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Photoluminescence in $SrTiO_3$†

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At 77 K photoluminescence from nominally pure, 0.05% Sm-doped and 0.005% Cr-doped $SrTiO_3$ gives identical spectra in the infrared (I.R.) with an intensity ratio of 1:20:400, respectively. In undoped and Sm-doped specimens, the intensity of emission is vanishingly weak at 4 K, in contrast to Cr-doped $SrTiO_3$, in which it is practically unchanged relative to that at 77 K. At 77 K, the spectrum consists of a narrow line at 1.5625 eV of half-width 0.5×10^{-3} eV, which we identify as the zero-phonon line, and 31 satellite lines, which are shown to be vibronics due to lattice phonons from the center and edge of the Brillouin zone. At 4 K the zero-phonon line is a doublet. Comparison with the reported lattice phonon spectrum is satisfactory. In addition, the data suggest the energies of several zone boundary phonons which have not been reported. In spite of identical emission spectra, undoped, Sm-doped, and Cr-doped specimens have different excitation spectra. This suggests energy transfer from Sm or Cr to a tightly bound center, isolated from the electronic energy bands, such as typically arise from rare-earth ions in ionic crystals. It is suggested that the center is an intrinsic defect or an exciton. In undoped $SrTiO_3$ an emission band in the visible—2.175 eV (77 K), 2.475 eV (4 K)—and its excitation spectrum are reported. The temperature dependence of both are anomalous. In contrast to the infrared emission, it is broad (half-width 0.63 eV) and structureless. Application of a dc electric field ~100 V/cm, at 4 K, induces oscillations in time of the visible emission, a property not shared by the I.R. emission.

INTRODUCTION

DURING the past 15 years numerous physical properties of $SrTiO_3$, mostly intrinsic, have been measured. Data and a bibliography have been compiled by Beals.[1] Photoluminescent and photoconductive properties have received little attention in spite of the fact that, according to our experience, these properties are marked.[2,3] Weber and Schaufele[4] have used the fluorescence of Eu^{3+} in $SrTiO_3$ as a tool to investigate the lattice vibrational spectrum of $SrTiO_3$. These workers also used the same system under pulsed excitation to study the decay modes of the Eu^{3+} fluorescence.[5] Similarly, Yamamoto *et al.*[6] have investigated the vibronic structure in fluorescence of some rare-earth ions in $SrTiO_3$ as well as other perovskites. Yasunaga and Nakada[7] have published two notes on photoconductivity in $SrTiO_3$. A preliminary report[3] on some aspects of photoluminescence and photoconductivity in undoped $SrTiO_3$ deals with oscillations in time, caused by an electric field, of an emission in the visible and of the photocurrent. Stokowski and Schawlow[8] first reported the emission of a narrow line in the infrared which occurs at the same wavelength for both undoped and chromium-doped crystals of $SrTiO_3$. The addition of Cr enhances the line significantly.[9] Similar results are obtained by the addition of Sm.[9] Stokowski and Schawlow note a splitting of this line at low temperature and relate the magnitude of the splitting, as a function of temperature, to the cubic-to-tetragonal phase transition[10] temperature at 110 K. In his experiments on undoped $SrTiO_3$, Sihvonen[11] found, besides the line reported by Stokowski and Schawlow, additional structure and showed a correlation between the intensity of the infrared emission (photocurrent) and the phase transitions in $SrTiO_3$.

The present work began when, independent of the other workers, we also noticed the infrared emission in undoped $SrTiO_3$. Following the report of Stokowski and Schawlow[8] the work was extended to Cr- and Sm-doped crystals.[12] In this report we wish to present the results of this laboratory with $SrTiO_3$ as far as some photoluminescent and photoconductive properties are concerned. It supplements and extends previous work and, as will be seen, differs in the matter of interpretation from Sihvonen's.

EXPERIMENTAL EQUIPMENT AND TECHNIQUES

The $SrTiO_3$ single crystals were either purchased from the National Lead Company or grown in this laboratory. The doping levels given are nominal. An emission spectrochemical analysis of a typical undoped

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[1] M. Douglas Beals, Internal Report, National Lead Co., Research Laboratory, South Amboy, N. J. (unpublished).

[2] L. Grabner, M. I. Cohen, and R. F. Blunt, Bull. Am. Phys. Soc. **11**, 86 (1966).

[3] L. Grabner, in *Interaction of Radiation with Solids*, edited by Adli Bishay (Plenum Press, Inc., New York, 1967), p. 155.

[4] M. J. Weber and R. F. Schaufele, Phys. Rev. **138**, A1544 (1965).

[5] M. J. Weber and R. F. Schaufele, J. Chem. Phys. **43**, 1702 (1965).

[6] Hajime Yamamoto, Shoji Makishima, and Shigeo Shionoya, J. Phys. Soc. Japan **23**, 1321 (1967).

[7] H. Yasunaga and I. Nakada, J. Phys. Soc. Japan **22**, 338 (1967); **24**, 218 (1968).

[8] S. E. Stokowski and A. L. Schawlow, Bull. Am. Phys. Soc. **11**, 886 (1966).

[9] S. E. Stokowski (private communication).

[10] Farrel W. Lytle, J. Appl. Phys. **35**, 2212 (1964).

[11] Y. T. Sihvonen, J. Appl. Phys. **38**, 4431 (1967).

[12] L. H. Grabner, Bull. Am. Phys. Soc. **12**, 1069 (1967).

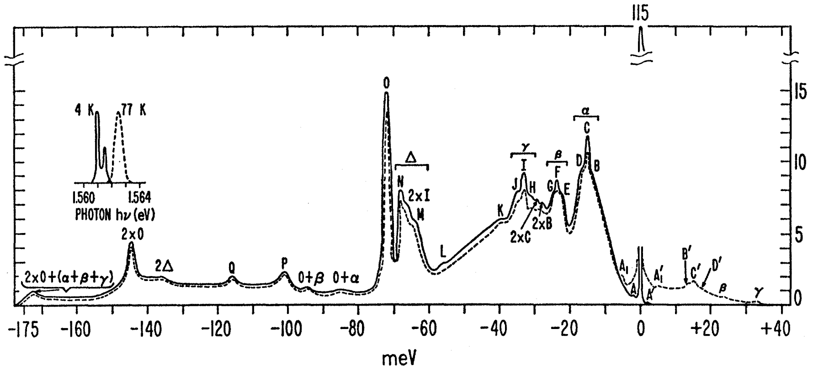

FIG. 1. Photoluminescence spectrum of $SrTiO_3$:0.005%Cr at 4 and 77 K. Photon energies are plotted with respect to zero-phonon line shown in inset. Intensities are about equal at 4 and 77 K. At 77 K, undoped $SrTiO_3$ and $SrTiO_3$:0.05%Sm give identical spectra as the Cr-doped specimen, but less intense by a factor of 400 and 20, respectively; at 4 K only very weak emission at the zero-phonon line remains. Letters label vibronics due to single and multiple phonon creation and annihilation. For example: 0, vibronic; 2×0, vibronic due to two-phonon creation of vibronic labeled as 0; 0+α, vibronic due to creation of 0 and α, the latter a group of vibronics which are unresolved.

sample yielded (ppm atomic):

Al	60–600	Li	<20
Ba	100–1000	Mg	8–80
Ca	50–500	Na	8–80
Cu	3–30	Rb	<2
Fe	30–300	Si	<7
K	<5		

Any other cation impurities were not present in concentrations larger than ~1 ppm, the lower limit of emission spectrochemical analysis. Specimens were cut to dimensions of approximately 1×5×10 mm, polished and etched. For the emission spectra, the exciting source was a 200-W high-pressure Hg arc lamp focused by quartz lenses on the sample to give an f/0.5 illumination aperture. The exciting radiation was filtered by a $CuSO_4$ solution (250 g/l, 2-cm path) contained in a quartz vessel. The emission, measured in a reflection geometry, was focused onto the slit of a monochromator (f/7) using a 1200 lines/mm diffraction grating blazed at 7500 Å. Before entering the monochromator the emission was filtered by a Schott RG9 (5 mm) glass filter, a long-wave-pass filter with negligible transmission ($<10^{-3}$%) below 7000 Å. For detection, a cooled photomultiplier with an S-1 response working into a preamplifier and phase-sensitive detector was used. For the excitation spectra, the total emission passed by the RG-9 filter was measured using as an exciting source a 450-W xenon arc lamp. The monochromator used was either the previously mentioned one using an 1800 lines/mm grating blazed at 5000 Å or a double monochromator using light flint prisms. The output of the monochromator was filtered by the $CuSO_4$ solution described previously. Contacts in the photoconductivity measurements were of melted indium. Lifetimes were measured in the usual manner; the flashtime of the xenon flash lamp used was 5×10^{-6} sec.

RESULTS AND DISCUSSION

A. Infrared Emission

Figure 1 shows the emission spectrum of $SrTiO_3$: 0.005% Cr at 4 and 77 K, respectively. The intensity of the emission at 4 and 77 K are equal within a factor of 2. At 77 K the spectra of undoped $SrTiO_3$ and $SrTiO_3$:0.05% Sm are identical with that shown in Fig. 1; the intensity, however, is uniformly reduced compared with $SrTiO_3$:Cr by a factor of 400 (undoped) and 20 ($SrTiO_3$:Sm). At 4 K, contrary to the Cr-doped sample, undoped $SrTiO_3$ and $SrTiO_3$:Sm show only very weak fluorescence at the principal line (1.561 eV, henceforth referred to as the zero-phonon line). In the case of $SrTiO_3$:Sm, the zero-phonon line rides on top of a background which we assume to be fluorescence due to the Sm. The spectrum shown in Fig. 1 is very similar to that found by Sihvonen[11] on undoped $SrTiO_3$, but is richer in detail. The splitting of the zero-phonon line, seen at 4 K, was previously reported by Stokowski and Schawlow[8] who find, in addition, that the energy difference between the two lines varies at T_c-T, where $T_c\approx110$ K, the temperature of the phase transition between the cubic and tetragonal phase. Experiments between 80 and 120 K again showed identical spectra for undoped, and Cr- and Sm-doped samples. However, in tracking the position of lines A_1 and A_1' with respect to the zero-phonon lines as a function of temperature above 80 K, both were found to be insensitive to temperature and disappeared above the 110 K phase transition. In agreement with Sihvonen,[11] we find an increase of the peak intensity of the zero-phonon line in undoped $SrTiO_3$ as the temperature increased from 88 to 110 K. In addition to $SrTiO_3$: 0.005% Cr, the emission spectrum of $SrTiO_3$:0.1% Cr was taken at 77 and 4 K. The spectrum is that shown in Fig. 1 but is a factor of 200 less intense than that of $SrTiO_3$:0.005%. Measurement of the absorption coefficient of $SrTiO_3$:0.1% Cr shows that the decrease of intensity is caused by the absorption of the emission line in the Cr absorption band to be discussed later. We find that in the heavily doped sample, the Cr absorption band extended further into the infrared than in the lightly doped sample, such that an overlap of the Cr absorption band with the emission reduced the latter. Similarly, a drastic reduction of the intensity of emission was also noticed in reduced and niobium-doped samples. Nb doping and reduction introduce free carriers. Free carrier absorption[13] in the region of emission reduces the intensity of fluorescence. For example, a Nb-doped sample containing 5×10^{18} electrons/cm^3 did not show emission. According to Baer[13] the free carrier absorption at 1.56 eV of a sample containing 5×10^{18} electrons/cm^3 is 30 cm^{-1}, which accounts for the result. Accordingly, all undoped samples were well oxidized. Neither the Cr- or Sm-doped samples showed significant carrier concentration.

We interpret[12] the emission spectrum shown in Fig. 1 as the emission of a zero-phonon line and satellite lines due to the creation or annihilation of one or more phonons (vibronics). Vibronic transitions can involve either lattice phonons or localized vibrational modes. We propose that the spectrum shown in Fig. 1 can be explained as being principally due to vibronics involving lattice phonons. To demonstrate this we first present Fig. 2 which is a compilation of data on the lattice vibrational spectrum of SrTiO$_3$ determined by Cowley[14] and other workers. Peaks in the vibronic spectrum are expected to appear at energies where there is a high density of phonon states within a narrow energy range as shown by the formulas for the one-phonon vibronic amplitude $I(\omega)$ at frequency ω from the zero-phonon line

$$I(\omega)\propto\rho(\omega)\begin{Bmatrix}\bar{n}(\omega)\\ \\ \bar{n}(\omega)+1\end{Bmatrix},$$

where $\rho(\omega)$ is the phonon density of states (frequency distribution), $\bar{n}(\omega)$ is the Bose statistical factor

$$[\exp(\hbar\omega/kT-1)]^{-1},$$

and $\bar{n}$ or $\bar{n}+1$ involve the process of phonon annihilation or creation, respectively. A high density of states occurs at points in the Brillouin zone where the energy versus q curves have zero slope. These are listed in Table I (unbracketed). Inspection of Fig. 1 shows vibronics due to both phonon annihilation and creation, the latter in single- and multiple-phonon creation. Our identification of the vibronics is shown in Table I (bracketed). Agreement of our assignments with the data summarized in Fig. 2 is quite satisfactory. Beyond that, however, we call attention to our assignment of the higher-energy vibronics M, O, and Q of Fig. 1 to zone boundary phonons which have not been reported so far. The reasonable agreement of some of the low-energy vibronics with zone boundary phonons, well-established by neutron diffraction[14] (see Fig. 2), gives us some confidence in our assignment of the vibronics M, O, and Q to zone boundary phonons.

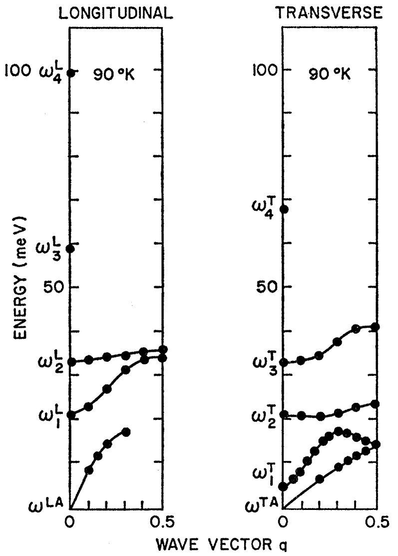

FIG. 2. Summary of reported data on lattice phonon spectrum of SrTiO$_3$. Phonon dispersion curves are from Cowley (Ref. 14). Remaining points at $q=0$ from W. G. Spitzer *et al.* [Phys. Rev. **126**, 1710 (1962)] and A. S. Barker, Jr. [Phys. Rev. **145**, 391 (1966)]. The wave vector is along the [100] direction.

At first sight one is inclined to identify A (2 meV) and A_1 (5 meV) as $q=0$ phonons of the temperature-dependent[14] lowest transverse-optic branch ω_1^T, the so-called "soft" or "ferroelectric" mode, at 4 and 77 K, respectively. As previously mentioned, we find the energy of A_1 with respect to the zero-phonon line to be insensitive to temperature in the range 80–110 K, and that A_1 disappears above 110 K, the cubic-tetragonal phase-transition temperature. Such behavior is inconsistent with a $q=0$ soft mode. A similar situation exists for the line A. Initially, it was thought to be the soft mode

TABLE I. Identification of vibronics (bracketed) of Fig. 1 with points of zero slope shown in Fig. 2.

q \ ω(meV)	[a] ω^{TA}	[a] $\omega_1{}^T$(90 K)	[a] $\omega_2{}^T$	[a] $\omega_3{}^T$	[b] $\omega_4{}^T$
0	0	5.2	21.1 (22.0 E)	32.9 (31.0 H)	67.4 (67.8 N)
0.3		17.4 (16.5 D)			
0.5	14.5 (15.0 C)	14.5 (15.0 C)	23.6 (23.8 F)	40.7 (39.5 K)	(72.0 O)
	[a] ω^{LA}	[a] $\omega_1{}^L$	[a] $\omega_2{}^L$	[c] $\omega_3{}^L$	[c] $\omega_4{}^L$
0	0	21.1 (22.0 E)	32.9 (31.0 H)	58.1 (57.0 L)	99.3 (10.0 P)
0.5		33.9 (33.0 I)	36.0 (35.0 J)	(64.0 M)	(116.0 Q)

[a] R. A. Cowley, Phys. Rev. **134**, A981 (1964).
[b] W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. **126**, 1710 (1962).
[c] A. S. Barker, Jr., Phys. Rev. **145**, 391 (1966).

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[13] W. S. Baer, Phys. Rev. **144**, 734 (1966).

[14] R. A. Cowley, Phys. Rev. **134**, A981 (1964).

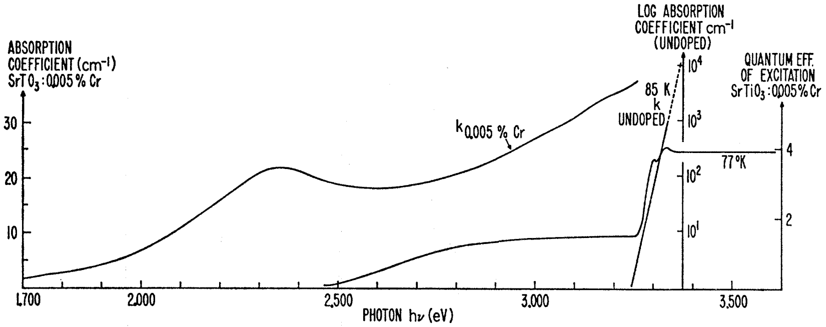

FIG. 3. Spectral dependence of external quantum efficiency (relative) for the excitation of the I.R. emission of $SrTiO_3$:Cr and its absorption coefficient (linear scale) at 77 K. The absorption coefficient of undoped $SrTiO_3$ is also plotted (logarithmic scale) for 85 K using the data of Cohen and Blunt (Ref. 17). External quantum efficiency = number of photons in emission/number of photons in excitation.

$\omega_1{}^T$ at $q=0$ at 4 K. However, Worlock and Fleury[15] in their experiments on the electric-field-induced Raman spectrum in $SrTiO_3$ at 8 K find A (as well as A_1) in the intrinsic (zero-field) Raman spectrum. Their experiments, however, demonstrate that A is not the soft mode but that it is located, instead, at 1.4 meV at 8 K. We suggest that A and A_1 may originate from localized phonons at twin boundaries: Above 110 K, in the cubic phase, the crystal is homogeneous; below 110 K the crystal is tetragonal but not homogeneous. It consists of a twin structure; the width of the twin lamellae is 10–30 μm, and the twin boundaries run parallel to the [110] direction.[10,16] As for the remaining peaks which have not been identified, namely, B (13.0 meV) and G (24.8 meV), we remark that either localized modes or phonons from points of the Brillouin zone other than the singular points selected will contribute to the vibronic spectrum. In addition, phonons from directions other than the [100] direction, the only direction for which data are available, will also contribute. In fact, we are surprised that most of the vibronics can be accounted for reasonably well by phonons from only one direction in the Brillouin zone.

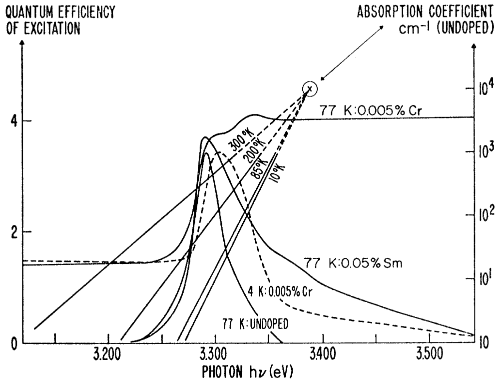

FIG. 4. Spectral dependence of external quantum efficiency for the excitation of the I.R. emission of undoped $SrTiO_3$ and $SrTiO_3$:Sm at 77 K, and $SrTiO_3$:Cr at 77 and 4 K. The complete curve for the latter is shown in Fig. 3 which is also valid at 4 K except in the region shown in the above figure. The external quantum efficiency for all curves is normalized at 2.290 eV. At 3.290 eV it is five times larger for $SrTiO_3$:Cr than for undoped $SrTiO_3$ and $SrTiO_3$:Sm which have equal external quantum efficiencies at 3.290 eV. The absorption coefficient of undoped $SrTiO_3$ is also plotted (logarithmic scale) using the data of Cohen and Blunt (Ref. 17).

As to the connection with other work, we mention that of Weber and Schaufele[4] on the vibronic spectrum of Eu^{3+} in $SrTiO_3$ as pertinent to ours. From a knowledge of the electronic transition in Eu^{3+}, these authors derive vibronic selection rules. Their vibronic data are fitted using zone-center phonons only. Vibronics due to zone boundary phonons are not observed in spite of the fact that most of them are allowed. In contrast: We cannot derive vibronic selection rules because, as will be shown later, we do not know the identity of the emitting center, let alone the states involved in the electronic transition. Further, our vibronic spectrum is richer, involving phonons at the center and boundary of the Brillouin zone. Finally, it is striking that our vibronic spectrum involves all the phonons except the "soft"-mode $q=0$ phonon which is either absent or very weak in our emission spectrum but is the strongest vibronic in $SrTiO_3$:Eu^{3+}.

B. Excitation Spectrum of the I.R. Emission

The excitation spectrum, at 77 K, of $SrTiO_3$:Cr is shown in Fig. 3, together with the absorption spectrum of this sample as taken by us, and the absorption spectrum of undoped $SrTiO_3$ as reported by Cohen and Blunt.[17] At 4 K the quantum efficiency and the excitation spectrum are unchanged except in the region of intrinsic absorption as shown in Fig. 4. Three notable facts emerge from these figures. First, the I.R. emission is excited in only one of the Cr absorption bands. Secondly, the quantum efficiency increases significantly in passing into the region of intrinsic absorption, which region, incidentally, coincides with the onset of the production of free charge carriers, known from monitoring the photocurrent. Finally, we call attention to the difference of the results at 77 and 4 K, respectively. At 4 K the quantum efficiency drops rapidly in the region of intrinsic absorption, whereas at 77 K it remains constant.

A question that presents itself is: Is the excitation in the region of intrinsic absorption essentially connected

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[15] J. M. Worlock and P. A. Fleury, Phys. Rev. Letters **19**, 1176 (1967).

[16] Estro Sawaguchi, Atsushi Kikuchi, and Yoichi Kodera, J. Phys. Soc. Japan **18**, 459 (1963).

[17] M. I. Cohen and R. F. Blunt, Phys. Rev. **168**, 929 (1968).

with Cr or is it an independent excitation process? If it is an independent excitation process, it should also be effective in undoped $SrTiO_3$ and $SrTiO_3$:Sm. That this is not the case is demonstrated in Fig. 4.

Figure 4 shows the excitation spectrum of undoped $SrTiO_3$ and $SrTiO_3$:Sm at 77 K. In contrast to $SrTiO_3$:Cr (77 K), these results show excitation only in the immediate region of intrinsic absorption with a reduction of the quantum efficiency by a factor of 5. At 4 K the emission is too weak to record an excitation spectrum, in contrast to $SrTiO_3$:Cr (4 K) which shows a quantum efficiency comparable with that of $SrTiO_3$:Cr (77 K) except well inside the region of intrinsic absorption.

The temperature dependence of the excitation spectrum of undoped $SrTiO_3$ is shown in Fig. 5. These curves were better fitted by three Gaussian curves than by two. Independent of temperature the peak heights are at 3.231, 3.258, and 3.283 eV, and have a half-width of 30 meV. In the excitation spectrum at 77 K, not shown in Fig. 5, the lower-energy band is barely noticeable.

Finally, Fig. 6 shows a simultaneous measurement of the excitation spectrum and the spectral response of photocurrent of undoped $SrTiO_3$. It should be noticed that the maximum of the excitation spectrum coincides with a minimum of the photocurrent. In this connection it should be mentioned that the spectral response of photocurrent shown in the figure can only be obtained under special conditions of illumination: The sample must be nonuniformly illuminated in that light and be kept away from the contacts as shown in inset (a) of Fig. 6. If the sample is uniformly illuminated between the contacts as shown in inset (b), the spectral response is very different: It follows exactly the excitation curve of the visible emission to be discussed later (see Fig. 8), and the photocurrent is orders of magnitude larger.

It is difficult to assimilate the data presented on the excitation spectra in terms of current models. Nevertheless, the following comments may be useful. Consider the result that the excitation spectra and quantum efficiency of undoped, Sm-doped, and Cr-doped $SrTiO_3$ differ in spite of identical emission spectra. This suggests energy transfer[18,19] from a "sensitizer," Cr or Sm in this case, to a common unspecified "activator." However, the increase of quantum efficiency in $SrTiO_3$:Cr which occurs when the region of intrinsic absorption is approached (see Figs. 3 and 4) points to the participation of free or trapped charges, generated by photoexcitation, in the excitation process. From electron-spin-resonance work Müller[20] has identified Cr as Cr^{3+} in $SrTiO_3$ and has pointed out that it very likely substitutes for Ti^{4+} on the basis of ionic radii. It is not known if the energy levels of Cr^{3+} lie between the highest valence band and lowest conduction band (energy gap) or not. Be that as it may, the participation of photogenerated carriers in the excitation process in $SrTiO_3$:Cr is perhaps understandable in terms of the trapping of a photogenerated electron in the conduction band by a state of the Cr^{2+} ion which *does* happen to lie in the energy gap and from which energy is then transferred to the "activator" (charge transfer band).

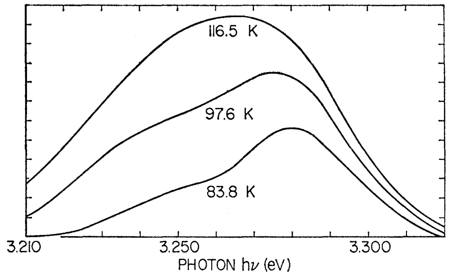

FIG. 5. Temperature dependence of the spectrum of external quantum efficiency for excitation (relative) of the I.R. emission of undoped $SrTiO_3$. Each curve is composed of two bands; the lower-energy band is increasing in intensity relative to the higher-energy band as the temperature increases. At 77 K (not shown) the lower-energy band is hardly noticeable.

Another point raised by the experiments on $SrTiO_3$:Cr is the absence of the so-called "*R* line." Our absorption spectrum (Fig. 3) is in good agreement with Müller's. He identifies the lower-energy band of the absorption spectrum as the $^4A_2 \rightarrow {}^4T_2$ transition, the higher-energy band as the $^4A_2 \rightarrow {}^4T_1$ transition. From the Tanabe-Sugano[21] calculations of the splitting of states of the d^3 configuration (Cr^{3+}) by an octahedral field, the *R* line is not expected to shift very much as

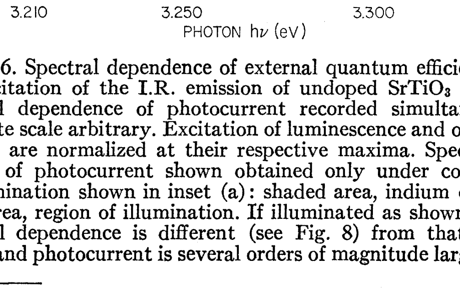

FIG. 6. Spectral dependence of external quantum efficiency for the excitation of the I.R. emission of undoped $SrTiO_3$ and the spectral dependence of photocurrent recorded simultaneously. Ordinate scale arbitrary. Excitation of luminescence and of photocurrent are normalized at their respective maxima. Spectral response of photocurrent shown obtained only under conditions of illumination shown in inset (a): shaded area, indium contact; dark area, region of illumination. If illuminated as shown in (b), spectral dependence is different (see Fig. 8) from that shown above and photocurrent is several orders of magnitude larger.

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[18] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

[19] R. Orbach, in *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Interscience Publishers, Inc., New York, 1967), p. 445.

[20] K. A. Müller, in *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962*, edited by W. Low (Academic Press Inc., New York, 1963).

[21] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 753 (1954).

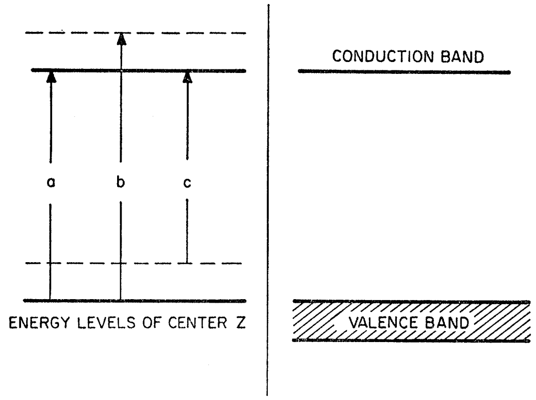

FIG. 7. Proposed model for excitation of I.R. emission in undoped $SrTiO_3$. The electronic energy levels of a "center Z," its phonon "sidebands," and a diagram of the electronic energy bands of $SrTiO_3$. It is postulated that the center Z is decoupled from the electronic energy bands and that excitation into the zero-phonon level of Z is suppressed by competition due to intrinsic absorption, but that excitation, with phonon cooperation, in which a phonon is annihilated, may be competitive because of the rapidly decreasing intrinsic absorption coefficient. (a): zero phonon absorption, (b): absorption with phonon creation, (c): absorption with phonon annihilation.

Cr^{3+} changes crystal environment. Thus, in ruby ($Al_2O_3:Cr^{3+}$), the $^2E \rightarrow {}^4A_2$ transition (R line) occurs at 6943 Å; in $MgO:Cr^{3+}$, at 6891 Å.[22] By analogy, R-line fluorescence in $SrTiO_3:Cr^{3+}$ is expected around 7000 Å. It might be thought that the I.R. emission in $SrTiO_3$ (zero-phonon line 7935 Å) is the R-line fluorescence and is due to Cr^{3+} as an impurity. According to the above argument, however, the wavelength of the I.R. emission is not that expected from R-line emission. Stronger evidence will be summarized later to show that the I.R. emission cannot be R-line emission.

Regarding the excitation spectrum of undoped $SrTiO_3$ (Figs. 4 and 5), we consider the following two points significant: (a) cutoff on the high-energy side at an intrinsic absorption coefficient of about 10 cm^{-1}, the onset of strong "band-to-band" absorption, and (b) drastic drop of fluorescence in going from 77 to 4 K. The first observation argues against the emission as being due to recombination radiation of a free charge, say, an electron, with a trapped charge (hole) as suggested by Sihvonen[11] since our experiments on photoconductivity show that free charge carriers are produced well beyond the energy at which excitation begins (see Fig. 8). In addition, two other points argue against the emission being due to recombination radiation. First, the half-width of the zero-phonon line is small (0.5 meV) compared to kT (7 meV) at 77 K; secondly, it is difficult to explain observation (b) under such an assumption since free and trapped charges are produced as well at 4 as at 77 K. We shall therefore assume that a "center," decoupled from the electronic energy bands, is responsible for the emission. As to observation (b), it then becomes tempting to ascribe it to a change of selection rule attributable to phase changes which $SrTiO_3$ is known to undergo as the temperature is lowered.[10] The phases are as follows: $T > 110$ K cubic (O_h), 110 K$>T>$65 K tetragonal, (D_{4h}), 65 K$>T>$35 K orthorhombic (D_{2h}), and $T < 35$ K possibly rhombohedral. However, the foregoing argument does not seem convincing because in going from higher to lower symmetry a forbidden transition usually becomes allowed, not the converse. An example of this in $SrTiO_3:Eu^{3+}$ is given by Weber and Schaufele[5]: Above 110 K the $^5D_0 \rightarrow {}^7F_2$ transition is forbidden and unobserved; below 110 K it is allowed and observed. We therefore reject the explanation that observation (b) is due to a change of selection rule caused by a change of phase.

We suggest that observations (a) and (b) can be qualitatively understood, using the following model. We assume a center Z decoupled from the electronic energy bands. As shown in Fig. 7, we also assume that the energy required to excite Z lies in a region of large intrinsic absorption coefficient, say, 100–1000 cm^{-1}, corresponding to band-to-band excitation. Associated with Z there is a zero-phonon line with absorption coefficient α_z. Since optical absorption is additive, the intrinsic absorption with absorption coefficient α_i will compete with "center" absorption α_z. We shall assume that $\alpha_i \gg \alpha_z$ at all temperatures. As shown in Fig. 7, if this is the case for the zero-phonon line, it is *a fortiori* so for absorption in Z with phonon cooperation in which a phonon is simultaneously *created.* However, absorption in Z with the simultaneous *annihilation* of phonon will shift to energies which are less than that of the zero-phonon line where competition against α_i rapidly becomes more favorable because of the steepness of α_i versus photon energy (see Fig. 4). We suggest then that the excitation spectrum of undoped $SrTiO_3$ shown in Fig. 5 represents the excitation of two-phonon sidebands (vibronics) in phonon annihilation and that the emission vanishes at 4 K because of the absence of a phonon population at that temperature. The competition between the localized center (decoupled from the electronic energy bands) and "intrinsic absorption" is illustrated in Fig. 6, which shows a *minimum* in the spectral response of photoconductivity at a *maximum* of the excitation spectrum. This result asserts that the center Z and the electronic energy bands are decoupled, for if they were strongly coupled, as they are in the free and bound excitons of the II–IV compounds, for example, a maximum in the photoconductivity spectrum would coincide with a maximum of the excitation spectrum as shown, for example, by Park and Reynolds[23] on CdS, who find coincidence of peaks in the spectral response of photoconductivity with absorption maxima due to free and bound excitons. Mention should also be made of the possibility that the zero-phonon line is

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[22] G. F. Imbush, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, Phys. Rev. **133**, A1029 (1964).

[23] Y. S. Park and D. C. Reynolds, Phys. Rev. **132**, 2450 (1963).

forbidden and that a vibronic of the zero-phonon line is allowed. An example is the $^5D_0 \rightarrow {}^2F_2$ transition in $SrTiO_3:Eu^{3+}$, mentioned previously, which is forbidden above the 110 K phase transition but allowed below; indeed, above 110 K the zero-phonon line is not observed but the vibronics are.[4] In such an event we would find it necessary to modify $\alpha_i \gg \alpha_z$ to $\alpha_i \gg \alpha_z$ (phonon creation), since phonons can be created even at low temperatures. We want to point out that an apparent difficulty for our model is presented by Sihvonen's[11] results on the temperature dependence of the emission and photoconductivity. In the emission versus T, Sihvonen finds two maxima, at 100 and 35 K; in the photoconductivity versus T, a maximum at 110 K and a minimum at 35 K. At first sight there does not seem room in our model to explain this observation. The model apparently asserts that the emission decrease with vibronic phonon population and hence with temperature. However, in the proposed mechanism two effects compete: intrinsic absorption and the phonon population in the vibronics. Both change with temperature (for the intrinsic absorption see Fig. 4). Thus, as the temperature is lowered, a decrease of intrinsic absorption at the energy of a vibronic can "uncover" a phonon sideband and it can be seen that the emission need not decrease monotonically. Nevertheless, the fact that the maxima occur at physically unique points, 110 K, the cubic → tetragonal phase transition, and 35 K, the so-called "para → ferroelectric" transition temperature, argues against our mechanism since these temperatures are not in any way unique in the proposed mechanism.

C. Visible Emission and Excitation in Undoped $SrTiO_3$

In addition to the infrared emission discussed so far, we wish to outline some properties of an emission band in the visible[2,3,11] which is a property of all undoped $SrTiO_3$ specimens that we have investigated. The emission spectrum is shown together with its excitation spectrum and the spectral response of photoconductivity in Fig. 8 at 4 and 77 K, respectively. The spectral response of photoconductivity is measured under uniform illumination as shown in inset (b) of Fig. 6, in contrast to the spectral-response measurements of photoconductivity shown in Fig. 6 which were measured under nonuniform illumination as shown in inset (a) of that figure.

The following observations may be of significance: The emission is a factor of 100 more intense at 4 than at 77 K and has the unusual property of oscillating in intensity[2,3] when a dc electric field is applied—most easily observed at 4 K. This property is not shared by the infrared emission and is accompanied by oscillations of the photoconductivity. At 4 K the threshold of the dc electric field which initiates oscillation is small, of the order of 100 V/cm, and decreases with the intensity of the exciting radiation. The frequency of the oscillations (observed only by eye so far, hence 10-Hz upper limit) increase with the intensity of the exciting radiation. This phenomenon is now under study and is mentioned in such preliminary form because it is a characteristic of the visible emission.

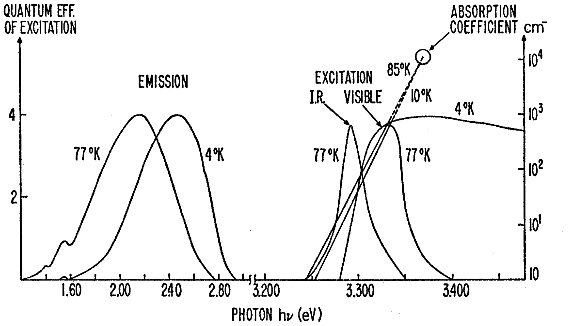

FIG. 8. Visible emission and its external quantum efficiency (relative) for excitation of undoped $SrTiO_3$ at 4 and 77 K. The spectral response of photocurrent is identical with that of the external quantum efficiency for excitation. The photocurrent was measured using the mode of illumination shown in inset (b) of Fig. 6. Excitation of the I.R. emission is shown for comparison. Emission and excitation spectra are normalized at their respective maxima. At 4 K the visible emission and photocurrent are about 100 times more intense than at 77 K.

The congruence of the excitation spectrum and the spectrum of photocurrent suggests the emission to be due to recombination radiation from the recombination of a free with a trapped charge carrier. However, the temperature dependence of both the emission and the excitation of emission are anomalous—emission: the large shift of the band with temperature (0.3 eV); excitation: decrease of excitation at high energies at 77 compared with 4 K. It will also be noticed that the emission spectrum at 4 K is skewed instead of bell-shaped, a result also noted by Sihvonen[11] at 24 K. As far as the emission is concerned, typically the spectral response of recombination radiation is not very sensitive to temperature. Random examples from the literature are Zn:Cu[24] and the so-called "blue" emission of TlCl.[25] As for the excitation spectrum, the contrast between the results at 4 and 77 K cannot be assimilated in a picture in which a photon is converted to a free-electron–hole pair of which one is trapped to subsequently recombine with the other. Note that the temperature dependence of the excitation spectrum of the visible emission is opposite to that found for the analogous data on the infrared emission in $SrTiO_3:Cr$ (see Fig. 4). In that case the temperature dependence of the excitation is such that it is constant beyond the "band edge" at 77 K and drops at higher energies at 4 K.

Finally, we would like to comment briefly on the differences obtained in the spectral response of photocurrent, depending on whether the area between the contacts is uniformly [inset (b), Fig. 6] or nonuni-

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[24] C. C. Klick, J. Opt. Soc. Am. **41**, 816 (1951).

[25] V. A. Sokolov, Opt. i Spektroskopiya **21**, 98 (1966) [English transl.: Opt. Spectry. (USSR) **21**, 53 (1966)].

formly illuminated [inset (a)]. The results obtained are shown in Fig. 8 and Fig. 6, respectively. Moreover, as previously mentioned, uniform illumination gives photocurrents that are orders of magnitude larger than nonuniform illumination. We suspect that, in the case of uniform illumination, the spectral response is distorted by space-charge-limited currents, i.e., the injection of charge carriers from replenishing contacts into the solid,[26,27] and that keeping light away from the contacts, as is done when the sample is nonuniformly illuminated, suppresses carrier injection and therefore leads to a "true" spectral response of photocurrent. Space-charge-limited currents are expected to play a significant role in $SrTiO_3$ because of its large static dielectric constant[28] (300 K, 300; 77 K, 2×10^3; 4 K, 2×10^4). We hope to comment on this aspect of the work in the future.

D. Miscellaneous Results

Lifetimes

Infrared emission:

$SrTiO_3$:0.005% Cr (4 and 77 K) = 20×10^{-3} sec,

$SrTiO_3$:0.1% Cr (4 and 77 K) = 5×10^{-3} sec,

$SrTiO_3$ (77 K) = 20×10^{-3} sec.

Visible emission:

$SrTiO_3$ (4 K) = 0.5×10^{-3} sec.

We observe that the equality of the lifetimes, at 77 K, of undoped $SrTiO_3$ and $SrTiO_3$:0.005% Cr is not in conflict with the view that energy transfer from a "sensitizer" (Cr in this case) to an "activator" is involved in the excitation-emission process if the lifetime is determined by the activator. Further evidence for energy transfer is contained in the decrease of the lifetime when the concentration of Cr is increased. This may be a sign of "concentration quenching"[29] involving energy transfer, in this case activator → activator, and final transfer from activator to an energy sink competing with activator emission. The "energy sink" is assumed to be a defect induced by the Cr.

Quenching of the Infrared Emission by an Electric Field

A dc electric field of $\sim10^3$ V/cm quenches the infrared emission by about 40%. This observation was made on the zero-phonon line of undoped $SrTiO_3$ at 77 K. In our experimental arrangement, the electric field was limited to $\sim10^3$ V/cm by the large photocurrents generated by the photoexcitation of free charge carriers.

In line with the proposed mechanism for the temperature quenching of the infrared emission discussed previously, the field quenching is possibly caused by a Franz-Keldysh[30,31] effect in which the intrinsic absorption edge is shifted to lower energies by an electric field, thus increasing α_i with respect to α_x. The observations of Frova and Boddy,[32] however, are in disagreement with a Franz-Keldysh effect in perovskite-type ferroelectrics. Their results on the electroabsorption of $KTaO_3$, a material closely related to $SrTiO_3$, show that the application of an electric field displaces the edge to *higher* energies, i.e., opposite to the Franz-Keldysh effect. If this is the case in $SrTiO_3$, our mechanism would predict an enhancement of the emission rather than the quenching which is observed.

Polarization of the Infrared Emission

Measurements of the polarization of the zero-phonon line for $SrTiO_3$:Cr at 4 K, a doublet at this temperature, gave the following ratios of peak intensities of the low-energy component to the high-energy component: unpolarized, 1.4; polarized parallel to the [100] axis, 1.6; polarized perpendicular to the [100] axis, 1.1. The radiation was measured perpendicular to a {010} face. The directions refer to a room-temperature alignment of the specimen. These measurements were found to be insensitive to the polarization of the incident radiation.

E. Nature of the I.R. and Visible Emission "Centers"

As to the nature of the center responsible for the I.R. emission, our experiments suggest a tightly bound center, isolated from the electronic energy bands, such as typically arise from rare-earth ions in ionic crystals. In spite of the fact that we cannot identify the center, our data exclude Cr or Sm as the emitting center. We have previously argued that the emission is unlikely to be *R*-line emission from Cr^{3+} since it occurs at 7935 Å instead of around 7000 Å. Be that as it may, our principal reasons for rejecting Cr^{3+} as the emitting center are as follows: (1) the large difference of the intensity of emission between undoped and Cr-doped $SrTiO_3$ when the temperature is changed from 77 to 4 K (Cr-doped, small change, undoped, large change); at 4 K vanishing intensity of emission. (2) The excitation spectra of Cr-doped and undoped $SrTiO_3$ are grossly different (see Figs. 3 and 4).

Samarium is rejected as the emitting center because the excitation of $SrTiO_3$:Sm is different from that of undoped $SrTiO_3$.

We find that the quantum efficiency for excitation varies by a factor of about 10 in samples from different boules of undoped $SrTiO_3$. Experience shows that if

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[26] M. A. Lampert, Rept. Progr. Phys. (London) **27**, 329 (1964).

[27] F. Stöckmann, in *Halbleiterprobleme* (Vieweg, Braunschweig, 1961), Vol. 6, p. 279; Acta Phys. Austriaca **20**, 71 (1965).

[28] H. E. Weaver, J. Phys. Chem. Solids **11**, 274 (1959).

[29] D. L. Dexter and James H. Schulman, J. Chem. Phys. **22**, 1063 (1954).

[30] W. Franz, Z. Naturforsch. **13a**, 484 (1958).

[31] L. V. Keldysh, Zh. Eksperim. i Teor. Fiz. **34**, 1138 (1958) [English transl.: Soviet Phys.—JETP **7**, 788 (1958)].

[32] A. Frova and P. J. Boddy, Phys. Rev. **153**, 606 (1967)

the emission is due to an impurity, much wider variations of the emission intensity are the rule. We suspect, therefore, that the center is either an intrinsic defect or intrinsic per se, viz., an exciton. If an exciton[33] is involved, it cannot be of the Wannier type in which an electron and hole, as effective mass particles, are loosely bound by a Coulomb interaction screened by a static dielectric constant since the static dielectric constant is so large.[28] Nor is it likely to be a Wannier exciton bound to an impurity, even disregarding the large static dielectric constant, as suggested by Sihvonen[11] because the binding energy would be far too large—about one-half the band gap. Rather, the electronic structure of an exciton would be that of a tightly bound electron and hole in which, because of the rapid motion with respect to each other, they are screened by the optical instead of the static dielectric constant, in short, a Frenkel-like exciton. In fact, experience shows that the latter type is to be expected in predominantly ionic crystals, of which $SrTiO_3$ is an example.

Finally we wish to add that the large "Stokes shift" between excitation and emission (1.67 eV) in undoped $SrTiO_3$ cannot be attributed to a "Frank-Condon" shift in which the center and surrounding lattice have different configurations with respect to each other in absorption and emission. This is because the emission is a narrow line rather than the broad band expected if such relaxation were involved.

As to the nature of the center responsible for the visible emission, it is noteworthy that, here, too, we find that the quantum efficiency for excitation of samples from different boules of undoped $SrTiO_3$ are identical within a factor of 10 (checked only at 4 K). Therefore, the comments made in this connection with the I.R. emission also apply. The possibility of a connection between the I.R. and visible emission cannot be dismissed in our opinion—a surmise already advanced by Sihvonen.[11] It may not be fortuitous that the quantum efficiency of undoped $SrTiO_3$, for the visible and I.R. emission, is fairly insensitive to the boule from which the sample is taken and that the visible emission, at 77, is small compared to that at 4 K whereas the opposite is true for I.R. emission.

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It is a pleasure to thank Dr. M. Douglas Beals of the National Lead Company for his cooperation in providing samples of $SrTiO_3$, and the members of the Solid State Physics Section of the National Bureau of Standards for assistance and illuminating discussions.

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[33] R. S. Knox, Solid State Phys. Suppl. **5** (1963).