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

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

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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

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

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 mea-

surements[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

† Research supported by the Army Research Office, Durham.
* National Science Foundation Predoctoral Fellow.
[1] W. Cochran, Advan. Phys. 9, 387 (1960); 10, 401 (1961).
[2] P. W. Anderson, in *Proceedings of the All-Union Conference on the Physics of Dielectrics* (Academy of Sciences, Moscow, USSR, 1958), p. 290.
[3] R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. 59, 673 (1941).
[4] A. S. Barker, Jr., and M. Tinkham, Phys. Rev. 125, 1527 (1962).
[5] W. G. Spitzer, R. C. Miller, D. A. Kleinman, and T. E. Howard, Phys. Rev. 126, 1710 (1962).

[6] J. M. Worlock and P. A. Fleury, Phys. Rev. Letters 19, 1176 (1967).
[7] R. Bell and G. Rupprecht, Phys. Rev. 129, 90 (1963).
[8] L. Rimai and G. A. deMars, Phys. Rev. 127, 702 (1962).
[9] K. A. Müller, Phys. Rev. Letters 2, 341 (1959).
[10] F. W. Lytle, J. Appl. Phys. 35, 2212 (1964).
[11] O. N. Tufte and E. L. Stelzer, Phys. Rev. 141, 675 (1966).
[12] P. A. Fleury, J. F. Scott, and J. M. Worlock, Phys. Rev. Letters 21, 16 (1968).
[13] W. Kaiser and R. Zurek, Phys. Letters 23, 668 (1966).

is seen. The experiments of Unoki and Sakudo[14] indicate that the transition is from the space group O_h^1 to the nonferroelectric space group D_{4h}^{18} and that it is due mainly to a rotation of the TiO_6 octahedra. Recently, experimental evidence has been obtained by Fleury et al.[12] that the transition is characterized by a soft phonon at the corner of the Brillouin zone whose frequency tends toward zero.

In a previous paper,[15] the authors described the sharp-line fluorescence and absorption of impurity-doped and undoped $SrTiO_3$. It was shown that the sharp-line emission at 7935 Å seen from Cr-doped and undoped $SrTiO_3$ is probably due to the Cr^{3+} ion. It is reported herein that the energy of the R-line transitions of Cr^{3+} and Mn^{4+} in $SrTiO_3$ show large and unusual shifts with temperature and applied electric fields. We find that these energy shifts are related to the behavior of the soft optical mode of $SrTiO_3$.

II. EXPERIMENTAL

The $SrTiO_3$ single crystals were obtained from the National Lead Co. The Cr-doped samples had concentrations of Cr_2O_3 from 0.005 to 0.05 wt%. The Mn-doped sample had 0.01-wt% MnO_2. The equipment used for observing the fluorescence and absorption of $SrTiO_3$ samples was described in Ref. 15.

Electric fields were applied to the $SrTiO_3$ samples by means of evaporated titanium electrodes deposited in vacuum. The layer of titanium was made thin enough so that it has a transmission about 10% in the optical region. Gold wires were attached to the electrodes by means of a silver paste.

The fluorescence was excited by an Hg-arc source focused through the semitransparent electrodes. The sample was masked to ensure that the fluorescence occurred in the region of uniform electric field. The mercury source was filtered so that only light in the region 5000–4100 Å was incident on the crystal. This decreased the amount of photoconductivity considerably. However, even with this filtering there was a sufficient amount of photoconductivity present to allow charges to flow. The charges move so as to compensate for the electric field inside the crystal. They create a surface layer where the electric field is high, but the bulk of the material experiences a small electric field. The time constant associated with the movement of these charges was about 10 sec. Therefore, in order to keep a large electric field present in the material, it was necessary to apply the field at a frequency of 70 Hz instead of dc.

The intensity is a function, $I(\mathcal{E},\nu)$, of both electric field ($\mathcal{E}$) and photon frequency (ν). The desired result $I(\mathcal{E},\nu)$ at $\mathcal{E}=$ constant. Two different methods were used to obtain this result. In the first method $\mathcal{E}$ varies,

[14] H. Unoki and T. Sakudo, J. Phys. Soc. Japan 23, 546 (1967).
[15] S. E. Stokowski and A. L. Schawlow, preceding paper, Phys. Rev. 178, 457 (1969).

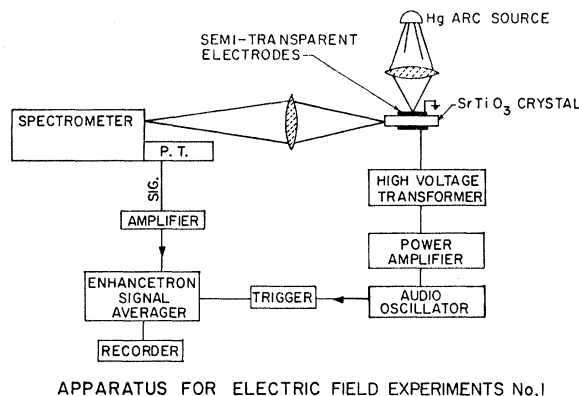APPARATUS FOR ELECTRIC FIELD EXPERIMENTS No.1

Fig. 1. Apparatus for electric field experiments.

but ν is kept constant. The intensity variation of the fluorescence at a given photon energy was measured through a cycle of the applied electric field. An Enhancetron signal averager was used to sum the intensity variation over many cycles. Figure 1 shows the experimental arrangement. The wavelength of the spectrometer was then varied point by point to give the spectrum as a function of electric field.

The second method essentially obtained $I(\mathcal{E},\nu)$ at constant $\mathcal{E}$ and varying ν. The fluorescence from the sample was chopped at 140 Hz, so that only when the 70-Hz field was at its maximum did light enter the detection system. Figure 2 shows the experimental arrangement. The signal and the reference from the audio oscillator were mixed by the PAR Model JB-5 phase-sensitive amplifier. This method gave $I(\mathcal{E},\nu)$ at the maximum of the 70-Hz electric field.

III. RESULTS

A. R-Line Shift versus Temperature

The temperature dependence of the average energy of the R lines is shown in Fig. 3. The R lines shift to higher frequencies as the temperature increases. There are several unusual features to be noted. First, a discontinu-
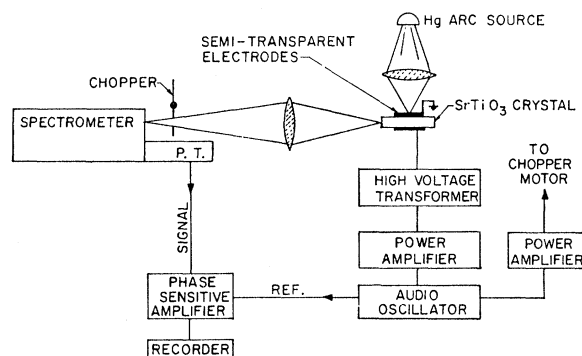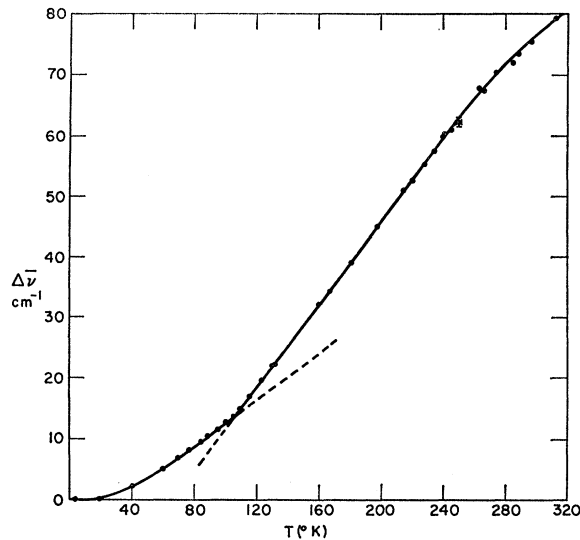

APPARATUS FOR ELECTRIC FIELD EXPERIMENTS No.2

Fig. 2. Apparatus for electric field experiments.

FIG. 3. Average position of the R lines of Cr^{3+} in $SrTiO_3$ versus temperature. At 4.2°K the average energy is 12 595.4 cm⁻¹. $[\Delta\bar{\nu}=\bar{\nu}(T)-\bar{\nu}(4.2°K).]$

ity in slope occurs at the transition temperature, $(107\pm1)°K$. The slope of the $\Delta\bar{\nu}$ versus T curve is 0.19 cm⁻¹/°K below 107°K and 0.34 cm⁻¹/°K above it. Second, the energy shift is linear in the temperature over a large range of temperatures. Finally, if the energy shift and the reciprocal dielectric constant $(1/\epsilon)$, as measured by Weaver,[16] are compared below 107°K, it is found that they have a similar temperature dependence. Therefore, below 107°K

$$E(T)-E(4.2°K)=\alpha\left(\frac{1}{\epsilon(T)}-\frac{1}{\epsilon(4.2°K)}\right), \quad (2)$$

where $E(T)$ is the energy of the R lines at temperature T and $\alpha=(1.83\pm0.05)\times10^4$ cm⁻¹ from our measurements. Thus, in this temperature region, the energy shift is proportional to the square of the soft-mode frequency, since $\epsilon\omega_s^2\cong$constant in $SrTiO_3$. Figure 4 demonstrates these features more dramatically. The solid line is a plot of $1/\epsilon$ and the dots are the experimental results for the line shift.

A comparison is made in Table I between the temperature shifts of the R line in MgO, Al_2O_3, and $SrTiO_3$. Note that the shift in $SrTiO_3$ is large and of opposite sign to that in the other substances.

The R line of Mn^{4+} in $SrTiO_3$ also shows a shift, but in the opposite direction to that of Cr^{3+}. Table II

TABLE I. Shift of the Cr^{3+} R line from 4.2 to 200°K (in cm⁻¹).

MgO	Al₂O₃	SrTiO₃
-8.4 [a]	-6.6 [b]	$+45$

[a] Reference 26.   [b] Reference 25.

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

compares the shifts for the two ions at different temperatures. Enough data have not been taken in order to determine if the Mn^{4+} R-line shift also follows the reciprocal dielectric constant. Nevertheless, since the temperature shift is much larger than for the same ion in Al_2O_3, and is comparable magnitude to that of Cr^{3+} in $SrTiO_3$, it seems likely that it also is influenced chiefly by the soft mode.

B. R-Line Shift with Electric Field

Figure 5 shows the actual experimental results of the electric-field shift of the R lines at 4.2°K. It will be noted that both lines move to shorter wavelengths as the field is increased. The observed hysteresis will be discussed later. By taking an average of the shift for increasing and decreasing electric fields, the results shown in Fig. 6 are obtained. Note that the shift is not linear in the field and, in fact, shows a different field dependence at the two temperatures 77 and 4.2°K. For comparison, the R lines in ruby shift 0.076 cm⁻¹ for an electric field of 10 kV/cm, and the shift is linear in the field at least up to 450 kV/cm.[17]

The R-line shift with field can also be compared to the change in dielectric constant. The field dependence of $1/\epsilon$ can be obtained by using a phenomenological thermodynamic theory first introduced by Devonshire.[18] The free energy per unit volume is expressed in terms of the temperature T and the macroscopic polarization P. We have, for one dimension,

$$A(T,P)=\tfrac{1}{2}\chi(T)P^2+\tfrac{1}{4}\xi(T)P^4+\cdots-EP, \quad (3)$$

where E is the macroscopic field inside the crystal. The free energy is minimized by setting $\partial A/\partial P=0$.
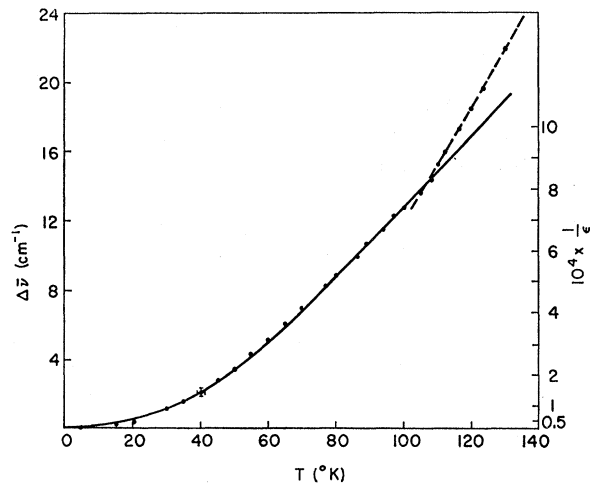

FIG. 4. Plot of $1/\epsilon$ versus temperature. The dots are the experimental points for the R-line shift versus temperature.

[17] A. A. Kaplyanskii and V. N. Medvedev, Fiz. Tverd. Tela **9**, 2704 (1967) [English transl.: Soviet Phys.—Solid State **9**, 2121 (1968)].
[18] A. F. Devonshire, Phil. Mag. **40**, 1040 (1949); Advan. Phys. **3**, 85 (1954).

The result is

$$\chi(T)P + \xi(T)P^3 - E = 0. \tag{4}$$

Assuming that $\epsilon \gg 1$ and differentiating by P again, we obtain

$$\frac{4\pi}{\epsilon}\frac{\partial E}{\partial P} \cong \chi(T) + 3\xi(T)P^2. \tag{5}$$

Solving Eqs. (3) and (4) for $1/\epsilon(\mathscr{E}) = \beta(\mathscr{E})$ in terms of the electric field ($\mathscr{E}$) we have,

$$\xi(3/4\pi)^3\mathscr{E}^2 = [\beta(\mathscr{E}) + 2\beta(0)]^2[\beta(\mathscr{E}) - \beta(0)]. \tag{6}$$

For large $\mathscr{E}$, Eq. (5) reduces to

$$\beta(\mathscr{E}) + \beta(0) \rightarrow (3/4\pi)(\xi\mathscr{E}^2)^{1/3}, \tag{7}$$

and for small $\mathscr{E}$,

$$\beta(\mathscr{E}) - \beta(0) \rightarrow (3\xi/64\pi^3)\epsilon^2(0)\mathscr{E}^2. \tag{8}$$

Figure 7 shows $\Delta\bar{\nu}$ plotted against $\epsilon(0)/\epsilon(\mathscr{E}) - 1$ using the value of $\xi = 6.9 \times 10^7$ $(cm^2/C)^2$ measured by Sawaguchi et al.[19] and Rupprecht et al.[20] The shift agrees well with the field dependence of the reciprocal dielectric constant, except that at 4.2°K the straight line drawn through the experimental points in Fig. 7 does not pass through zero. The reason for this is unknown, but the possible explanations for this include : (1) a spontaneous polarization induced by the application of the electronic field, or (2) residual fields due to trapped space charge in the sample.

$$\Delta\bar{\nu}(\mathscr{E}) = \alpha\left(\frac{1}{\epsilon(\mathscr{E},T)} - \frac{1}{\epsilon(0,T)}\right), \tag{9}$$

where $\alpha = (7.0 \pm 0.3) \times 10^3$ cm^{-1} for a field applied parallel to [001].

Note that

$$P^2 = \frac{4\pi}{3\xi}\left(\frac{1}{\epsilon(\mathscr{E})} - \frac{1}{\epsilon(0)}\right) \tag{10}$$
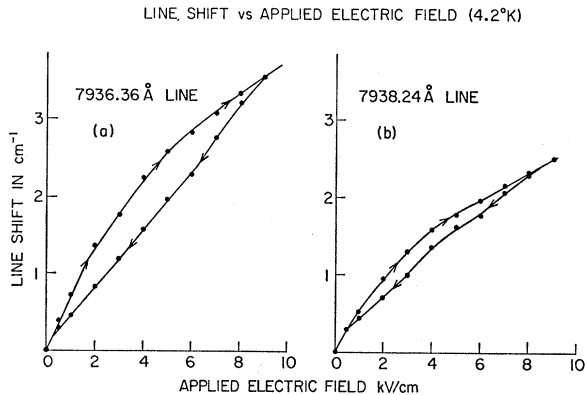
LINE SHIFT vs APPLIED ELECTRIC FIELD (4.2°K)

FIG. 5. Shift of the R lines versus applied electric field at 4.2°K.

[19] E. Sawaguchi, A. Kikuchi, and Y. Kodera, J. Phys. Soc. Japan 17, 1666 (1962).
[20] G. Rupprecht and R. O. Bell, Phys. Rev. 135, A748 (1964).

LINE SHIFT vs APPLIED ELECTRIC FIELD
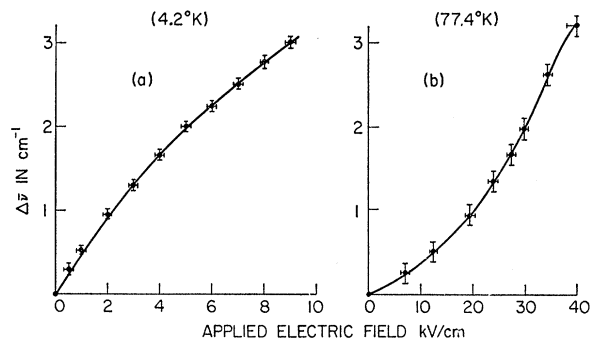

FIG. 6. Average shift of the center position of the R lines versus electric field.

from Eqs. (2)–(7). This relation shows that the R-line shift with electric field is proportional to the square of the polarization. Because the polarization induced by the field is partially ionic, there is a displacement of the Cr³⁺ with respect to its surrounding octahedron. Thus, these results indicate that the energy of the R lines depends on the square of this relative displacement.

There is also an increase in the splitting of the R lines upon application of the electric field as seen in Fig. 5. This would be the expected result from a displacement of the Cr³⁺ ion, because the magnitude of the noncubic field is increased.

The occurrence of the "hysteresis" must now be explained. It could be due to a small amount of photo-conductivity present in the sample. As the field is applied, charges will flow toward the surface of the crystal, thereby decreasing the field in the bulk. This, in turn, leads to a decrease in the R-line shift. The actual field in the bulk will be a sum of the measured applied field minus that set up by the compensating charges. But the flow of charges through a resistive medium lags the applied field in phase. Therefore,

$$\mathscr{E}_{bulk} = \mathscr{E}_{app}e^{i\omega t} - \mathscr{E}_{charge}e^{i(\omega t - \phi)}.$$

As a result the field in the bulk will be somewhat advanced in phase over the applied field leading to a curve similar to the one seen. The "hysteresis" decreased somewhat when the frequency was raised to 200 Hz, supporting the above explanation. At 77°K, the R lines are much broader, and hence no "hysteresis" could be observed with experimental error. This problem with the photoconductivity can be avoided by going to higher frequencies. Because the Enhancetron had a

TABLE II. Temperature shift of the R lines of Cr³⁺ and Mn⁴⁺ in SrTiO₃ (in cm⁻¹).

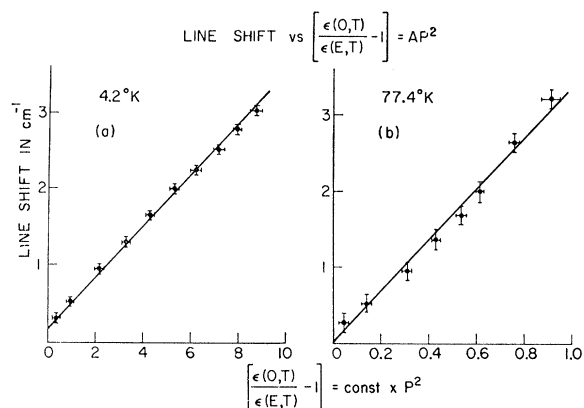|	Mn⁴⁺	Cr³⁺
4.2°K	0	0
20°K	−0.6	+0.4
77°K	−10	+8.2

FIG. 7. R-line shift versus $\epsilon(0,T)/\epsilon(E,T)-1$, where E is the applied electric field. The constant $A = 4\pi/3\xi\epsilon(0,T)$.

maximum repetition rate of 60 Hz, higher frequencies could not be used in this experiment.

Another possible source for the "hysteresis" could be the reorientation of the tetragonal domains. It has been noted by Sakudo et al.[21] that domains oriented parallel to an applied electric field disappear from the spin-resonance spectrum of Gd^{3+}. If there is a small amount of anisotropy in the dielectric constant, then for a given field a larger polarization can be induced for domains parallel to the field (c domains). Therefore, the c domains will have a larger R-line shift than the a domains (domains$\perp E$). If there is a time constant (τ) associated with the switching of domains, then a "hysteresis" would appear for frequencies such that $\omega\tau\cong 1$.

IV. DISCUSSION

We have just shown in Sec. III that the energy of the R lines depends on the square of the relative displacement of the Cr^{3+} ion and its surroundings when an electric field is applied to $SrTiO_3$. But in addition to field-induced changes in the equilibrium positions of the ions, there is the vibration of the crystalline lattice. Since the energy of the R lines depends on the position of the Cr^{3+} ion with respect to its neighbors, the phonons interact with the impurity ion. This interaction will produce thermal shifts of the R lines because the number of interacting phonons depends on the temperature.

In general, the interaction between the impurity-ion electrons and the phonons can be expanded in terms of the relative displacement (δu) of the ions divided by the interionic distance (d). Thus, the form of the interaction for one dimension is

$$\mathcal{3C}' = C\left(\frac{\delta u}{d}\right) + D\left(\frac{\delta u}{d}\right)^2 + \cdots, \qquad (11)$$

where C and D contain operators which act on the

[21] T. Sakudo, H. Unoki, and Y. Fujii, J. Phys. Soc. Japan 21, 2739 (1967).

electronic states. Up to second order in the perturbation $\mathcal{3C}'$ the R-line shift with temperature can be expressed as follows:

$$\Delta\bar{\nu} = A \sum_{k,j} g(k,j)\langle\delta u_{k,j}{}^2\rangle = A \sum g(k,j)\frac{\bar{n}(k,j)+\frac{1}{2}}{\omega(k,j)}. \qquad (12)$$

The k and j refer to the wave vector and phonon branch, respectively. The $g(k,j)$ is a coupling parameter between the mode (k,j) and the impurity ion. The $\bar{n}(k,j)$ is the thermal occupation number of the mode (k,j) and $\langle\delta u_{k,j}{}^2\rangle$ is the mean-squared relative displacement.

The reason why $\Delta\bar{\nu}$ and $1/\epsilon$ or $\omega_s{}^2$ show the similar temperature dependences below 107°K can now be explained. The soft-mode frequency is temperature-dependent because of anharmonic interactions with other phonons. In the quasiharmonic approximation some anharmonic terms can be included in the harmonic part of the Hamiltonian by renormalization. This technique is described in a paper by Cowley.[22] Silverman and Joseph[23] have applied the quasiharmonic approximation to calculating the temperature dependence of the soft mode in paraelectric materials. A recent paper by Nettleton[24] has extended this theory to both the field and temperature dependence of the soft mode. His result for the soft-mode frequency can be written in the form

$$\omega_s{}^2 = -\omega_0{}^2 + A \sum_{k,j} G(k,j)\frac{n(k,j)+\frac{1}{2}}{\omega(k,j)} + B[u(\mathcal{E})]^2, \qquad (13)$$

where ω_0 is the frequency in the harmonic approximation, the $G(k,j)$ are the anharmonic coupling parameters, $u(\mathcal{E})$ is the relative displacement of the positive and negative ions under the influence of the electric field, and the $\omega(k,j)$ are the renormalized frequencies. Note that the harmonic frequency is imaginary, i.e., the crystal is unstable to vibrations of this mode in the harmonic approximation.

It can be seen that the R-line shift $\Delta\bar{\nu}$ and $\omega_s{}^2$ are related if $G(k,j)$ is similar to $g(k,j)$ of Eq. (12). It also can be seen that both $\omega_s{}^2$ and $\Delta\bar{\nu}$ depend on the square of the ionic polarization when an electric field is applied.

But $\Delta\bar{\nu}$ and $\omega_s{}^2$ have much different behaviors in the region of 107°K. The tetragonal transition has no effect at all on $\omega_s{}^2$, whereas $\Delta\bar{\nu}$ versus T has a slope discontinuity at 107°K. As mentioned previously, the transition is characterized by a soft phonon at the corner of the Brillouin zone tending toward zero as the transition temperature is approached from above. Below 107°K the number of phonons at $k=0$ increases by a factor of 2. The soft phonon at the zone boundary splits into two soft phonons at $k=0$, as experimentally seen by Fleury et al.[12] We expect that the ionic displacements in this mode change considerably at the transition. If the

[22] R. A. Cowley, Phil. Mag. 11, 673 (1965).
[23] B. D. Silverman and R. I. Joseph, Phys. Rev. 129, 2062 (1963).
[24] R. E. Nettleton, Ann. Physik 20, 136 (1967).

impurity is coupled to this mode, there will be a change of the coupling parameter at the transition. The discontinuity in the slope could be explained by a combination of a change in the coupling parameters and the accompanying distortion in the tetragonal phase. Nevertheless, the details of why this might be so are not known as yet. In summary, it can be said that the zone corner soft phonon affects the R-line thermal shift, even though it does not affect the temperature dependence of ω_s^2.

What sort of temperature dependence can be expected on the basis of this theory. McCumber and Sturge,[25] and Imbusch et al.[26] considered the impurity-ion interaction with the acoustic phonons and in the Debye approximation. In this case the relative displacement is given by the elastic strain

$$\delta u \cong \left(\frac{\partial u}{\partial x}\bigg|_{x=0}\right) d = kud.$$

Therefore, $g(\mathbf{k},j)$ is proportional to k^2. The sum in Eq. (12) can be converted to an integral over $|\mathbf{k}|$ with the assumption of spherical symmetry for the dispersion curves. In the Debye approximation, $|\mathbf{k}| = \omega/v$, thus, Eq. (12) becomes

$$\Delta\bar{\nu} = 4\pi A g_A \int_0^{\omega_D} [\bar{n}(\omega) + \tfrac{1}{2}]\omega^3 d\omega, \tag{14}$$

where ω_D is the Debye frequency. This is the total heat of the host crystal for a Debye spectrum of phonons.

Measurements of thermal line shifts in many materials have satisfied this theory quite well. In particular, the line-shift data of Cr^{3+} and V^{2+} in MgO and Cr^{3+} in Al$_2$O$_3$ are linear in the total heat from 4 to 300°K.[26,27] The local mode vibration of H$^-$ in the alkali halides also has a thermal shift proportional to the total heat.[28] Now compare the R-line shift of Cr^{3+}:SrTiO$_3$ with the integral of the specific-heat data of Todd and Lorenson.[29] This is shown in Fig. 8. It is obvious that the total heat theory is not applicable to SrTiO$_3$:Cr^{3+}.

The difference between SrTiO$_3$ and other materials, such as Al$_2$O$_3$ and MgO, is the existence of soft optical phonon modes. Because the energy levels of an impurity ion depend on its displacement with respect to its surroundings, one would expect that optical phonons would be more strongly interacting because of the opposing motion of the positive and negative ions.

[25] D. E. McCumber and M. D. Sturge, J. Appl. Phys. 34, 1682 (1963).

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

[27] A. L. Schawlow, in Proceedings of the Third International Congress of Quantum Electronics, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964), p. 645.

[28] S. S. Mitra and R. S. Singh, Phys. Rev. Letters 16, 694 (1966).

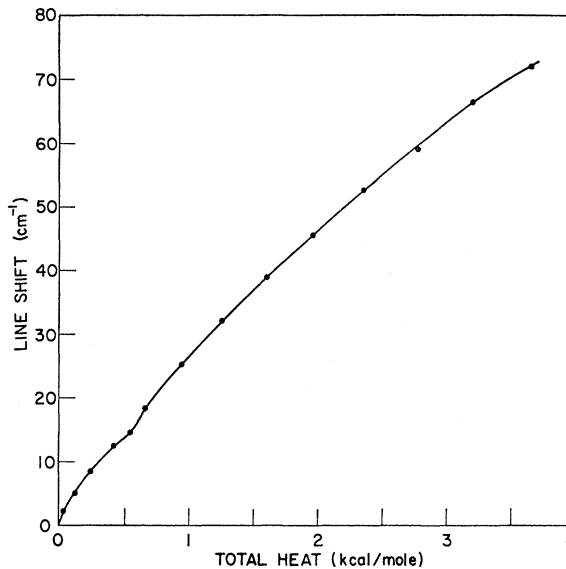[29] S. S. Todd and R. E. Lorenson, J. Am. Chem. Soc. 74, 2043 (1952).

FIG. 8. Line shift versus $\int C_p dT$ for SrTiO$_3$ (C_p is the specific heat of SrTiO$_3$ as measured by Todd and Lorenson, Ref. 29).

Optical modes were not considered in the explanation of the line shift in ruby and MgO because these modes are not populated in the temperature ranges of interest. (In MgO the optical phonons have frequencies in the range 350–500 cm^{-1}.) Thus, they make a very small contribution to the thermal line shift in these substances. However, in SrTiO$_3$ the presence of low-frequency optical modes means that optical modes have to be considered in this material. Since one of the soft modes consists primarily of a vibration of the titanium against the surrounding oxygen ion, it should have a strong interaction with an impurity at the Ti site.

Because the R-line shift and the reciprocal dielectric constant depend linearly on the temperature above 70°K, the important phonons contributing to the temperature dependence must have energies less than 100 cm^{-1} or so. In the previous paragraph we argued that the lowest optical phonon branch should have the primary contribution to the temperature dependence, with a smaller contribution from the acoustic phonons. Using Barrett's[30] theory, Weaver[16] did a fit of $1/\epsilon$ to an Einstein oscillator and had reasonable success with a value of 70 cm^{-1}. Barrett's assumption of an interaction with a single Einstein mode is probably oversimplified. Nevertheless, the reasonable fit obtained by Weaver with a single phonon of 70 cm^{-1} indicates that the important phonons must lie in the region of this frequency. The exact temperature dependence could be obtained from Eq. (3) if the coupling constant $G(\mathbf{k},j)$ were known. Since the frequencies $\omega(\mathbf{k},j)$, which appear in Eq. (13), are the renormalized quasiharmonic frequencies, the temperature dependence of ω_s would be difficult to calculate. However, the frequencies of the

[30] J. H. Barrett, Phys. Rev. 86, 118 (1952).

soft-phonon branch at low **k** values increase rapidly with temperature; therefore, their relative contribution to the integral in Eq. (13) will decrease as the temperature increases. Thus, it is likely that the major contribution comes from frequencies in the region near 70 cm^{-1}.

Thermal expansion can also contribute to the R-line shift because of the change in the lattice parameter.[31] In ruby it is observed experimentally that hydrostatic pressure shifts the R lines linearly to lower energies.[32] The decrease in distance between the impurity and the surrounding ions tends to increase covalency because of the greater overlap of the $3d$ orbitals with the surrounding ligands. This lowers the energy of the R lines. Thus, as the temperature is lowered, thermal contraction shifts the lines to the red. Therefore, in the temperature range where the thermal expansion is linear, the line shift will be linear in temperature.

The x-ray data of Lytle[10] shows that the thermal expansion is approximately linear in the region 120–300°K. The thermal strain $(\Delta a_0/a_0)$ developed over this temperature range is 1.9×10^{-3}. The line shift is 66 cm^{-1} for the same temperature range. This means that in order for thermal expansion to explain the R-line shift, the shift must be 3.4×10^4 cm^{-1} per unit cubic strain. This can be checked experimentally by applying pressure to the crystal and observing how far the R-line shifts.

Uniaxial pressures were applied to SrTiO$_3$ at 77°K along the [001], [110], and [111] directions. For pressures up to 25 kg/mm^2 along [001] the R-line shift was 0.1 cm^{-1}/(kg/mm^2).

The cubic strain induced by a uniaxial pressure is

$$e(A_1) = (S_{11} + 2S_{12})P,$$

where the S_{11} and S_{12} are the elastic compliances. The values for the compliances are taken from the results of Rupprecht and Winter.[33] At 77°K they are

$$S_{11} \cong 5.4 \times 10^{-13} \text{ cm}^2/\text{dyn},$$

$$S_{12} \cong -0.83 \times 10^{-13} \text{ cm}^2/\text{dyn}.$$

Thus, a pressure of 1 kg/mm^2 produces a cubic strain of 3.8×10^{-5}. The shift was found to be almost independent of stress direction; therefore, the important term is the cubic symmetry term. As a result, the R-line shift is 2.6×10^3 cm^{-1} per unit strain of cubic symmetry. This is about a factor of 10 too small to explain the R-line shift on the basis of thermal expansion.

One effect seen at low pressures should be mentioned here. When the stress was applied along the [001] axis, a large shift [~ 1.2 cm^{-1}/(kg/mm^2)] was seen for pressures <1 kg/mm^2. This large shift could be due to the reorientation of the tetragnal domains under uniaxial pressure. A reorientation of the domains would change the relative intensities of the two components of the R lines. Since these components are not resolved at 77°K, a large change in relative intensities would produce a shift in the peak. There is experimental evidence for the reorientation of domains under uniaxial pressure. If the SrTiO$_3$ crystal is observed optically through crossed polarizers, the domain pattern is seen to be very sensitive to stress. In fact, the domain size can be increased by cooling the crystal through the transition temperature under uniaxial stress.

V. CONCLUSIONS

The presence of a temperature-dependent optical phonon and a phase transition in SrTiO$_3$ leads to unusual shifts of the Cr^{3+} R lines. It has been shown that the change in the R-line frequency with an electric field is directly related to the square of the relative displacement of the Cr^{3+} ion and its surroundings. The temperature dependence of the R-line frequency has been explained on the basis of interaction with the soft phonons present in SrTiO$_3$. A direct comparison between theory and experiment could be made once more is known about the phonon dispersion curves and the anharmonic coupling coefficients. The effect of the tetragonal transition on the Cr^{3+} fluorescence wavelength is still only qualitatively explained, but perhaps this problem can be solved when more is known about the interaction between the zone corner soft phonon and the impurity.

ACKNOWLEDGMENT

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