## ELECTRIC FIELD EFFECTS ON THE SPECTRUM OF CHROMIUM IN STRONTIUM TITANATE\*

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An electric field of 4 kV/cm applied to a crystal of  $SrTiO_3:Cr^{3+}$  at 4.2°K shifts the chromium R lines by about 2 cm<sup>-1</sup> and increases their integrated intensity by 8%. The intensity increase is attributed to an induced electric dipole transition made possible when the  $Cr^{3+}$  ion is displaced from the center of symmetry by the applied electric field.

In a purely cubic crystal field, as in MgO or in  $SrTiO_3$  at temperatures above  $110^{\circ}K$ , the  $Cr^{3+}$ fluorescence has a single zero-phonon line corresponding to the transition from the  ${}^{2}E$  to the  ${}^{4}A_{2}$ level. If the site symmetry is reduced, as by an external stress which retains inversion symmetry, from cubic to tetragonal, trigonal, or rhombic, both levels split but the transition remains a weak magnetic dipole with an oscillator strength around  $10^{-9}$ . If, however, the  $Cr^{3+}$  ion is removed from the center of symmetry, as it is in aluminum oxide, an electric dipole transition becomes possible, and it can have an oscillator strength of the order of  $10^{-7}$ . Therefore, it seemed possible that a strong electric field applied to the crystal might displace the  $Cr^{3+}$  ions from center of the  $O^{2-}$  octahedron and permit some electric dipole transition. However, attempts to observe a field-induced intensity increase were made without success by Imbusch<sup>1</sup> in MgO: $Cr^{3+}$  and by Sturge<sup>2</sup> in SrF<sub>2</sub>:Sm<sup>2+</sup>. We have, therefore, applied an electric field to the highly polarizable crystal SrTiO<sub>3</sub> to observe the effects on the spectra of chromium impurities.

In preliminary studies,<sup>3,4</sup> it was found that small amounts of chromium in strontium titanate produce sharp lines at 7936.36 and 7938.24 Å at  $4.2^{\circ}$ K, observable in emission and absorption with no Stokes shift. These are the two *R* lines, which coalesce as a transition temperature of 107°K is approached and the tetragonal field component is removed. At  $4.2^{\circ}$ K the individual lines have a width of  $0.5 \text{ cm}^{-1}$ . Polarization studies show that the transition is magnetic dipole. If all the Cr<sup>3+</sup> ions are in equivalent titanium sites, the oscillator strength is given approximately by  $1.4 \times 10^{-9}$  from absorption measurements.

The  $Cr^{3+}$  zero-phonon lines display symmetry properties appropriate to titanium substitutional sites, both above and below the transition. Unlike MgO: $Cr^{3+}$ , no lines from sites of lower symmetry are seen, such as could arise from the close proximity of a charge compensation defect. The charge defect, introduced when a Ti<sup>4+</sup> ion is replaced by a  $Cr^{3+}$  ion, is probably compensated by some mechanism that is not localized at the impurity.

As in MgO:Cr<sup>3+</sup>, the zero-phonon lines are accompanied by vibrational sidebands whose integrated intensity is many times larger than the lines. Thus the fluorescence lifetime and the population of the excited state are limited by the sidebands, and are little changed by a moderate fractional increase in the zero-phonon oscillator strength. Since the population is unchanged, the fluorescence intensity of the zero-phonon line will change in proportion to the oscillator strength.

Strontium titanate exhibits some photoconductivity when visible light is used to excite the fluorescence. This causes an applied electric field to be neutralized with a time constant of about 10 sec. For this reason, all electric field experiments had to be performed with an alternating field, and so field frequencies from 60 to 1000 Hz were used.

The applied electric field caused the R lines to shift to shorter wavelengths and to move slightly farther apart, as shown in Fig. 1. On applying 4 kV/cm, the higher frequency line moved 2.0



FIG. 1. Wave number of the  $SrTiO_3:Cr^{3+}$  zero-phonon lines as a function of applied electric field. At 77°K the lines are not resolved.

 $cm^{-1}$ , and the lower frequency line moved 1.5  $cm^{-1}$ , so that the separation increased from 3 to  $3.5 \text{ cm}^{-1}$ . The field was applied along the [111] direction. These shifts are more than a hundred times larger than the field-induced shifts observed in ruby by Kaiser, Sugano, and Wood,<sup>5</sup> who found a shift of 0.012 cm<sup>-1</sup> for 4 kV/cm. Such large shifts are to be expected in strontium titanate because of its high polarizability, shown by a dielectric constant of 20000. It would appear from Fig. 1 that at 4.2°K the shift curve has a finite slope at zero field, which would not be possible for an ion at a center of symmetry. However, the linewidths are large enough to prevent accurate measurements of the very small shifts corresponding to a few hundred volts per cm. Our preliminary investigations have shown that both temperature and field shifts are proportional to the change in the reciprocal of the dielectric constant. This relationship, together with the dielectric constant measurements of Sawaguchi, Kikuchi, and Kodera,<sup>6</sup> indicates a shift curve which flattens in the very low-field region where we were not able to make accurate measurements.

Because of these shifts, with a high-resolution spectrometer set on the peak of a line, there was an apparent change of intensity when the electric field was applied. This masked any real change of the integrated line intensity. Therefore, the exit slit of the spectrometer was opened to provide a bandpass of about 13 cm<sup>-1</sup>. The entrance slit width was one-tenth of this. Then both emission lines could be made to remain within the transmitted region during the full cycle of the alternating field. A phase-sensitive detector was used, tuned to twice the frequency of the applied electric field.

As the spectrometer was scanned toward increasing wavelengths, the detector output shown in Fig. 2 was obtained. At A, the spectrometer



FIG. 2. Signal from the synchronous detector, as the optical spectrometer is tuned slowly while an ac modulating field is applied to the  $SrTiO_3:Cr^{3+}$  crystal.

bandpass began to admit part of the line when the field was applied, so that a positive signal is observed. Since the field-induced shift is greater than the linewidth, the detector output at the peak, B, is proportional to the intensity of the shorter-wavelength line component. This is just as in Stark-modulation microwave spectroscopy of gases when the extent of modulation exceeds the linewidth.

At C, both lines lie within the slit and the output is fairly flat. But the output is nonzero and is, in fact, about 8% of the peak at B. This can come only from an overall change in intensity induced by the electric field. From measurements at fields of 2 and 4 kV/cm, it is found that the percentage of induced intensity change is approximately proportional to the square of the dielectric polarization  $P^2$ . That is, the electric dipole matrix element is proportional to P as would be expected. The results shown in Fig. 2 were obtained with unpolarized light, but similar positive intensity changes were also obtained with each linear polarization.

The crystalline field at the Cr site in ruby can be expanded as follows:

 $V = B_0^0 + B_1^0 r \cos\theta + B_2^0 r^2 (3\cos^2\theta - 1)$ 

+ higher order terms.

These coefficients have been calculated for ruby by McClure using a point-charge model.<sup>7</sup> He found that the coefficient of the dominant term of odd symmetry  $B_1^0$  is -3.65 eV/Å. The electric dipole moment matrix element should be approximately proportional to this coefficient. The electric dipole oscillator strength induced in SrTiO<sub>3</sub> by a field of 4 kV/cm is  $0.08 \times 1.4 \times 10^{-9} = 1.1$  $\times 10^{-10}$ , while that of Cr<sup>3+</sup> in ruby is  $3.3 \times 10^{-7}$ . Since the oscillator strength is proportional to the square of the matrix element and hence approximately proportional to  $(B_1^{0})^2$ , we can estimate the induced  $B_1^0$  as  $6.5 \times 10^{-2}$  eV/Å. From a point-change calculation over nearest-neighbor ions, this value of  $B_1^{0}$  in strontium titanate corresponds to a chromium-ion displacement of 0.008 Å.

To assess how reasonable this measurement of the field-induced ionic displacement is, we can compare it with an estimate from the dielectric polarization. For an applied field of 4 kV/cm, the dielectric polarization is  $3.7 \times 10^{-6}$  C/cm<sup>2</sup>. This can be compared with the spontaneous polarization in BaTiO<sub>3</sub>, which is  $3 \times 10^{-5}$  C/cm<sup>2</sup> near 120°C. About 30% of this is due to the ionic displacement of the Ti ion,<sup>8</sup> which is 0.1 Å in BaTiO<sub>3</sub>. Therefore, the effective ionic charge of the Ti ion is  $e^* = 0.3P_S/(\Delta x)N_0$ . With  $N_0 = 2.7 \times 10^{22}/\text{cm}^3$ ,  $e^*$  is ~2.1 electronic charges. If the Ti ion is assumed to have about the same effective charge in SrTiO<sub>3</sub>, then the displacement of the Ti ion must be about 0.012 Å. This estimate also contains important uncertainties, but it is quite consistent with the value deduced from the induced optical transition.

This is the first observation of an electricfield-induced intensity change of a sharp line in a solid. Such effects for vibrational spectra of symmetric molecules were predicted by Condon<sup>9</sup> and observed by Crawford and Dagg.<sup>10</sup> For ions in a solid, observation is complicated by the magnetic dipole transitions which can have appreciable intensity even when an electric dipole transition is completely forbidden by symmetry. But now that the effect has been observed, the induced electric dipole transition can be measured as a function of the induced polarization which is also a measurable quantity. Further studies will be needed to confirm that the induced dipole transition is the only factor contributing to the intensity change. It is conceivable that part of the change might be an increased magnetic dipole intensity arising from changes in the crystal-field parameters when the electric field is applied. This question could be decided by polarization measurements, preferably in a magnetic field, but such studies are greatly complicated by the domain structure of the crystals.

The field-induced intensity change observed here may permit observed oscillator strengths to be used for estimates of the relationship between fields and displacements of ions. It also provides a new way to modulate the fluorescence intensity.

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## PHONON-LIMITED DRIFT OF THE ELECTRON BUBBLE IN SUPERFLUID HELIUM\*

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We present measurements of the negative ion mobility in He II for  $T \leq 0.5^{\circ}$ K. We show that the usual kinetic-theory approach to ion drift in He II is inadequate, and we describe a more realistic model. It is found that <u>inelastic</u> phonon scattering is the dominant process determining the mobility of the electron bubble at these temperatures.

The limiting drift velocities of ions<sup>1</sup> in He II, under the influence of an electric field, have been investigated in some detail by Meyer and Reif.<sup>2-4</sup> Their results showed that at low fields the ion drift velocity  $v_D$  is linearly proportional to the applied electric field E, where the proportionality constant  $\mu$  (the mobility) is temperature dependent. At higher temperatures, where roton scattering dominates,  $\mu$  was seen to vary roughly as the inverse of the roton number density, while at their lowest temperatures ( $T \sim 0.5^{\circ}$ K) phonon scattering became important. According to the data of Meyer and Reif, the temperature dependence of the phonon-limited mobility  $\mu_p$  is  $\mu_p \propto T^{-l}$  where  $l = 3.3 \pm 0.3$  for positive ions and

 $l=2.4\pm0.4$  for negative ions. This qualitatively implies that  $\mu_p$  varies as the inverse of the phonon number density.

The interpretation of this behavior has generally proceeded along the lines of elementary kinetic theory. The ion moving through the field of thermal excitations is treated as analogous to a particle moving through a gas. In the limit where  $v_D$  is much less than the mean thermal velocity of the ion, such a model yields

$$v_{D} = (eE/M)\tau = \text{const}En^{-1}, \qquad (1)$$

where e is the ion charge, M the ion effective mass, E the electric field,  $\tau$  the relaxation time, and n the number density of scatterers. Equation