PHYSICAL REVIEW VOLUME 178, NUMBER 2 10 FEBRUARY 1969

Spectroscopic Studies of $SrTiO_3$ Using Impurity-Ion Probes*

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(Received 1 July 1968)

Sharp-line fluorescence and absorption in the region of 7935 Å were observed in Cr^{3+}-doped and undoped $SrTiO_3$. It is reasonably established that the fluorescence and absorption are due to the $^2E \leftrightarrow {}^4A_2$ transition (R line) of the Cr^{3+} ion. Polarization and absorption measurements indicate that the R-line transition is magnetic dipole. Fluorescence from Mn^{4+}-doped $SrTiO_3$ was seen at about 7230 Å. At low temperatures, a temperature-dependent splitting of the R-line transition of Cr^{3+} is seen. It is shown that this is due to the lifting of the degeneracy of the ^2E state by the temperature-dependent tetragonal field present in $SrTiO_3$ below 103±2°K. These results are compared with previous measurements on rare-earth ions in $SrTiO_3$. The possible origin of the tetragonal transition is discussed.

I. INTRODUCTION

The interesting properties of the substance $SrTiO_3$ have made it a popular subject for study in the past few years. The presence of a temperature-dependent soft optical lattice mode in $SrTiO_3$ has been of primary interest to researchers.[1,2] The temperature dependence of this mode is manifested in many properties of the crystal, such as the dielectric constant, electrostriction,[3] and thermal conductivity.[4] At room temperature $SrTiO_3$ has the cubic perovskite structure (space group, O_h^1), but transforms into a tetragonal structure at about 103°K (probable space group, D_{4h}^{18}). This transition is apparently of second order or higher and has been studied by several methods.[5–7]

The work reported herein was undertaken with the idea of studying the properties of $SrTiO_3$ with the aid of impurity ions as probes of the local crystalline environment. The transition-metal ions of the ($3d^3$) configuration were chosen as probes because they normally have sharp-line optical transitions and have been studied in a large number of materials. However, until recently fluorescence from $SrTiO_3$ had been seen only with rare-earth doping. Broad-band optical absorption, but no sharp-line absorption, had been observed in $SrTiO_3$ doped with Cr^{3+} and Mn^{4+}. The absence of the familiar chromium spectrum was thought to be unusual, and therefore a more careful search for sharp-line absorption or fluorescence was undertaken. Samples of $SrTiO_3$ doped with from 0.005 to 0.05 wt% of Cr_2O_3, nominally pure samples, and one doped with 0.01 wt% of MnO_2 were used in this search. Both sharp-line fluorescence and absorption were subsequently found in the Cr-doped $SrTiO_3$, and fluorescence was observed from the Mn-doped and nominally "pure" $SrTiO_3$.[8–10] In this paper we describe some of the characteristics of the fluorescence and absorption spectra in $SrTiO_3$ and discuss the possible sources of the transitions.

Previous work on Cr^{3+} and Mn^{4+} in $SrTiO_3$ was mainly concerned with the electron spin-resonance properties of these ions in their ground states. Müller[11] showed that the Cr^{3+} ion is in a site of cubic symmetry at room temperature. Because of the cubic symmetry and narrow linewidth of the spin resonance, it is unlikely that the Cr^{3+} ion goes into an interstitial site. Also, since the Cr^{3+} ion has almost the same ionic radius as Ti^{4+}, it should replace Ti^{4+} rather than Sr^{2+}. However, the replacement of Ti^{4+} by Cr^{3+} introduces a charge defect into the lattice. The defect is compensated, probably by an oxygen vacancy, either locally or at a distant site. Because the spin resonance shows the Cr^{3+} ion is in a cubic site, the compensation takes place nonlocally.

II. EXPERIMENTAL TECHNIQUES AND EQUIPMENT

The doped and undoped single crystals of $SrTiO_3$ were grown by the National Lead Co. The fluorescence spectra of the $SrTiO_3$ samples were excited by a 1000-W PEK Labs AH-6 high-pressure mercury arc. The light from this source passed through a saturated $CuSO_4$ solution, which filtered out most of the red and infrared light. The fluorescence from the sample was analyzed by a $\frac{3}{4}$-m or a 1.8-m focal length grating spectrometer and detected by a cooled RCA 7102 photomultiplier. In order to improve the signal-to-noise ratio in absorption measurements, a Nuclear Data model-800 Enhancetron signal averager was utilized. The Enhancetron summed the signal from repeated scans of the spectrometer. In some cases a Bausch and Lomb dual-grating spectrograph with dispersions of 4 and 8 Å/mm was used, and the spectra were recorded on 1-N photographic plates.

The sample was cooled by cold helium gas from the boil-off of liquid helium. The flow rate of the gas pro-

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* Research supported by the Army Research Office, Durham.
† National Science Foundation Predoctoral Fellow.
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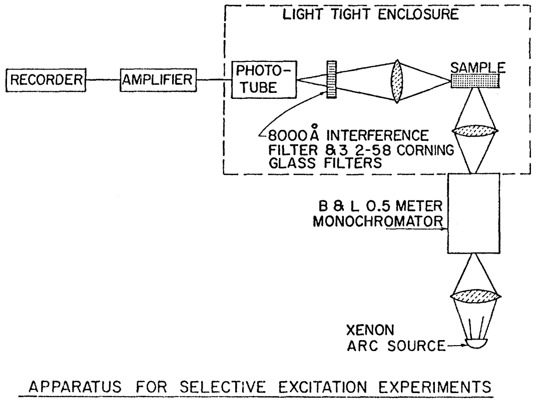

FIG. 1. Apparatus for selective excitation experiments.

vided the course control on the temperature; and a heater attached to the sample holder, the fine control. The temperature of sample was measured by means of an Au (2.1% Co) versus Cu thermocouple attached to the sample with G.E. 7031 glue.

In order to help in the identification of the impurity center, experiments were done in which the fluorescence was selectively excited by narrow-band radiation. Figure 1 shows the experimental arrangement.

The lifetime of the fluorescence was also determined. The fluorescence was excited by a 200-μsec pulse from a xenon flash tube. The output from a photomultiplier detector was amplified by a logarithmic amplifier and displayed on an oscilloscope. The log amplifier was limited to lifetimes longer than 0.5 msec.

III. $SrTiO_3:Cr^{3+}$

Figure 2 shows the fluorescence spectrum of $SrTiO_3$ doped with 0.05 wt% of Cr_2O_3. At 20°K the spectrum consists of a zero-phonon doublet split by 2.9 cm^{-1} at 12 595.8 cm^{-1} plus associated phonon sidebands. The linewidth of the no-phonon lines is about 0.5 cm^{-1} at 4.2°K. Only a single line is seen at 77°K with a width of 5 cm^{-1}. The lifetime of this fluorescence is 18.5 msec at 4.2°K, 18 msec at 77°K, and drops to 5 msec at 175°K.

The sharp lines also appear in the absorption spectrum at the same energy as the emission lines; i.e., there is no Stokes shift. The peak absorption coefficient at 2°K is about 0.026 cm^{-1} for a $SrTiO_3$ sample doped with 0.05% Cr_2O_3. A sample doped with 0.005% Cr_2O_3 gave a peak absorption coefficient of 0.003 cm^{-1}. This shows that the concentration of the absorbing center is roughly proportional to the concentration of Cr^{3+} ions. Assuming that the lines have a Gaussian shape and that the density of Cr^{3+} ions is given by the nominal value of doping, the calculated oscillator strength (f) of the transitions is approximately 1.4×10^{-9}. This number is a lower limit of f because the actual number of Cr^{3+} ions in cubic sites is usually lower than the nominal value of doping.

The same fluorescence, but no absorption, was also seen in undoped samples of $SrTiO_3$. However, the intensity of fluorescence was much weaker and temperature-dependent. The intensity drops by a factor of about 100 from 77 to 20°K. This is similar to the data obtained by Sihvonen.[10] Other than the temperature variation of the intensity, the fluorescence spectrum in the undoped samples is identical with that seen in the Cr-doped $SrTiO_3$.

The presence of a no-phonon doublet means that there is a splitting of the excited state or the ground state or that the lines originate from ions in slightly inequivalent sites. If there is rapid thermalization between the energy levels, then the population of the levels will have a Boltzmann distribution. If this splitting is due to ions in inequivalent sites, then the energy transfer must be rapid compared to the lifetime of the excited state in order that a Boltzmann distribution be attained. This is rather unlikely for a dilute impurity system because of the low probability of energy exchange. Because 2.9 cm^{-1} is equivalent to 4.2°K, there should be change in the relative intensities of the two lines if the temperature is lowered from 20 to 2°K. Experimentally it is found that in absorption the relative intensities remain constant, but that in fluorescence the intensity of the higher-frequency component decreases relative to that of the lower-frequency component. This indicates that the energy splitting is in the excited state.

The data presented so far indicate that the fluorescence and absorption are due to the $^2E \leftrightarrow {}^4A_2$ transition (R line) of the Cr^{3+} ion. The ^2E excited state would be split by the tetragonal field present in $SrTiO_3$ below 103°K, which is what is observed. The fact that the fluorescence can be seen in undoped $SrTiO_3$ may seem unusual. But this does not rule out the possibility that it is the chromium fluorescence. Cr^{3+} has broad pumping bands and a narrow emission line which often shows nearly unity quantum efficiency. The undoped $SrTiO_3$ crystals contain on the order of 1 ppm of Cr impurities.

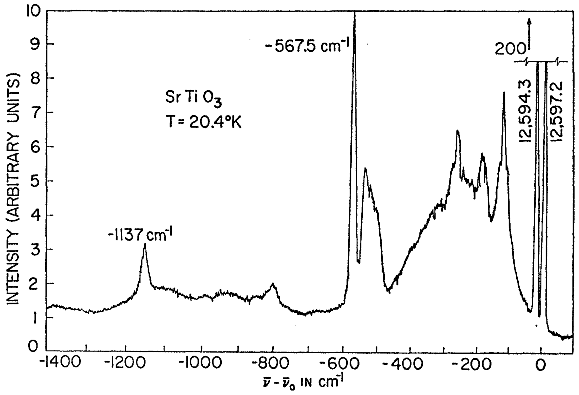

FIG. 2. The fluorescence spectrum of $SrTiO_3$ doped with 0.005-wt% Cr_2O_3 (the splitting of the doublet has been exaggerated for clarity).

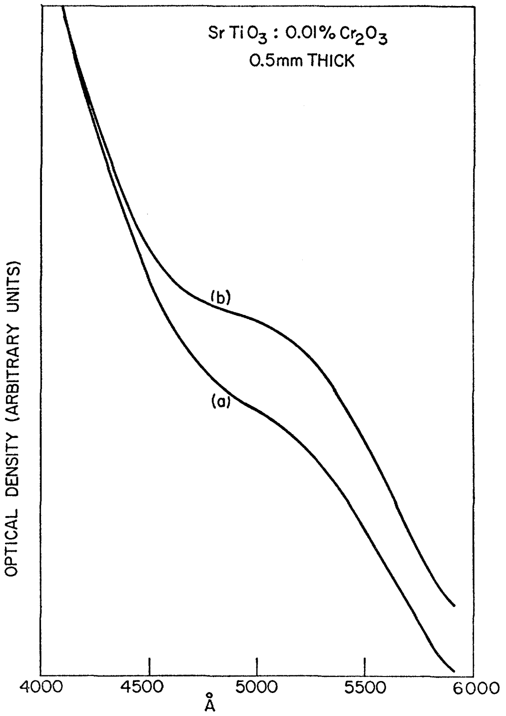

FIG. 3. Absorption of $SrTiO_3:Cr^{3+}$ (a) after being in dark for four hours; (b) after exposure to white light.

With an efficient mechanism of energy excitation and high quantum efficiency, the fluorescence from an impurity of this concentration could still be seen. The quantum efficiency of Cr^{3+} in Al_2O_3 and in MgO is so high that fluorescence can be seen very easily in samples with 1 ppm of chromium.

Chromium-doped $SrTiO_3$, though, is unusual in at least one respect. The position of the *R* lines is much farther to the red than normally found. Nevertheless, this low energy for the *R* lines is not unreasonable. For Cr^{3+} surrounded by six nearest-neighbor ions, the known position of the *R* lines varies from 6807 Å in emerald to 7337 Å in $LaAlO_3$.[12,13] In the highly covalent substance $K_3[Cr(CN)_6]$ the *R*-line energy is about 12 300 cm^{-1}.[14] According to the crystal theory as worked out by Tanabe and Sugano,[15] a low value of the *R*-line energy indicates a low value for the parameter *B*, which is a measure of the electron-electron interaction between the valence *d* electrons. The value of *B* would have to be about 600 cm^{-1} in order to explain the low energy of the *R* lines. The electron-electron interaction between the *d* electrons could be reduced because of increased covalency in $SrTiO_3$. Increasing the covalency normally lowers the *e-e* interaction, because the impurity ion electrons spend some of their time on the ligands, thereby becoming less localized.[16]

In order to get a better estimate of the crystal-field parameters, *Dq* and *B*, of Cr^{3+} ion in $SrTiO_3$, it is helpful to know the energies of the $^4T_2$ and $^4T_1$ states. However, the ^4T absorption bands, normally seen in Cr^{3+}-doped materials, are not seen in the room-temperature absorption of $SrTiO_3:Cr^{3+}$. Instead there is a strong broad-band absorption which has a slight peak at 5150 Å as is shown in Fig. 3(a). This peak also appears in reduced samples of $SrTiO_3$. After heating the crystals of $SrTiO_3:Cr^{3+}$ at 950°C in vacuum, this absorption decreases. The crystal can be returned to its original state by heating in air or oxygen. This is similar to the effect seen by Gandy[17] in cobalt- and iron-doped samples of $SrTiO_3$.

This absorption is also affected by exposure to visible light as shown in Fig. 3. The same effect is also seen in Co-doped $SrTiO_3$. This photo-effect is rather long lived, on the order of minutes. It could be due to the excitation by infrared radiation of an electron from the valence band to an acceptor site. The increased absorption at 5100 Å would then correspond to the excitation of this electron into the conduction band. The presence of such an acceptor site could also lead to quenching of photoconductivity by infrared radiation. This is illustrated in Fig. 4. Such a quenching has been observed by Grabner.[18]

It is likely that the strong broad-band absorption seen in Cr-doped $SrTiO_3$ is not due to the Cr^{3+} ion, but to the Ti^{3+} ion or a defect introduced in the growth process. A 0.01% Cr_2O_3-doped sample has a nominal concentration of 4×10^{18} Cr^{3+} ions/cm^3. The $^4T_1$ and $^4T_2$ bands should have absorption coefficients of about 0.3 and 0.6 cm^{-1}, respectively, based on Cr^{3+} in Al_2O_3.[19] However, the absorption coefficient of a 0.01% $Cr_2O_3:SrTiO_3$ sample is about 16 cm^{-1} at 6150 Å and 37 cm^{-1} at 4700 Å. Therefore, the Cr^{3+} ^4T band absorption is completely masked by this other absorption.

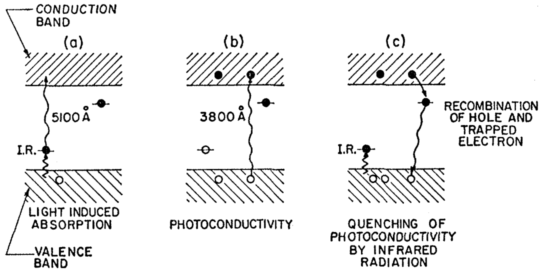

FIG. 4. Properties of $SrTiO_3$ due to the presence of acceptor and donor sites.

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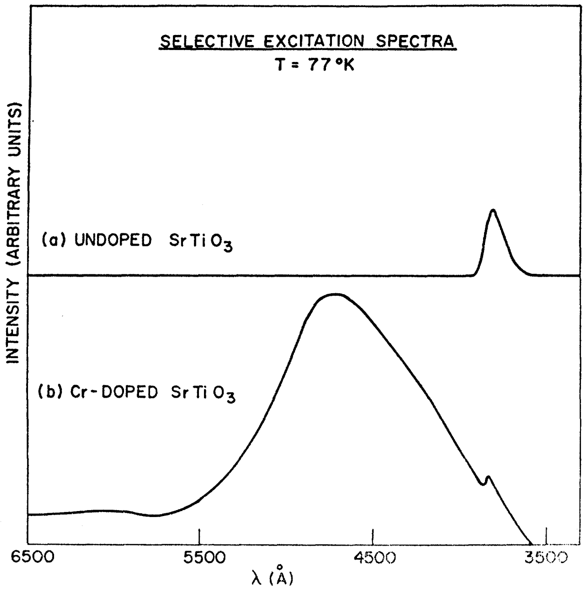

Fig. 5. Selective excitation spectra of undoped and Cr-doped $SrTiO_3$ (uncorrected for system response).

In order to determine what the energy of the $^4T_1$ and $^4T_2$ bands might be, the fluorescence was selectively excited by narrow-band radiation. The results are shown in Fig. 5 for doped and undoped $SrTiO_3$. The peaks in the selective excitation spectrum of the Cr-doped $SrTiO_3$ occur at 6150, 4700, and 3800 Å. The undoped sample has a peak only at 3800 Å. The $^4T_2$ and $^4T_1$ bands of the Cr^{3+} ion could be identified with the maxima at 6150 and 4700 Å, respectively. The parameters, Dq and B, would then have the approximate values 1530 and 560 cm^{-1}, respectively.

The 3800-Å peak corresponds to excitation of electrons into the conduction band. It is likely that energy is being transferred from the conduction band to the impurity system. For the undoped sample this is the primary mechanism for excitation. The strong fluorescence of the Cr^{3+} ion in undoped $SrTiO_3$ could be explained by an efficient host-impurity energy transfer. This energy-transfer hypothesis is supported by some results obtained by Weber.[20] He noticed that some undoped samples showed a millisecond buildup in the fluorescence after a 5-μsec pulsed excitation. This was not seen in Cr-doped samples.

The intensity decrease of the fluorescence at low temperature is due to the loss of this energy transfer from the conduction band. Below 80°K Sihvonen[10] and Grabner[18] observed a broad-band fluorescence at 5400 Å which increased in intensity as the temperature was lowered. The infrared and green emissions may be competing processes for the energy absorbed at the band edge. The energy transfer to the infrared emission may require the assistance of a phonon, which explains why it disappears at low temperature.

We would like to summarize some of the evidence that the fluorescent center in $SrTiO_3$ is the Cr^{3+} ion.

1. The sharp-line absorption is proportional to the concentration of Cr^{3+} ions.
2. Only two no-phonon transitions are seen. This is consistent with the known energy-level scheme of the Cr^{3+} ion. The ^2E_g excited state is split by the tetragonal field present in $SrTiO_3$ below 103°K. The $^4A_{2g}$ ground state is also split by the field; however, the splitting[11] is 8×10^{-4} cm^{-1} at 77°K, which is too small to be observed optically.
3. The selective excitation spectrum has two peaks, which can be ascribed to the $^4T_2$ and $^4T_1$ bands.

IV. POLARIZATION OF *R* LINES

Because of the tetragonal distortion at low temperatures the ^2E_g level is split into two components, normally given the labels u and v. In general the transitions from these levels to the ground state are polarized with respect to the tetragonal axis. However, $SrTiO_3$ has tetragonal domains. This means that the tetragonal axis lies along different directions in different domains. Therefore, if the three differently oriented domains are equally probable, then no polarization of the transitions will be seen because then the material is essentially isotropic.

Experimentally this is not the situation. The intensities of the R-line components, R_u and R_v, do vary with the polarization. Each line reaches its maximum or minimum when the polarization is parallel to one of the cubic axes. The intensity ratio $I_u:I_v$ also varies with the polarization. For instance, in one experiment $I_u:I_v$ was equal to two for the polarization vector parallel to [001]. By rotating the plane of polarization by 90°, the ratio $I_u:I_v$ became $\frac{1}{2}$. However, the intensity ratio for a given polarization varied from sample to sample, and even varied in the same sample after heating and cooling through the tetragonal transition. This indicates that the polarization is due to unequal numbers of the three differently oriented domains. The relative numbers of these domains can change each time the crystal is heated and cooled through the 107°K transition. Because of the observed polarization of the R lines, something can be said about the magnetic or electric dipole character of the transitions.

Table I. Relative intensity of R lines split by a tetragonal field.

		The light is emitted along the X axis			
	c axis parallel to	**E** vector‖Z axis		**E** vector‖Y axis	
		u	v	u	v
Magnetic dipole	z axis (Z)	3	1	0	4
	y axis (Y)	0	4	3	1
	x axis (X)	3	1	3	1
Electric dipole	z axis (Z)	0	0	3	1
	y axis (Y)	3	1	0	0
	x axis (X)	3	1	3	1

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[20] M. J. Weber (private communication).

The intensities of the R_u and R_v lines for polarization parallel and perpendicular to the tetragonal axis has been calculated by Imbusch *et al.*[21] Two different results are obtained depending on whether the transitions are magnetic or electric dipole. An odd component of the crystalline field could allow the electric dipole transition, and it is assumed that this odd field is parallel to the tetragonal axis. The intensity ratios of the two R lines from the differently oriented systems are given in Table I.

First consider magnetic dipole transitions. If the amount of emission from each domain is the same, then the intensity is $(3+3+0)=6$ for the u component and $(1+1+4)=6$ for the v component. The intensities of the lines are equal. A change of the polarization vector **E** from the z to the y axis reverses the contribution from (Y) and (Z) domains. If there is an equal amount of light from each, then there is no change in the relative intensity of the u and v components. However, if the (Y) and (Z) domains contribute an unequal amount to the total intensity, then the u component will be stronger in one polarization and the v component stronger in the other.

Now consider electric dipole transitions. With equal amounts of the three domains the intensity ratio is 3:1 in favor of the u component. However, if the light from the (Y) and (Z) domains is not equal, then rotating the **E** vector by 90° will change the intensity of the R lines, but *not* the ratio of the intensities. Therefore, because the intensity ratio *does* change when the polarization is changed, the transition must be mainly of magnetic dipole character. This indicates that the Cr^{3+} ion must be situated in a site which has approximate inversion symmetry.

V. TEMPERATURE DEPENDENCE OF *R*-LINE SPLITTING

Rimai and deMars[5] found that the field of tetragonal symmetry seen by the Gd^{3+} ion in SrTiO$_3$ is temperature-dependent. Near the transition temperature the field varies as $(T_c-T)^{1/2}$ where $T_c=110\pm2.5$°K from their experimental data. Since Gd^{3+} is believed to substitute for the Sr^{2+} ion and Cr^{3+} for the Ti^{4+} ion, it is interesting to compare the temperature dependence of the tetragonal field at the Sr^{2+} site with that at the Ti^{4+} site. Because the degeneracy of the ^2E state of Cr^{3+} ion is lifted by an axial field, the R-line splitting can be used for observing any variation of the tetragonal field with temperature. The R-line splitting is temperature-dependent as shown in Fig. 6. It has a temperature dependence similar to that of the tetragonal splitting of the Gd^{3+} spin-resonance spectrum, also shown in Fig. 6. However, the transition temperature appears to be slightly lower in our samples, perhaps because of the impurity doping.

TABLE II. Splittings of the ^2E_g and $^4A_{2g}$ states of Cr^{3+} in MgO and SrTiO$_3$.

	MgO	SrTiO$_3$
	Uniaxial pressure (77°K) [cm^{-1}/10^{-3}$(a/c-1)$]	(80°K) (cm^{-1})
$\Delta(^2E_g)$	1.3 [a]	1.5 [c]
$2D(^4A_{2g})$	1.8×10^{-3} [b]	8.0×10^{-4} [d]

[a] Reference 23.
[b] Reference 24.
[c] This work.
[d] Reference 11.

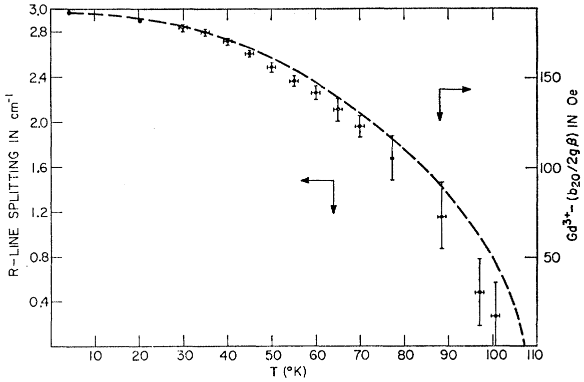

FIG. 6. R-line splitting of Cr^{3+} in SrTiO$_3$ versus temperature (points with error bars). The tetragonal splitting of the Gd^{3+} ground state versus temperature is shown as a dashed line. (Gd^{3+} data taken from Rimai and deMars, Ref. 5.)

A word should be said on how these results were obtained since the two R lines cannot be resolved above 65°K. It is fortunate that the intensity ratio of the two lines can be varied by rotating the plane of polarization, as mentioned in the previous section. Therefore, above 65°K the peak of the observed line shifts if the plane of polarization is rotated. The true separation of the R lines can then be calculated from the observed shift and the relative intensity of the two components as a function of polarization. The relative intensity was measured at 20°K, where the lines are completely resolvable.

The results of Unoki and Sakudo[22] indicate that the tetragonal transition consists primarily of a rotation of the TiO$_6$ octahedra. If these octahedra remain regular, then the tetragonal field at the titanium site is only provided by the ions beyond the nearest-neighbor oxygen ions. In order to determine whether or not the oxygen octahedron might be distorted, the magnitude of the R-line splitting in SrTiO$_3$ should be compared to that of Cr^{3+} in a substance where the amount of tetragonal distortion can be determined. MgO:Cr^{3+} is such a material. Since MgO is cubic, the tetragonal field is only present if uniaxial pressure is applied along a cubic axis. Table II compares the splittings of the ^2E and $^4A_2$ states in MgO and SrTiO$_3$.

Under an axial pressure along [100] of 22×10^8 dyn/cm^2 the ^2E splitting of Cr^{3+}:MgO is 1.4 cm^{-1}. The

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[21] G. F. Imbusch, A. L. Schawlow, A. D. May, and S. Sugano, Phys. Rev. 140, A830 (1965).

[22] H. Unoki and T. Sakudo, J. Phys. Soc. Japan 23, 546 (1967).

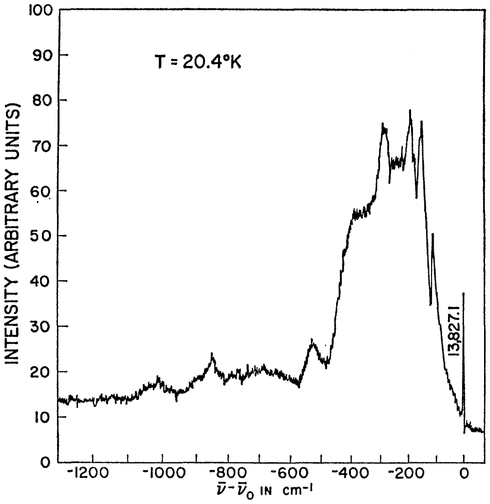

FIG. 7. Fluorescence spectrum of $SrTiO_3$ doped with 0.01% MnO_2.

tetragonal $(a/c-1)$ at this pressure, as calculated from the elastic constants given in Refs. 23 and 24 is approximately 10^{-3}. The corresponding splitting in $SrTiO_3$ is 1.5 cm^{-1} for a $(c/a-1)\cong 3\times 10^{-4}$. The order of magnitude of the R-line splitting is about the same in the two materials. However, in MgO the nearest-neighbor oxygen octahedron is tetragonally distorted by the uniaxial pressure. Therefore, it is likely that the oxygen octahedron in $SrTiO_3$ is not regular below the tetragonal transition.

VI. TETRAGONAL PHASE TRANSITION IN $SrTiO_3$

The "soft-mode" theory of ferroelectricity has been very successful in explaining the properties of ferroelectrics above their Curie temperatures. This is because ferroelectricity in the perovskites is essentially the result of the relative displacement of positive and negative ions. Thus, it can be analyzed in terms of the normal modes of the lattice. The transition to ferroelectricity can be considered as the result of an instability in one of the lattice modes of vibration. The soft mode is just this mode. Therefore, the displacements of the ions below the transition temperature might be expected to resemble the displacements in the soft-mode vibration. Also, by looking at the distorted structure in the ferroelectric state, something can be said about the possible symmetry of the soft mode.

But the ferroelectric transition is not the only one of interest in the perovskites. The other common transition is one in which the ideal cubic perovskite lattice transforms into an orthorhombic or tetragonal form. The transition is normally from the space group O_h^1 to D_{2h}^{16} or D_{4h}^{18}. This transition is essentially characterized by a rotation and tilting of the oxygen octahedra, and given a name, "puckering" transition, by Francombe and Lewis.[25] They ascribed the transition to an instability in the B-O-B ion chains. (They use the formula ABO_3 to represent a general perovskite.) This occurs because if the A ion is small, the B-O-B chains can buckle in order to maintain a given B-O bond length as the crystal contracts.

Because this transition is characterized by a regular displacement of the ions, it can be analyzed in terms of the lattice modes. However, in contrast to the case of ferroelectricity, the size of the unit cell increases. Thus, the unstable lattice mode would not be at $\mathbf{k}=0$, but near the zone boundary. This concept has been used by Silverman[26] in explaining the occurrence of antiferroelectricity. It has some support from the calculations of Cowley.[1] For $SrTiO_3$ he did a shell-model calculation of the phonon dispersion curves in high-symmetry directions. He noted that some of the models gave negative frequencies for k vectors at the zone boundary along [110] and [111] at 90°K. The displacements of the ions in these unstable modes consist primarily of a rotation of the TiO_6 octahedra.

After the present manuscript had been submitted, Fleury, Scott, and Worlock[27] reported on Raman scattering in $SrTiO_3$ at low temperatures. Their data indicate strongly the existence of a temperature-dependent soft mode at the corner of the Brillouin zone. Such soft modes may be found in other perovskites, such as $KMnF_3$,[28] which have a transition similar to that in $SrTiO_3$.

VII. Mn^{4+} IN $SrTiO_3$

The fluorescence from $SrTiO_3$ doped with 0.01% MnO_2 is shown in Fig. 7. It has only been seen in manganese-doped $SrTiO_3$. The no-phonon line has an energy of 13 827.1 cm^{-1} at 20.4°K. At 4.2°K a doublet split by 1.2 cm^{-1} is observed. The lifetime of the fluorescence is about 5 msec at 77°K. The selective excitation spectrum has a peak at 5785 Å, but no peak at 3800 Å. If the energies of the ^2E and $^4T_2$ states are taken to be 13 827 and 17 300 cm^{-1}, respectively, then $B\cong 670$ cm^{-1} and $Dq\cong 1730$ cm^{-1}. Using these values for Dq and B, the predicted energy for the $^4T_1$ band is 25 400 cm^{-1} (3950 Å). This is where the strong absorption to the conduction band begins. The energy absorbed at this frequency is obviously not transferred to the Mn^{4+} ion as it is for the chromium.

There are other differences between the Mn^{4+} and Cr^{3+} fluorescences. The no-phonon transition of Mn^{4+} is very much weaker compared to its phonon sidebands; whereas, for Cr^{3+}, the peak R-line intensity is much

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larger than that of its sidebands. The sidebands of SrTiO$_3$:Mn^{4+} also have appreciable intensity out more than 2000 cm^{-1} from the no-phonon line. This may be the same effect noted by Yamamoto *et al.*[29] in rare-earth emission from SrTiO$_3$.

VIII. PHONON SIDEBANDS

Figure 8 gives a comparison of the phonon sidebands of Mn^{4+} and Cr^{3+} in SrTiO$_3$. The two sidebands have many common features, but there are some major differences. The sharp peak at 568 cm^{-1} could be due to a local mode around the Cr^{3+} ion. However, the local mode is probably not the result of a mass defect because Cr^{3+} has a mass of 52 and Mn^{4+}, 55. They both replace the Ti^{4+} ion of mass 48, but only the Cr fluorescence has this 568-cm^{-1} peak. More likely the mode would be due to a change in the force constants or to the presence of the charge defect of Cr^{3+}. This 568-cm^{-1} phonon also appears in the two-phonon spectrum at 1137 cm^{-1}.

The intensity at a given frequency in the sideband depends on the magnitude of the electron-phonon coupling and the phonon density of states at the phonon frequency. Normally peaks in the density of phonon states will occur at high-symmetry points in the Brillouin zone, such as at the center of the zone or at the boundary. Some of the peaks in the sidebands should, therefore, correspond to the frequencies of phonons at the Γ point (center of zone) or the *X* point (zone boundary along [001]). Table III makes a comparison between the phonon sideband peaks and the frequencies of phonons at the Γ or *X* points obtained by neutron scattering[1] or infrared measurements.[30]

TABLE III. Comparison of peaks of phonon sidebands in SrTiO$_3$ with phonon frequencies obtained by other methods (cm^{-1}).

Fluorescence[a]			Point in	ir[c]
Cr^{3+}	Mn^{4+}	Neutron[b]	Brillouin zone	300°K
		91.0 42.3[d]	Γ TO$_1$	86
108.3	106.9			
110.8		115	*X* TA, *X* TO$_1$	
119.6	119.7			
123.5	126			
	132	133	Δ TO$_1$	
136.0				
	144	∼150	*X* LA	
177	180	167	Γ LO$_1$	172.8
			Γ TO$_2$	176
187	188	187	*X* TO$_2$	
218	218			
231	230	230	2*X* TA, 2*X* TO$_1$	
248	245			
262	263	266	Γ LO$_2$, Γ TO$_3$	
276	276	270, 283	*X* LO$_1$, *X* LO$_2$	
316				
	386		Γ LO$_3$	473
501				
518	512		*X* LO$_3$	
533			Γ TO$_4$	544
567.5				
676	672	656	2*X* TO$_3$	
746				
796	836		Γ LO$_4$	804
922	870			
1063	1002			
1137	1242			

[a] $T=20.4$°K.
[b] Reference 1, $T=296$°K.
[c] Reference 23.
[d] $T=90$°K.

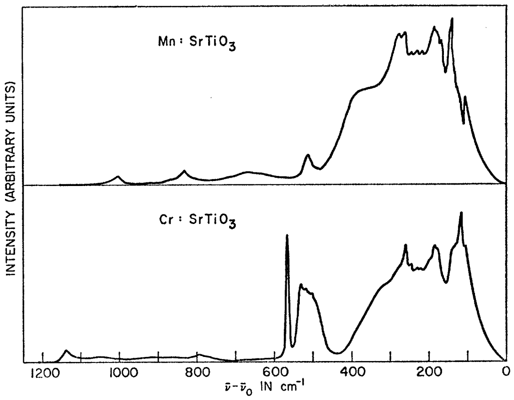

FIG. 8. Comparison of phonon sidebands for Cr^{3+} and Mn^{4+} in SrTiO$_3$.

A number of the peaks correspond to known phonon frequencies at the zone center and at the zone boundary. Most of the other peaks are due to combinations or overtones of these phonons. Further information about the phonon frequencies at the zone boundary in SrTiO$_3$ has been obtained by Nilsen and Skinner[31] using Raman scattering. In particular, the sideband peaks at 518 and 512 cm^{-1} in Cr^{3+}- and Mn^{4+}-doped samples, respectively, coincide with Nilsen and Skinner's assignment of 516 cm^{-1} as the energy of the LO$_3$ phonon branch at the zone boundary.

IX. CONCLUSION

There is a considerable amount of evidence that the sharp-line transitions seen in Cr-doped and undoped SrTiO$_3$ are the *R* lines of the Cr^{3+} ion. The primary objections to the fluorescent center being Cr^{3+} is that the *R* lines are low in energy and that the emission can be seen in undoped SrTiO$_3$. However, it is likely that covalency may be the cause of the crystal-field parameters being much reduced in SrTiO$_3$. The selective excitation results indicate that there is an efficient energy transfer from the host to the fluorescent center which helps to explain why the fluorescence can still be seen in undoped SrTiO$_3$. Besides the Cr^{3+} ion other

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types of impurity or defect centers are present as evidenced by the broad-band fluorescence and absorption in the region around 5200 Å. The magnitude of the tetragonal splitting of the *R* line does indicate that the oxygen octahedra do distort in the tetragonal phase. The properties and character of the tetragonal transition in $SrTiO_3$ and other perovskites are interesting enough to deserve further study. Certainly, a search should be made in other perovskites, such as $KMnF_3$, for a soft phonon mode at the Brillouin zone corner.

ACKNOWLEDGMENTS

The authors would like to thank Dr. R. M. Macfarlane for several helpful discussions and Dr. M. J. Weber for communicating his results to us.

PHYSICAL REVIEW VOLUME 178, NUMBER 2 10 FEBRUARY 1969

Dielectric-Related Optical Line Shifts in $SrTiO_3$:Cr^{3+} †

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(Received 1 July 1968)

Very unusual and large shifts of the *R* lines of Cr^{3+} with temperature and applied electric fields were observed. Below the tetragonal transition temperature, these shifts were found to have a behavior similar to that of the reciprocal dielectric constant of $SrTiO_3$. The electric field shift is shown to be due to the ionic polarization induced by the electric field. The *R*-line thermal shift cannot be explained by the usual theory of interaction with the acoustic lattice modes. The temperature dependence of the dielectric constant and the *R*-line shift is discussed in terms of interaction with the low-frequency optical-phonon branch. The tetragonal transition of $SrTiO_3$ at 107°K is instrumental in producing a discontinuity in the slope of the *R*-line shift versus temperature.

I. INTRODUCTION

A MEMBER of the perovskite family, $SrTiO_3$ has been the subject of a large variety of investigations in recent years. This interest in $SrTiO_3$ has occurred for several reasons. One is that the lattice dynamical theory of ferroelectricity introduced by Cochran[1] and Anderson[2] was first confirmed in $SrTiO_3$. This theory, suggested by the Lyddane-Sachs-Teller[3] relation, predicts that

$$\epsilon_0\omega_s^2 \cong \text{constant}, \qquad (1)$$

where ϵ_0 is the static dielectric constant and ω_s is the frequency at the zone center of a transverse optical mode (soft mode). Because the dielectric constant of $SrTiO_3$ is strongly temperature- and electric-field-dependent, a similar behavior should be seen in the frequency ω_s. Such a temperature-dependent mode was found by spectroscopic measurements of Barker and Tinkham[4] and those of Spitzer *et al.*[5] The recent measurements[6] of ω_s using an electric-field-induced Raman effect have confirmed the validity of Eq. (1) down to 8°K and up to applied electric fields of 10 kV/cm.

At about 107°K, $SrTiO_3$ undergoes a transition from a cubic to tetragonal structure. This structural transition has been one of the more studied characteristics of $SrTiO_3$. The transition has been observed in measurements of the elastic constant,[7] spin resonance of impurity ions,[8,9] optical birefringence,[10] piezoresistivity,[11] Raman scattering,[12] and Brillouin scattering.[13] The phase transition, though, has no effect at all on the measured dielectric constant.[7] A plot of the reciprocal dielectric constant against temperature does not even have a change of slope at 107°K.

The most useful measurements have been made on the electron spin resonance of Fe^{3+} and Gd^{3+} in $SrTiO_3$.[14,8] These measurements show that the tetragonal distortion from cubic symmetry increases as the temperature is lowered. The transition is at least of second order because the tetragonal distortion goes smoothly to zero at the transition temperature and no thermal hysteresis

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† Research supported by the Army Research Office, Durham.

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