

FIG. 3. Temperature dependence of the gap Δ_I for sc band structure (dotted curve) and for 6% deviation from sc ($\lambda/2w=0.06$, solid curve). At less than 5% deviation the Δ_I curve becomes second order again, whereas at or above 10% $T_I \rightarrow 0$ and the insulating phase disappears. This calculation is for $\tilde{g}=0.1 \times 2w$. The temperature is plotted in units of $kT=2w \times 10^{-2}$.

We conclude that the observed effects of pressure and strain on T_I are explained by the strain dependence of the band structure (i.e., the "mix" of next-nearest-neighbor to nearest-neighbor overlap depends sensitively on lattice parameter) rather than by the effects of strain on the absolute or relative magnitudes of \tilde{g} , $\hbar\omega$, bandwidth, or U .

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ELECTRIC FIELD DEPENDENCE OF A HYDROGEN IMPURITY MODE IN SrTiO_3

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The temperature and electric field dependence of a 3500-cm^{-1} absorption band arising from hydrogen impurities in SrTiO_3 crystals have been measured. The phase transition at 102°K from a cubic to a tetragonal structure as well as externally applied electric fields at low temperature cause a multitude of symmetrically different positions for the impurity. The corresponding frequency shifts can be correlated with the structural changes in the crystal and with the behavior of the low-frequency phonons.

Strontium titanate is known to undergo a non-ferroelectric phase transition at about 110°K . Quite some detailed knowledge has been obtained about this transition.¹⁻⁵ A more intriguing aspect of strontium titanate is the ferroelectric phase transition at lower temperature which has never been found. Although the crystal apparently never reaches instability, many physical properties show a behavior analogous to those

in crystals that do eventually reach a ferroelectric phase transition. The high response to external electric fields and the large frequency shifts with temperature of some of the Raman-active lattice vibrations are the most typical in this respect.⁶

It has also been reported that certain spectroscopic features of impurities in those crystals follow closely⁷ the temperature-dependent di-

electric constant. The relation between these two properties is not quite understood, but it is clear that the response which is shown by the impurities might give detailed information on a microscopic scale about the changes in the crystal with change of temperature and under the influence of an external electric field.

It is known that hydrogen may be present in strontium titanate crystals in fairly large amounts.⁸ This impurity gives rise to an absorption band associated with an OH vibration at about 3500 cm^{-1} . We report here some high-resolution measurements on this absorption band, made with a Perkin-Elmer E 14 spectrophotometer. The SrTiO_3 crystal, fitted between two electrodes, was placed in an immersion cryostat in which temperatures as low as 1.7°K could be obtained.

The temperature dependence of the absorption band at 3500 cm^{-1} from room temperature down to 1.7°K , without external electric field, is shown in Fig. 1. This plot shows the almost linear behavior of the frequency shift with temperature in the cubic phase. At 102°K SrTiO_3 undergoes a phase transition from cubic to tetragonal symmetry. Around this temperature the absorption band splits into three components. Each component shows a different temperature dependence upon further cooling. A common feature is that the derivative of the frequency-versus-temperature curves tends towards zero as the temperature approaches 0°K . The phase transition at 102°K goes with a small rotation of the oxygen octahedra.^{3,9} This rotation gives rise to three symmetrically different positions on the O-O junctions on which the hydrogen would

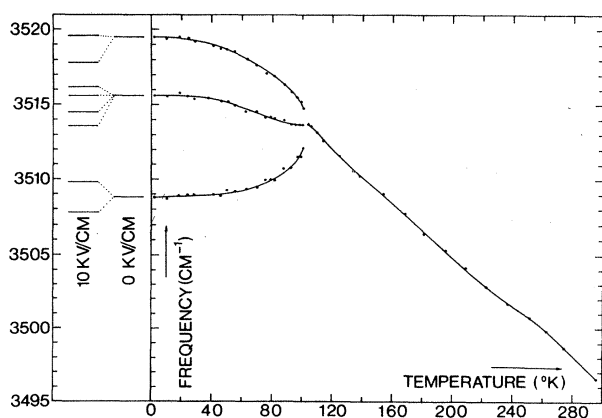


FIG. 1. The temperature dependence of the frequency of the hydrogen impurities in SrTiO_3 . In the left part the split under the influence of a dc electric field in a $[112]$ direction at 1.7°K is shown.

probably be located. The three absorption frequencies show a similar temperature dependent behavior as the rotation angle θ of the TiO_6 octahedra, below 102°K .⁹

This static explanation of the splitting in three bands at the phase transition is confirmed by the spectra that arise when a dc electric field is applied. The components in which each of the three bands split under the influence of an external electric field are indicated in Fig. 1. The amount of splitting appears to be proportional to the strength of the field. Many of the components are very sensitive to the direction of polarization of the infrared radiation. An example of an experimental spectrum with radiation polarized parallel and perpendicular to the electric field direction is given in Fig. 2. The number of components and their relative intensity as well as the magnitude of the splitting with applied electric field depend strongly on the orientation of the field direction with respect to the crystallographic axes. Although quantitative interpretation is hard to achieve due to the fact that the shape and apparent intensities of the bands are determined by the slit width, the experimental results are in good qualitative agreement with the static picture. Different OH dipoles at sites of different symmetry give rise to the multitude of absorption peaks. Tunneling between different dipole orientations does not seem to be of any consequence for the spectra. The shifts of the 3500-cm^{-1} peak are therefore a direct measure for the shifts of the energy levels in the potential well for the vibration of the hydrogen between two oxygen atoms of the crystal lattice. Hence the behavior of this frequency with temperature changes and under the influence of an external electric field can be directly correlated with the configurational changes of the lattice. A first conclusion is that the earlier ideas about the behavior of the SrTiO_3 lattice are confirmed.

In Fig. 3 the response to an electric field at constant temperature of two absorption bands (marked A and B in Fig. 2) is shown. Accurate measurements could only be performed with fields higher than 3 kV/cm . The frequency shift is a linear function of the field, but the line does not go through the origin for zero field. This may mean that there is a small spontaneous polarization whether or not induced by the applied field, or simply that the frequency shift does not depend linearly on the electric field for low fields. Only for a very simple frequency-

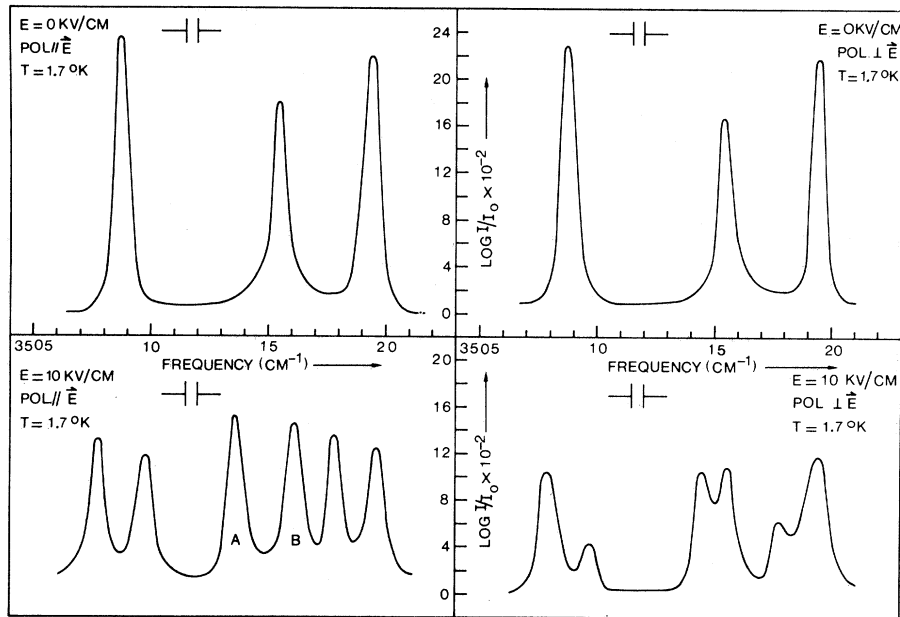


FIG. 2. Experimental spectra of the hydrogen impurities in SrTiO_3 . The dc electric field is applied in a $[112]$ direction. The spectral slit width is indicated in the figure.

polarization relation could this imply a nonlinear behavior of the polarization with the applied field such as $E^{2/3}$ as expected near a ferroelectric phase transition. The most striking feature in Fig. 3 is the asymptotic behavior of the temperature dependence of the frequency split for lower temperatures at a constant electric field. Between 100 and 30°K the increasing frequency split is suggestive of a ferroelectric phase transition at some lower temperature. At the approach to this temperature, however, the situation becomes stabilized.

It is as yet not clear what the relation is between the frequencies of the hydrogen impurity and the frequencies of the lattice modes that are held responsible for the phase transition at 102°K and for the quasiferroelectric behavior. These lattice modes have been studied by Raman scattering.^{4,6}

It is obvious to assume that the impurity modes near 102°K show a large anharmonic interaction with the soft zone-boundary phonons. Because the frequency of these phonons changes rapidly as the temperature is lowered,⁴ a strong temperature dependence of the impurity-mode frequencies can be expected.

Below 102°K the frequency of the ferroelectric phonons decreases monotonically with decreasing temperature,⁶ which causes, at low temperatures, a dominant interaction of the impurity modes with these phonons, partially because of the

larger anharmonicity and partially because of the higher population of the latter.

These arguments may give an explanation for some typical experimental features, such as the increasing response of the impurity-mode frequencies in an electric field with decreasing temperature down to 30°K, and an asymptotic temperature dependence of the frequency split at lower temperatures at constant field, be-

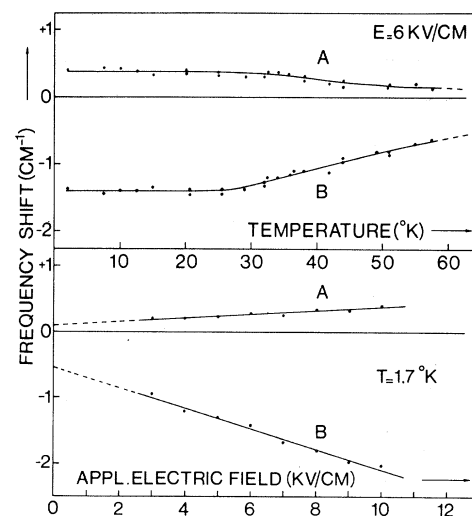


FIG. 3. Temperature and electric field dependence of two hydrogen impurity frequencies in SrTiO_3 . The dc electric field is applied in a $[112]$ direction. The dashed parts of the lines are extrapolations.

cause the soft-phonon-mode frequencies behave in a similar way.

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$g_{9/2}$ - $d_{5/2}$ INTERACTIONS IN Nb^{96} AND Nb^{92} †

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The reaction $\text{Zr}^{96}(\text{He}^3, t)\text{Nb}^{96}$ was studied and six states belonging to the $(\pi g_{9/2})(\nu d_{5/2})^{-1}$ configuration were identified. The energies and spin assignments agree well with those derived by use of the Pandya transformation from the known states of Nb^{92} belonging to the $(\pi g_{9/2})(\nu d_{5/2})$ configuration.

The low-lying states of $^{96}\text{Nb}_{55}$, previously unreported, should be well represented by the $(\pi g_{9/2})(\nu d_{5/2})^{-1}$ configuration, since both the f - p proton shell ($Z=40$) and the $d_{5/2}$ neutron subshell ($N=56$) are reasonably complete in Zr^{96} . The spectrum of low-lying states in Nb^{96} would therefore yield a set of $g_{9/2}$ - $d_{5/2}$ matrix elements. The comparison of these with the corresponding $g_{9/2}$ - $d_{5/2}$ matrix elements from Nb^{92} affords a rare opportunity for the study of the importance of changing configuration admixtures.

We have chosen to study the low-lying states in Nb^{96} by the charge-exchange (He^3, t) reaction on Zr^{96} . The (He^3, t) reaction has recently been studied for nuclei in the $1f_{7/2}$ shell,¹⁻⁴ and the $A \approx 90$ region.^{5,6} This reaction selects proton-particle, neutron-hole excitations of the target ground state. The reaction $\text{Zr}^{90}(\text{He}^3, t)\text{Nb}^{90}$, for instance, strongly excites nine low-lying states that were identified⁵ with the nine $T=4$ states expected from the $(\pi g_{9/2})(\nu g_{9/2})^{-1}$ configuration. Thus the low-lying Nb^{96} states that should be strongly excited in the reaction $\text{Zr}^{96}(\text{He}^3, t)\text{Nb}^{96}$ are those of the $(\pi g_{9/2})(\nu d_{5/2})^{-1}$ configuration. Admixtures of configurations involving $\pi(g_{9/2})^2$ and $\nu(d_{5/2})^{-2}(s_{1/2})^2$ in the ground state of Zr^{96} could give rise to weak excitations of other states below 1.5 MeV excitation in Nb^{96} . Configurations involving $(\nu g_{9/2})^{-1}$ or $(\pi d_{5/2})$ components should occur at excitation energies of 3 MeV or more because of the gap in single-particle states at

$N, Z = 50$.

We have studied the reaction $\text{Zr}^{96}(\text{He}^3, t)\text{Nb}^{96}$ with the 21-MeV He^3 beam from the Argonne tandem Van de Graaff accelerator. The target was a rolled foil of Zr metal enriched⁷ to 85% in Zr^{96} . The thickness of the foil was 220 $\mu\text{g}/\text{cm}^2$, representing a target thickness of ~ 30 keV. Tritons were detected in the Argonne split-pole spectrograph by means of photographic emulsions which were later scanned in a computer-controlled automatic plate scanner.⁸ A typical spectrum for the excitation region below 0.9 MeV is shown in Fig. 1. The peaks are not completely resolved, but a least-squares fitting program has enabled us to extract meaningful information on the energies and yields of individual peaks.

The angular distributions for the six most prominent states below 2 MeV are displayed in Fig. 2. It is clear that the six strongly excited states are reasonable candidates for those expected in the $\pi g_{9/2}(\nu d_{5/2})^{-1}$ multiplet. The angular distributions are remarkably similar for two pairs of states, and different for the remaining two states.

In our attempt to ascertain the spin values for these states, we have been guided by empirical rules noted in previous (He^3, t) reaction studies: (1) The shapes of the angular distributions for even-parity states of odd J are similar to those for states with the next larger even J ; and (2) in