

ment in the electronic wave function outside a solid surface. This feature is unique to INS among the electron spectroscopies used to determine surface electronic structure.

Because the effective neutralization energy of the ion is ~ 2 eV less than the free-space value,⁵ we can estimate the distance s_m where neutralization occurs. Equating $\Delta E_n = 2$ eV to the principal interaction term, namely the image interaction $(3.6 \text{ eV } \text{\AA})/s_m$, we obtain $s_m \sim 1.8 \text{ \AA}$ as the distance of the ion from the image plane. This simple image interaction has been shown to hold with good accuracy to 1.5 \AA .¹¹ From the equation $s_m = (1/a) \ln(A/av)$ given earlier we obtain $\Delta s_m = (1/a) \ln(v_2/v_1)$ as the difference in neutralization distances for ions of velocities v_1 and v_2 . The parameter a that specifies the rate of exponential falloff of $R_i(s)$ is taken as 2λ , where $\exp(-\lambda s)$ is the rate of decay outside the surface of a p wave function at $E - E_{\text{vac}} \sim -7$ eV, the principal determinant of where neutralization occurs. From $\lambda = (2mE_i/\hbar^2)^{1/2}$ with $E_i = 7$ eV we obtain $a = 2.8 \text{ \AA}^{-1}$. This estimate agrees closely with the variation of charge density outside the Si surface calculated by Appelbaum and Hamann.¹² Adding the 2-eV image acceleration to the experimental ion energies we obtain $v_2/v_1 = (\frac{22}{12})^{1/2} = 1.35$ and $s_m \sim (1/2.8) \times \ln(1.35) \sim 0.1 \text{ \AA}$. Hence the relative change in the Hg d orbital components that we see in the $U(E)$ functions of Fig. 2 occurs over a distance increment of $\sim 0.1 \text{ \AA}$ at an ion-surface separation of $\sim 2 \text{ \AA}$.

The observed changes in the Hg d orbital intensity have only relative significance. The absolute magnitude cannot be determined because we do not know *a priori* either the electron escape probability function or the factor R_2 used in the

one-curve method.

We conclude that ion-neutralization spectroscopy using our new one-curve debroadening procedure yields information about the relative variation of wave-function components outside a surface. We believe this to be a significant addition to the capabilities of electron spectroscopies because we expect it to help us understand the intensity differences of orbital resonances in chemisorption systems as observed by INS and UPS. This, in turn, should yield information about the wave-function character of particular orbital resonances.

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Model for the Low-Temperature Lattice Anomaly in SrTiO₃ and KTaO₃ †

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The low-temperature anomaly in the lattice dynamics of SrTiO₃ and KTaO₃ is described as resulting from an anharmonic coupling between an optical and an acoustic branch. The numerical calculations performed for ω_{TQ} at the center of the Brillouin zone give an excellent fit to the available data from 4 to 300 K. It is shown that the ferroelectric phase transition in SrTiO₃ is prevented by the zero-point fluctuations of the acoustic mode.

Strontium titanate and potassium tantalate are incipient ferroelectrics. Their static dielectric constant follows a Curie-Weiss law down to about

50 K. Below this temperature, however, although continuously increasing to such values as 3×10^4 for SrTiO₃ and 5×10^3 for KTaO₃, the dielectric

constant deviates from the Curie-Weiss behavior, remaining finite, and the crystals do not reach the ferroelectric state.¹⁻⁴ That deviation was interpreted as resulting from a quantum effect of the ionic polarizabilities,⁵ or from zero-point fluctuations of the lattice.⁶ Following Cochran,⁷ the ferroelectricity of many compounds has been associated with a lattice instability for one or more normal modes, the so-called soft modes. Experiments with infrared-light reflection,⁸⁻¹⁰ neutron scattering,¹¹⁻¹⁴ and Raman¹⁵ scattering have shown that one of the F_{1u} optical modes in SrTiO_3 and KTaO_3 decreases its frequency at low temperatures, in very good agreement with the Lyddane-Sachs-Teller relation. This critical F_{1u} mode, here designated by F_{1u}^1 , is probably composed mostly by the motion of the Ti (Ta) ion against the framework of the other ions.^{13,16,17} Some theoretical investigations of the temperature variation of the ferroelectric mode in SrTiO_3 were published, with results in qualitative agreement with the measurements above 50 K.¹⁸⁻²⁰

In this Letter we propose a very simple model to describe the behavior of the ferroelectric soft mode in SrTiO_3 and KTaO_3 . The motivation for

the model is the unusual coupling existing between the $F_{1u}^1(\text{TO})$ and the acoustic transverse mode $F_{1u}(\text{TA})$, for waves traveling along one of the $[100]$ directions.^{14,21} Besides the frequency variation of the TO phonon, the TA phonon in both crystals shows a decrease in frequency at low temperatures which is completely unexpected for a crystal with inversion symmetry. The dispersion of both TO and TA phonons and its temperature variation are highly anisotropic. Axe, Harada, and Shirane¹⁴ introduced a harmonic coupling between $F_{1u}^1(\text{TO})$ and $F_{1u}(\text{TA})$ for points outside the center of the Brillouin zone (BZ) to explain the dispersion of these modes. The harmonic coupling, however, cannot be responsible for the temperature variation of the mode frequencies. We admit that the Ti (Ta) is loosely bound inside the oxygen octahedron and that its transverse mode, i.e., the $F_{1u}^1(\text{TO})$, is stabilized by the thermal fluctuations of the strain through a fourth-order coupling. Let $Q(\vec{q})$ and $X(\vec{q})$ be normal mode coordinates in the harmonic approximation, respectively, for $F_{1u}^1(\text{TO})$ and $F_{1u}(\text{TA})$, and consider waves parallel to a crystallographic axis. The model Hamiltonian is

$$\begin{aligned}
 H = & \frac{1}{2} \sum_q P_Q(q)P_Q(-q) + \frac{1}{2} \sum_q P_X(q)P_X(-q) + \frac{1}{2} \sum_q \omega_{\text{TO}}^2(q)Q(q)Q(-q) \\
 & + \frac{1}{2} \sum_q \omega_{\text{TA}}^2(q)X(q)X(-q) + \sum_{\substack{q, q', q'', q''' \\ q'' q'''}} C(q, q', q'', q''') Q(q)Q(q')X(q'')X(q''') \\
 & + \frac{1}{4} \sum_{\substack{q, q', q'', q''' \\ q'' q'''}} \Gamma(q, q', q'', q''') Q(q)Q(q')Q(q'')Q(q'''), \quad q + q' + q'' + q''' = n2\pi/a,
 \end{aligned} \quad (1)$$

where a is the lattice parameter and n is an integer, or zero. The last contribution, which might become apparent at higher temperatures, will be neglected in the present treatment. Applying a molecular-field approximation to decouple the modes and considering the renormalized modes as quasi harmonic, we obtain the renormalized frequencies

$$\begin{aligned}
 \bar{\omega}_{\text{TO}}^2(q) &= \omega_{\text{TO}}^2(q) + N^{-1} \sum_{q'} C(q, -q, q', -q') [\hbar/\bar{\omega}_{\text{TA}}(q')] \left\{ \frac{1}{2} + n[\bar{\omega}_{\text{TA}}(q')] \right\}, \\
 \bar{\omega}_{\text{TA}}^2(q) &= \omega_{\text{TA}}^2(q) + N^{-1} \sum_{q'} C(q', -q', q, -q) [\hbar/\bar{\omega}_{\text{TO}}(q')] \left\{ \frac{1}{2} + n[\bar{\omega}_{\text{TO}}(q')] \right\},
 \end{aligned} \quad (2)$$

where $n(\omega) = (e^{\hbar\omega/kT} - 1)^{-1}$.

The knowledge of the function $C(q, -q, q', -q')$ would make possible the self-consistent solution of the system above to obtain the temperature variation of $\bar{\omega}_{\text{TO}}(q)$ and $\bar{\omega}_{\text{TA}}(q)$. However, in the present approach we confine our attention to the optical mode at the center of the BZ and substitute the summation over the acoustic modes by an effective term:

$$\bar{\omega}_{\text{TO}}^2(0) = \omega_{\text{TO}}^2(0) + (C^3/\Omega) \left[\frac{1}{2} + n(\Omega) \right]. \quad (3)$$

The effective frequency for the acoustic modes,

Ω , is a function of temperature, but its variation will have a small effect on $\bar{\omega}_{\text{TO}}(0)$, since at low temperature, where $n(\Omega)/\Omega$ is more critically dependent on Ω , the acoustic mode varies little. Figures 1 and 2 show the best fit of $\bar{\omega}_{\text{TO}}(0)$ defined by Eq. (3) to selected experimental data. In the fitting procedure, more attention was given to the Raman data, because of their higher resolution. The agreement with experiments is excellent. A more rigorous test of the model would in fact require more precise data. There

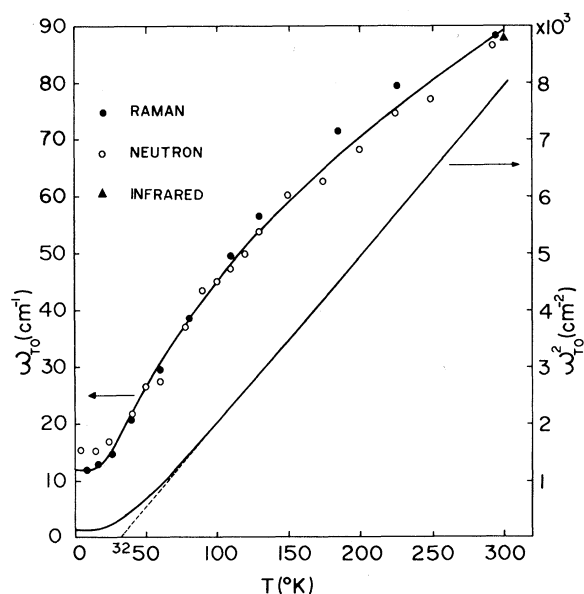


FIG. 1. Fit of the model to selected data of $\bar{\omega}_{\text{TO}}$ in SrTiO_3 . Raman data from Ref. 14; neutron data from Ref. 12; infrared data from Ref. 9. The calculated values of $\bar{\omega}_{\text{TO}}^2$ were also included in the figure. More attention was given to the Raman data.

are differences between the Raman and neutron scattering data which cannot be explained by the finite resolution of the measurements, as pointed out by Yamada and Shirane.¹³ The same authors

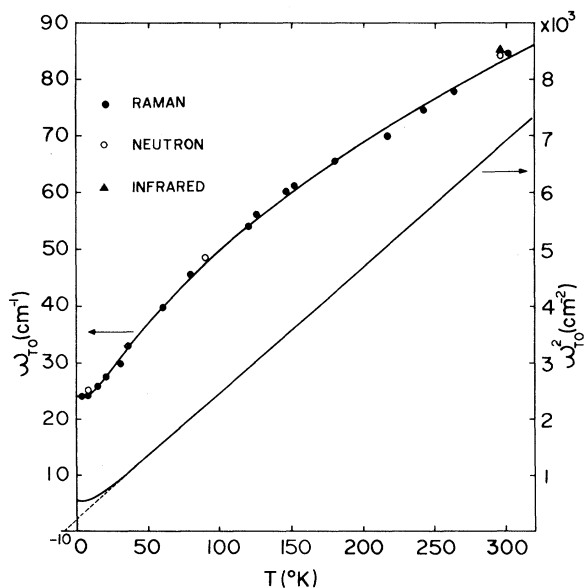


FIG. 2. Fit of the model to selected data of $\bar{\omega}_{\text{TO}}$ in KTaO_3 . Raman data from Ref. 14; neutron data from Ref. 13; infrared data from Ref. 10. The calculated values of $\bar{\omega}_{\text{TO}}^2$ were also included in the figure. More attention was given to the Raman data.

noted that the frequency of the optical mode of SrTiO_3 at 4.2 K changed when the crystal was kept refrigerated overnight and associated that fact with a sluggish phase transition around 10 K. After the evidence of strong coupling between the optical and acoustic modes, however, we have to admit that static strains of the crystal can have a large influence in the optical-mode frequency, especially at low temperature; the static strains could be minimized by a slow cooling of the sample.

The parameters used to fit the experiments are listed in Table I. The harmonic frequency of the TO mode is imaginary in SrTiO_3 , as required for the phase transition. However, the zero-point fluctuations of the TA mode are large enough to stabilize the TO mode, and so prevent the crystal from going to the ferroelectric state, which classically should occur at 32 ± 2 K, as demonstrated by the behavior of $\omega_{\text{TO}}^2(0)$ shown in Fig. 1. On the other hand, the harmonic frequency, although very small, is real in KTaO_3 . This results in a classical Curie temperature of -10 ± 2 K; i.e., even classically the crystal would not have a phase transition. The Curie temperature obtained for SrTiO_3 is in excellent agreement with the available data of the static dielectric constant. For KTaO_3 , the dielectric constant obtained by Wemple does not follow rigorously a Curie-Weiss law, so that one cannot extrapolate a precise Curie temperature. For both materials, the deviation from the Curie-Weiss law is explained by quantum effects on the acoustic-phonon correlation $\langle X(q)X(-q) \rangle$, confirming the suggestion of Silverman.⁶

The small effective frequency found in KTaO_3 is consistent with the low frequencies experimentally found for the acoustic phonons in this crystal. From the dispersion curves for the TA branch in SrTiO_3 and KTaO_3 at low temperature one sees that Ω corresponds to wave vectors $q_0 \cong 0.35 \text{ \AA}^{-1}$ in SrTiO_3 and $q_0 \cong 0.25 \text{ \AA}^{-1}$ in KTaO_3 . We conclude that the anharmonic coupling between the acoustic and optical branches is larger

TABLE I. Temperature-independent parameters used to fit the temperature variation of the TO mode; all the parameters are given in cm^{-1} .

	ω_{TO}	Ω	C
SrTiO_3	$i35.1$	62.3	55.5
KTaO_3	13.8	23.6	26.3

for q around q_0 . This is also the region where the harmonic coupling is larger.^{14, 21}

As a final remark we compare the lattice anomalies in SrTiO₃ and KTaO₃ with the transitions in BaTiO₃ and KNbO₃. In all these isomorph ABO₃ crystals the anomaly results from the weak bounds of the ion B , and we should admit similar models for them. BaTiO₃ and KNbO₃, usually described as displacive ferroelectrics, were recently investigated^{22, 23} from the order-disorder point of view. The distinction between the displacive and the order-disorder behavior does not result from fundamental differences in the crystal machinery. Both behaviors may result from the same model, depending on the values of the parameters involved. Both require a "static" potential possessing equivalent minima at two or more configurations. The displacive behavior may result when the "dynamic" potential resulting from anharmonic interactions is large enough to stabilize the anomalous mode at high temperatures. The renormalized frequency of the mode, classically, is $\bar{\omega}^2 = -\omega_0^2 + AT$, with the temperature $T_0 = \omega_0^2/A$ below the melting point. However, these conditions are not sufficient to cause a ferroelectric phase transition at T_0 ; in fact, the minimization of the free energy may favor the paraelectric state until a temperature T_c ($T_c < T_0$), where the crystal undergoes an order-disorder transition to a ferroelectric state. These ideas can be illustrated by a very simple model. Suppose that the motion of one ion is described by the potential

$$V = -\frac{1}{2}\omega_0^2 x^2 + \frac{1}{2}ATx^2 + \frac{1}{4}\Gamma x^4. \quad (4)$$

This potential has, below T_0 , two minima at $x_1 = +x_0$ and $x_2 = -x_0$, where $x_0^2 = A(T_0 - T)/\Gamma$. The interaction between ions of different cells gives a contribution $-Bx_0^2(n_1 - n_2)^2$ to the internal energy per unit cell, where n_i are the probabilities of occupation of the two minimum positions.²³ The ferroelectric-transition temperature is

$$T_c = \frac{T_0}{1 + \Gamma k/2AB}. \quad (5)$$

The crystal should then be considered ordered paraelectric above T_0 (this phase will not occur for crystals like potassium dihydrogen phosphate

and NaNO₂ because T_0 is above the melting point), disordered paraelectric between T_c and T_0 , and ferroelectric below T_c . The anomalous mode will be highly damped at temperatures below and not too far from T_0 .

A more complete analysis of the TO-TA coupling is in progress.

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