orbach spin-lattice relaxation process.

PHOTOINDUCED REVERSIBLE CHARGE-TRANSFER PROCESSES IN TRANSITION-METAL–DOPED SINGLE-CRYSTAL SrTiO₃ AND TiO₂†

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When $SrTiO_3$ or TiO_2 doped with certain transition elements is irradiated with light in the region 0.39 to 0.43 μ, broad visible absorption bands with peak absorption as high as 100 cm^{-1} are introduced. The study of optical and EPR spectra of Fe/Mo doped crystals under the influence of light and various heat treatments shows that the effect is due to a transfer of charge between Fe and Mo ions such that the nonabsorbing Fe^{3+} and Mo^{6+} ions become Fe^{4+} and Mo^{5+} with absorption bands in the visible.

We have observed large reversible changes in the optical absorption of certain transition-metal–doped $SrTiO_3$ and TiO_2 single crystals after irradiation with visible light in the region 0.39-0.43 μ. The effect can be explained as a photoinduced transfer of charge between the transition metal ion and another defect center present in the crystal. When Mo co-doping is used, the transfer of charge takes place between two known impurities and the size of the effect can be made quite large by increasing the concentration of both dopants.

Such photoinduced charge-transfer processes have been reported before in other inorganic crystals. For example, defect centers in alkali halides and certain glasses have been found to be photochromic.[1,2] Reversible color changes in TiO_2, $SrTiO_3$, and other oxide powders have also been reported.[3] However, these early experiments depended on surface effects, according to some authors.[3] Only qualitative results from visual observation were reported, although the models proposed to explain these effects have some similarity to ours. Charge-transfer processes in phosphors have been studied recently, especially by EPR techniques.[4] In most cases the change in absorption coefficient is not large and the quantum efficiency of coloration is often quite small. We have observed peak absorption-coefficient changes in the visible greater than

100 cm^{-1} for samples of 0.5-mm thickness or less and quantum efficiencies of approximately 10%. The combined study of the optical and EPR spectra of these materials under the influence of bleaching and coloring light and after various heat treatments permits an identification of the valence states of the various ions responsible for the optical absorption.

Figure 1 shows the optical absorption spectra for Fe/Mo-doped $SrTiO_3$ and TiO_2 at 77°K. Pure $SrTiO_3$ and TiO_2 are transparent in the visible. When either crystal is doped with Fe, a small amount of visible absorption is introduced. This appears as a smearing out of the band edge absorption to longer wavelengths, as shown in Fig. 1. When the sample is irradiated with light in the vicinity of 0.40 μ, several broad absorption bands are introduced, covering the entire visible region. The individual absorption bands are not well distinguished in a plot such as Fig. 1 because at least one of the absorption peaks usually occurs close to the smeared-out band-edge absorption region. They become more distinct when the difference between the induced and normal optical absorption is plotted. The interpretation and uniqueness of these bands is further demonstrated by the heat-treatment experiments discussed later.

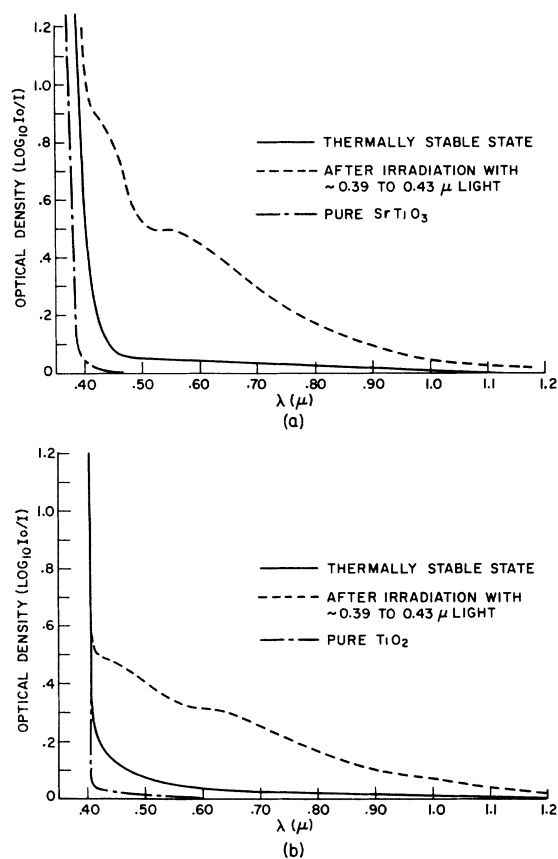The thermal bleaching rate of the photoinduced state varies widely, depending on both dopant

FIG. 1. Optical density of (a) $SrTiO_3$ and (b) TiO_2 doped with Fe and Mo before and after irradiation with blue light in the region 0.39-0.43 μ. $T = 77°K$; sample thickness = 0.25 mm.
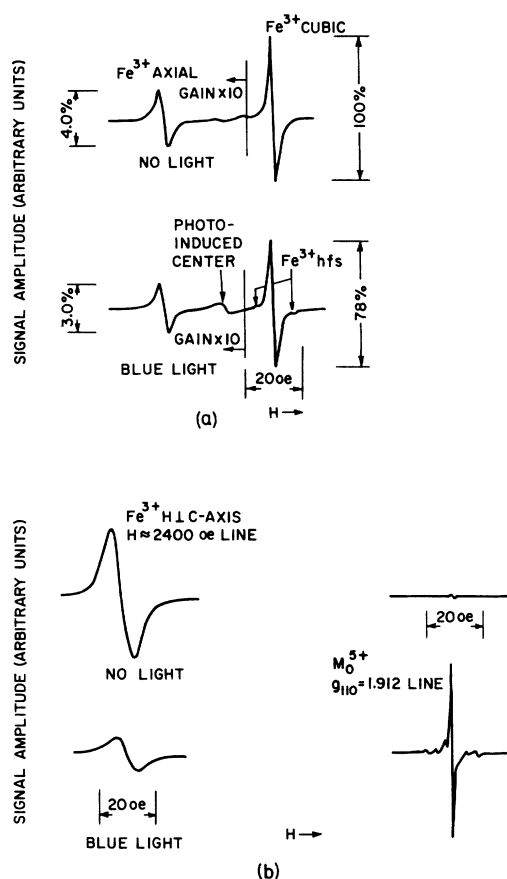

FIG. 2. EPR spectra observed in (a) $SrTiO_3$ and (b) TiO_2 doped with Fe and Mo before and after irradiation with blue light. The $SrTiO_3$ sample is 0.125 mm thick and the TiO_2 sample is 0.50 mm thick. $T = 77°K$. These samples were cut from the same crystal boules that were used to obtain the data shown in Fig. 1.

and host material. Fe/Mo-doped $SrTiO_3$ has a thermal decay time of several minutes at 300°K, whereas singly doped $SrTiO_3$:Fe decays in less than a second. At 77°K, however, both have a long thermal decay time and the induced optical absorption is similar except that the double-doped sample has increased absorption at long wavelengths. In TiO_2 the room-temperature decay time is very short, even when doped with Fe and Mo, and the spectra must be measured at 77 °K.

Study of the EPR spectra present in these materials has enabled us to determine the mechanism of the effect. The EPR spectra of Fe^{3+} in both TiO_2 and $SrTiO_3$ have been previously reported.[5,6] Iron enters both hosts substitutionally on the Ti^{4+} sites. Charge compensation presumably takes place through oxygen vacancies. This is observed[7] indirectly through the appearance of the strong axial spectra of Fe^{3+} in $SrTiO_3$. Mo^{5+} has also been observed in TiO_2, but not in cubic $SrTiO_3$, probably because the ground state is an

orbital triplet.[8] One of the EPR lines of Fe^{3+} in TiO_2 is shown in Fig. 2(b). The upper trace is observed in the thermally stable state. The Mo^{5+} resonance is absent or very small. After irradiation with approximately 0.40-μ light from a 500-W Hg lamp with $CuSO_4$ solution and Corning 7-59 filters, the Fe^{3+} resonance decreases and the Mo^{5+} resonance appears. An estimate of the number of Fe^{3+} centers removed and the number of Mo^{5+} centers created shows that they are approximately equal, within a factor of 2. The $SrTiO_3$ sample shows a similar decrease in the Fe^{3+} resonance, but the Mo^{5+} resonance cannot be seen in this case. Instead, a new isotropic defect center with $g = 2.012$ is observed, but the number of centers contributing to this line is probably not more than 20% of the centers switched. It may be an additional electron trap whose importance diminishes as the Mo concentration is

increased. The actual number of Fe centers contributing to the photoinduced absorption varies between 5×10^{16} and $10^{18}/cm^3$ depending on the dopant concentration. The fraction of Fe^{3+} centers switching varies from a few percent for highly doped samples to 40% when the total Fe concentration is at the $10^{17}/cm^3$ level. The change in the number of Fe^{3+} centers as estimated from the EPR data correlates well with the corresponding change in absorption coefficient. In Fig. 2 the percentage change of Fe^{3+} centers is less in the $SrTiO_3$ sample than the TiO_2 sample, even though the optical density change is greater. This is because the $SrTiO_3$ sample contains considerably more Fe.

We interpret the above changes in the EPR spectra as a light-induced transfer of charge between Fe and Mo centers via the conduction or valence bands. We believe the Fe and Mo originally enter the crystal as Fe^{3+} and Mo^{6+}, respectively. Measurements of the Fe and Mo concentrations by atomic absorption spectroscopy show that the total amount of Fe present is close to the amount of Fe^{3+} present as estimated from the EPR data and that approximately equal amounts of Mo are incorporated into the crystal. Neither the Fe^{3+} nor the Mo^{6+} have significant optical absorption in the visible except near the band edge. After irradiation with approximately 4000-Å light (pumping the Fe^{3+} or Mo^{6+} bands), Fe^{4+} and Mo^{5+} are created. Both these ions have visible absorption, thus leading to the observed photochromism. The role of the Mo is that of electron trap and the thermal decay of the absorbing state is determined, among other things, by the depth of this trap. When Mo is not present, another defect center acts as an electron trap, possibly the oxygen vacancy. In this case, the thermal decay rate is much faster and the optical absorption band due to Mo^{5+} is missing. These observations are supported by heat-treatment experiments which we now discuss.

Oxidation and reduction of $SrTiO_3$ and TiO_2 changes the number of oxygen vacancies present in the crystal. This in turn affects the valence state of the impurity ions since overall charge compensation must be preserved. The effect of heat treatment on the optical absorption of transition-metal–doped $SrTiO_3$ was first reported by Gandy.[9] Fe-doped $SrTiO_3$ is usually amber in color. If reduced in an atmosphere of air at $p \approx 1$ mm, $T = 800°C$, the crystal becomes almost transparent. Furthermore, the removed bands are the same as the light-induced bands except

for the long-wavelength region. The EPR spectrum of Fe^{3+} before and after reduction shows that the amount of Fe^{3+} has not increased by more than 10%. The reduction should create more vacancies which can cause the reduction of the 5-10% of Fe^{4+} originally present to Fe^{3+}. Therefore, the photoinduced band must come from Fe^{4+} which is created by light. The same is true for Mo. Singly doped $SrTiO_3$:Mo is colorless. After moderate reduction it turns blue with a broad band centered around 0.65 μ. This band also contributes to the photoinduced optical absorption. The 0.65-μ band can be associated with Mo^{5+} on the basis of the EPR spectrum, and the colorless state with Mo^{6+}. Mo^{6+}, having no d electrons, would be expected to be colorless. In addition, it is found that Mo charge-compensates Fe in the double-doped samples as seen by decreased optical absorption in the visible and a decrease in the Fe^{3+} axial spectra. Since the EPR spectra as well as ionic radii considerations point to the Mo being in a Ti^{4+} site, the initial charge state would have to be 6^+. As pointed out by Gandy, the optical absorption changes resulting from oxidation and reduction are completely reversible. None of the reduction treatments used here is severe enough to reduce Ti^{4+} and produce free carriers as observed by Baer.[10]

Our model can be summarized as follows: Initially the impurity ions are Fe^{3+} and Mo^{6+}. After blue-light irradiation, a charge transfer takes place through either the conduction or valence band and the ions become Fe^{4+} and Mo^{5+}. The first two have no optical absorption in the visible, whereas the latter two both absorb in the visible. Similar optical absorption changes have been observed at temperatures of 300, 77, and 4.2°K. When Mo is not present, other centers may act as electron traps. The number of centers switching can be higher than $10^{18}/cm^3$, and the oscillator strength has been estimated from Smakula's equation to be approximately 0.3. The exact nature of the optical bands is not known as yet, and the experimental evidence does not distinguish between an electron or hole transfer. The effect can also be observed in Ni-, Cr-, and Co-doped crystals and to a lesser extent with other transition-metal ions. These will be discussed in more detail elsewhere. The effect reported here could have considerable importance in quantum electronic applications.

edge the experimental assistance of R. Nielsen
for the heat treatment experiments.

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EUROPIUM-TERMINATED CHROMIUM FLUORESCENCE IN EuAlO$_3$:Cr^{3+}

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An optical emission process is observed in which a Cr^{3+} ion, initially in the ^2E_g excit-
ed state, simultaneously emits a photon and excites a neighboring Eu^{3+} ion to an excited
^7F_J level. Transitions terminating on $J = 1$ through 5 have been found.

In the optical-emission spectrum of Cr^{3+}-
doped EuAlO$_3$ we observe, in addition to the two
transitions from the crystal-field-split ^2E_g lev-
els to $^4A_{2g}$ levels, a number of strong lines at
longer wavelengths. The additional lines are not
associated with the emission of single Cr^{3+},
Eu^{3+}, or other impurity ions, but consist of a
compound process in which a Cr^{3+} ion makes a
transition from the ^2E_g to $^4A_{2g}$ levels while a
neighboring Eu^{3+} ion simultaneously goes to an
excited state, and the energy difference is emit-
ted as a photon. The effect is closely related to,
but distinct from, the excitation of ion pairs ob-
served by Varsanyi and Dieke.[1] It is quite dif-
ferent from the satellite lines observed in the
spectrum of dark ruby, as there the level struc-
ture is determined not by single-ion levels, but
by chromium-pair levels.[2]

The crystal has the orthorhombic crystal
structure, D_{2h}^{16}-$Pbnm$, with four molecules in
the unit cell.[3] There are two magnetically in-
equivalent rare-earth ion sites having C_{1h} (mir-
ror plane) symmetry, and four inequivalent alu-
minum sites with C_i (inversion) symmetry. The
Cr^{3+} substitutes for Al^{3+}, and the presence of a
center of symmetry requires the transitions to
be magnetic dipole.

Figure 1(a) shows the emission spectrum at
77 °K in the immediate vicinity of the chromium
R lines. Compare this with the emission from
the isomorphic crystal YAlO$_3$:Cr^{3+}, Fig. 1(b),
which shows the expected emission of two R lines
and a very weak vibronic spectrum. The latter,
when examined under higher gain, has a complex
structure and shows no simple relation to Fig.
1(a). Thus the lines in Fig. 1(a) are not vibron-
ics.

Paramagnetic-resonance measurements fur-
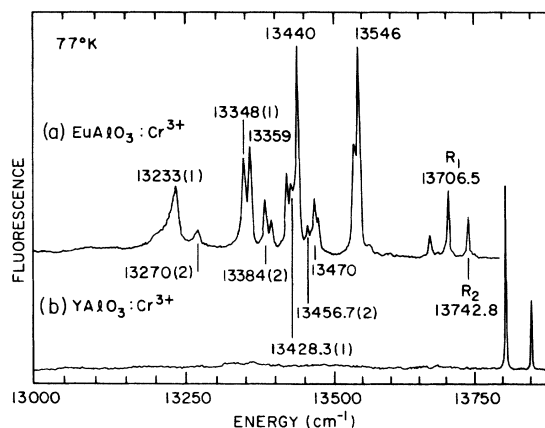ther indicate that Cr^{3+} is found only on the four
inequivalent sites.[4]

FIG. 1. (a) Emission spectrum of EuAlO$_3$:Cr^{3+} at
77°K. The temperature dependence of several of the
satellite lines relative to the R_1 and R_2 lines is denoted
by the bracketed 1 and 2, respectively. (b) R-line
emission from YAlO$_3$:Cr^{3+} at 77°K.