

Anharmonic Effects in KTaO_3 : Ferroelectric Mode, Thermal Expansion, and Compressibility*

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(Received 7 February 1973)

The effects of temperature and pressure on the static dielectric constant and lattice parameter of KTaO_3 have been measured. Combined with literature data, the present results allow a determination of the pressure and temperature dependence of the soft-ferroelectric-mode frequency ω_f over a wide temperature range (0–500°K). The isobaric anharmonic self-energy shift of ω_f is separated into its pure-volume (thermal-strain) and pure-temperature contributions. Though small, the thermal-strain contribution is not negligible, amounting to 7% of the measured frequency at 300°K and 10% at 500°K. It acts to reduce the influence of the pure-temperature anharmonicities. The soft-mode Grüneisen parameter γ_f is very large at low temperatures (460 at 4°K) and decreases rapidly with increasing temperature—unique properties of the soft mode. It is estimated that the strictly harmonic frequency ω_0 of the soft mode is just barely imaginary, and thus all of the stabilization of ω_f at 0°K ($\geq 21 \pm 4 \text{ cm}^{-1}$) is provided by zero-point anharmonicities. At high pressure, ω_0 becomes real. Interpreted in terms of the perturbation and self-consistent phonon treatments, the high-temperature stabilization of ω_f is dominated by quartic anharmonicities, but the nonlinear high-temperature $\omega_f^2(T)$ response suggests the importance of higher-order anharmonicities.

I. INTRODUCTION

It is now very well established both theoretically and experimentally that the dielectric properties and the temperature-induced ferroelectric (FE) transitions in many perovskites such as PbTiO_3 , BaTiO_3 , and SrTiO_3 can be understood in terms of soft transverse-optic (TO) phonons.^{1–6} The paraelectric (PE) → FE transition results from an instability of the lattice against a long-wavelength ($\vec{q} \approx 0$) TO mode caused by the cancellation of the short-range forces by the Coulomb forces. The large increase in the static dielectric constant with decreasing temperature in the PE phase is a direct consequence of the softening (i. e., decrease) of the frequency of this so-called FE mode. Many of the other physical properties of these crystals are also strongly influenced either directly or indirectly by this mode or by its coupling to other lattice modes. Thus, for example, the ultrasonic properties, thermal conductivity, and critical scattering are dominated by interactions with this FE mode.^{1,7}

The temperature (T) dependence of the frequency of the FE mode as well as that of any normal mode of vibration of the crystal results from anharmonic interactions among the modes. This T dependence arises in two different ways. First, there is a pure-volume effect associated with the thermal expansion of the crystal. Secondly, there is a pure-temperature effect which is present even when the crystal is held at constant volume. Constant-pressure (isobaric) measurements of the T dependence of the phonon frequencies and other associated physical properties yield changes due

to the combination of the two effects. However, measurements of both the pressure and temperature dependences of these properties, combined with a knowledge of the compressibility and thermal expansivity, allow a separation of the volume-dependent and volume-independent (i. e., pure-temperature) contributions, and, under suitable conditions, make it possible to determine the magnitude and origin of the anharmonicity. In the case of the FE mode in the perovskites it is generally acknowledged that the pure-temperature effect dominates⁸; however, recent high-pressure studies have indicated that the pure-volume effects can also be quite important.^{9,10} Owing to the lack of sufficient data, heretofore no detailed quantitative separation of the pure-volume and pure-temperature contributions to the isobaric T dependence of the frequency of the soft mode has been made, over an extended temperature range, for any perovskite. We believe that such a separation is important from the theoretical point of view and necessary for continued progress in the understanding of the lattice dynamics of these crystals.

Motivated by the above considerations we examine in this paper the temperature dependence of the soft-FE-mode frequency ω_f of potassium tantalate, KTaO_3 . This crystal is ideal for this purpose. It has the cubic perovskite structure (space group $Pm\bar{3}m$) and remains cubic and paraelectric down to the lowest temperatures; however, it is just barely stable against the FE mode at 4°K.¹¹ This avoids possible complications associated with phase transitions (as is the case in SrTiO_3) and allows us to examine the behavior of the soft mode over a wide temperature range. Fur-

thermore, the FE mode in KTaO_3 is underdamped and well defined, and its temperature dependence at 1 bar has been extensively studied by far-infrared,^{12,13} Raman,⁵ and inelastic-neutron-scattering⁴ techniques. The T dependence of the dielectric constant has also been studied by several authors.^{10,14-16}

In this work we measured the temperature (4–500 °K) and pressure (0–4.5 kbar) dependences of the static dielectric constant of KTaO_3 . Combined with literature data, the results allow us to deduce both the temperature and pressure dependences of ω_f over the whole temperature range. We have also measured the thermal expansion and compressibility of KTaO_3 using x-ray diffraction techniques. The results will now be presented and discussed.

II. THERMAL EXPANSIVITY AND COMPRESSIBILITY

The variation of the lattice parameter a_0 with temperature at 1 bar is shown in Fig. 1. The data points were determined using three different experimental methods. At $T \geq 298$ °K a high-temperature x-ray furnace¹⁷ was used. This furnace mounts directly on a standard goniometer head which in turn fits on a Picker single-crystal diffractometer. The sample was a single crystal ground in the form of a small sphere. The two points at 265 and 200 °K were obtained using the same arrangement but without the furnace cover and by blowing cold nitrogen gas directly on the crystal specimen. The lattice constant was deter-

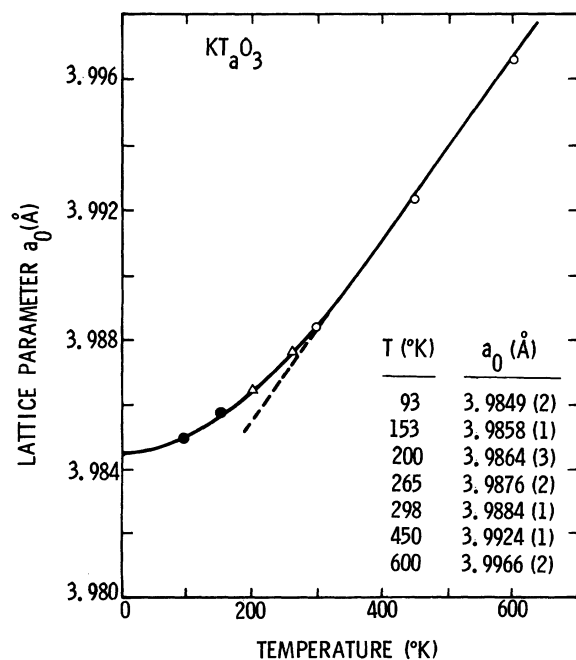


FIG. 1. Variation of the lattice parameter of KTaO_3 with temperature at 1 bar.

mined from least-squares fit of the data from 14 high- 2θ Bragg peaks. The data points at 153 and 93 °K were obtained by measuring high- 2θ values on Debye-Scherrer film taken with a 15-cm-diam camera. Copper $K\alpha$ radiation with $\lambda_{\alpha_1} = 1.54051$ Å was used for all of the measurements.

Our room-temperature (298 °K) value $a_0 = 3.9884(1)$ Å is in excellent agreement with the earlier value 3.9885(1) Å of Vousden.¹⁸ The curve drawn through the data in Fig. 1 extrapolates smoothly to the 8 °K value $a_0 = 3.9842$ Å deduced from the measurements of Demurov and Venevtsev.¹⁸ (At higher temperatures there is some discrepancy in Ref. 16 between the text and their Fig. 5 which gives a_0 vs T .) Our results show curvature in the $a_0(T)$ behavior up to near room temperature—a feature characteristic of materials with high (~ 1000 °K) Debye temperatures. Above 298 °K the response is linear, and in this high-temperature regime the linear expansivity of KTaO_3 is $\alpha_a \equiv (\partial \ln a_0 / \partial T)_P = (6.8 \pm 0.3) \times 10^{-6} \text{ }^\circ\text{K}^{-1}$ and the volume expansivity is simply $\alpha \equiv (\partial \ln V / \partial T)_P = 3\alpha_a = (2.04 \pm 0.09) \times 10^{-5} \text{ }^\circ\text{K}^{-1}$.

The pressure dependence of a_0 was determined to 3 kbar at 296 °K from single-crystal measurements performed in a beryllium high-pressure cell.¹⁹ The lattice constant was obtained from a least-squares fit of the data for 8 Bragg peaks with high 2θ obtained using $\text{Cu}K\alpha$ radiation. The decrease in a_0 is linear over the range covered with a linear compressibility $\kappa_a \equiv -(\partial \ln a_0 / \partial P)_T = (1.50 \pm 0.05) \times 10^{-4} \text{ kbar}^{-1}$. The volume compressibility is $\kappa = 3\kappa_a \equiv -(\partial \ln V / \partial P)_T = (4.50 \pm 0.15) \times 10^{-4} \text{ kbar}^{-1}$, a relatively small value.

In our later considerations, the variation of κ with temperature will be needed. Examination of literature data on materials with comparable κ to that of KTaO_3 , e.g., SrTiO_3 and TiO_2 , shows that for such materials κ is weakly T dependent, increasing by $\sim 2\%$ per 100 °K increase in T . A similar change is suggested for KTaO_3 by Barrett's 2–300 °K data for the elastic constants c_{11} and c_{44} .²⁰ Thus for the present purposes a linear variation in κ of 2% per 100 °K is assumed over the whole temperature range. It can be easily shown that any uncertainty in this assumption will not materially affect our later conclusions.

III. TEMPERATURE AND PRESSURE DEPENDENCE OF DIELECTRIC CONSTANT AND SOFT-MODE FREQUENCY

A. Dielectric Constant

The dielectric constant measurements were made on a single-crystal sample (0.491 cm² in area by 0.122 cm thick) cut from the same boule²¹ as the samples recently used by Abel.¹⁰ The crystal was optically clear with no coloration and cut with the large faces parallel to the [100] crystal face. The large faces were vapor coated with aluminum elec-

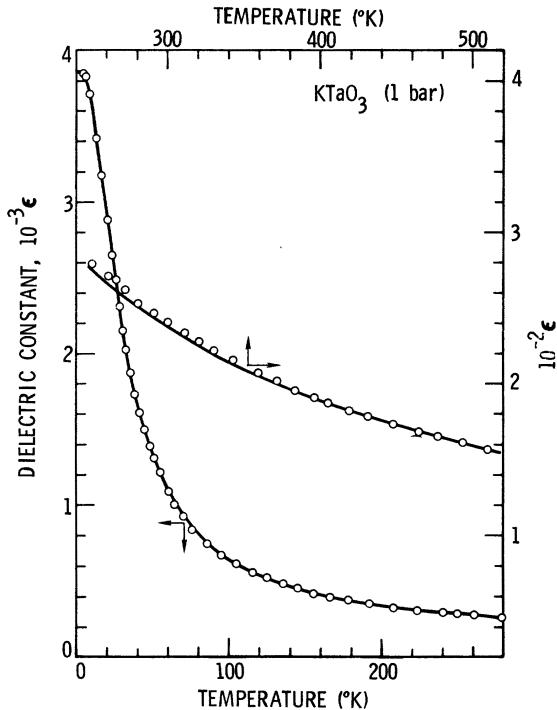


FIG. 2. Temperature dependence of the static dielectric constant of KTaO_3 at 1 bar. The solid line represents a least-squares fit of the data to Eq. (1). Note change in scale to emphasize the high-temperature response.

trodes. Sample capacitance was measured at 100 kHz with a General Radio type-1615A capacitance bridge employing a three-terminal technique. The accuracy of the capacitance is estimated to be better than $\pm 0.2\%$. Sample conductivity was very low with the loss $\tan \delta < 0.003$ at all temperatures and pressures. The details of the temperature and pressure measurements are similar to those reported earlier.^{22, 23} Temperature changes were measured to $\pm 0.1^\circ\text{K}$ and the accuracy of the pressure is better than $\pm 1\%$.

The present dielectric constant (ϵ) data overlap with and extend beyond the recent results obtained by Abel¹⁰ at this laboratory. Figure 2 shows the variation of ϵ with T at 1 bar. The data are in excellent agreement with Abel's results over the 4–300°K range of overlap of the two measurements. The solid line in Fig. 2 is a least-squares fit of the data to the expression

$$\epsilon = A + \frac{B}{\frac{1}{2}T_1 \coth(T_1/2T) - T_0}, \quad (1)$$

with $A = 47.5$ (const), $B = 5.45 \times 10^4$ °K, $T_1 = 56.9$ °K, and $T_0 = 13.1$ °K. This expression was first derived (with $A = 0$) by Barrett²⁴ and recently used by Abel to describe the deviations from the simple Curie-Weiss law at both low and high temperature. Note that Eq. (1) reduces to $\epsilon = A + B/(\frac{1}{2}T_1 - T_0)$

$\equiv \text{const}$ as $T \rightarrow 0^\circ\text{K}$ and to $\epsilon = A + B/(T - T_0)$ —a modified Curie-Weiss law—at high T . The pressure dependence of the parameters B , T_1 , and T_0 was the subject of Abel's work and will not be discussed here. We note that the $\epsilon(T)$ data can also be fit over the whole temperature range by the expression given by Silverman and Joseph²⁵ determined from a perturbation lattice dynamic treatment.

Figure 3 shows the fractional changes in ϵ with pressure at several temperatures. KTaO_3 has a rather low compressibility and these changes are linear over the pressure range indicated. The temperature dependence of the logarithmic pressure and temperature derivatives $(\partial \ln \epsilon / \partial P)_T$ and $(\partial \ln \epsilon / \partial T)_{1 \text{ bar}}$ are shown in Fig. 4. Note that $(\partial \ln \epsilon / \partial P)_T$ is large at low T ($-39\%/ \text{kbar}$ at 4°K) and decreases (in magnitude) rapidly and monotonically with increasing T reaching a value of $-1.36\%/ \text{kbar}$ at 450°K . The temperature derivative $(\partial \ln \epsilon / \partial T)$, on the other hand, starts out $= 0$ at 0°K , as it must, reaches a sharp maximum (in magnitude) of $-2.8\%/^\circ\text{K}$ at $\sim 30^\circ\text{K}$ and then decreases monotonically with increasing T .

B. Soft-Mode Frequency ω_f

The temperature dependence of ω_f for KTaO_3 has been reported by several groups and the results, expressed as ω_f^2 vs T are summarized in Fig. 5. Typical reported error bars are indicated. The large increase in ω_f with increasing T is responsible for the $\epsilon(T)$ behavior in Fig. 2 since the two quantities are related by a Lyddane-Sachs-Teller relationship such that^{1, 9}

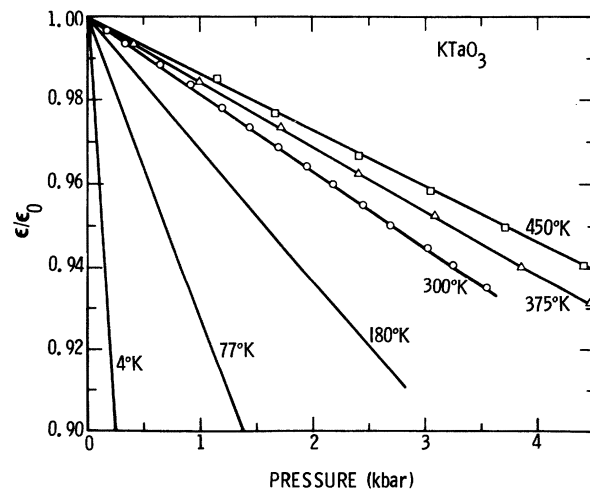


FIG. 3. Fractional change of the static dielectric constant of KTaO_3 with pressure at different temperatures. Data for $T \geq 300^\circ\text{K}$ are from the present work whereas those below 300°K are from Abel's work (Ref. 10) also done at this laboratory.

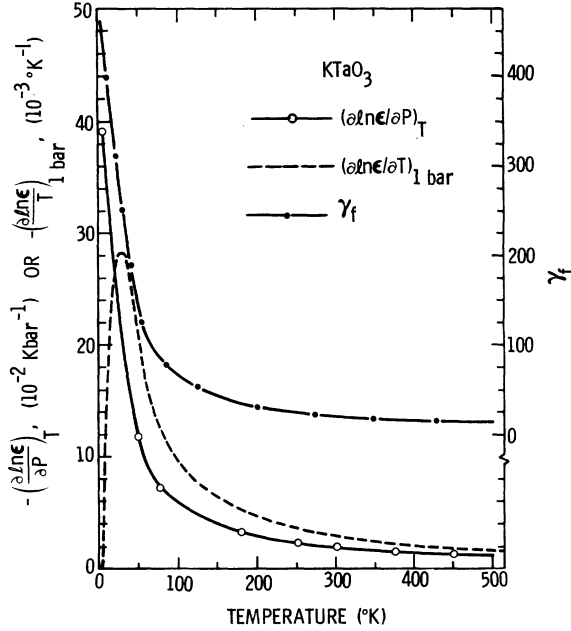


FIG. 4. Temperature dependences of the logarithmic pressure and temperature derivatives of the static dielectric constant and of the soft-mode Grüneisen parameter γ_f for KTaO_3 .

$$\epsilon \omega_f^2 = \text{const.} \quad (2)$$

That Eq. (2) holds very well for KTaO_3 is shown by the solid line in Fig. 5, which is deduced from our $\epsilon(T)$ data, and where the constant ($= 1.81 \times 10^6 \text{ cm}^{-2}$) was evaluated solely from the known room-temperature (300°K) values of $\epsilon = 239$ and $\omega_f = 87 \text{ cm}^{-1}$ (the average of the three experimental values). Within the uncertainties in the directly measured ω_f 's the agreement between the solid line and the data is excellent. It is worth noting that unlike SrTiO_3 , where $\omega_f^2(T)$ is linear over a relatively large temperature range above $\sim 50^\circ\text{K}$,²⁶ the behavior of KTaO_3 is rather nonlinear (Fig. 5). This is of course also manifested by the fact that $\epsilon(T)$ in Fig. 2 does not obey a simple Curie-Weiss law.

From Fig. 5 it is seen that measurements of ϵ give us direct information on ω_f . We make use of this fact in deducing the effect of pressure on ω_f from the $\epsilon(P)$ data. This is necessary because $\omega_f(P)$ is relatively difficult to measure directly and has not been done. From Eq. (2) it follows that

$$\left(\frac{\partial \ln \omega_f}{\partial P} \right)_T = -\frac{1}{2} \left(\frac{\partial \ln \epsilon}{\partial P} \right)_T \quad (3a)$$

and

$$\left(\frac{\partial \ln \omega_f}{\partial T} \right)_P = -\frac{1}{2} \left(\frac{\partial \ln \epsilon}{\partial T} \right)_P \quad (3b)$$

The pressure and temperature dependence of ω_f are then readily deduced from the results in Figs. 2-4 and Table I.

The soft-mode Grüneisen parameter,⁹ or so-called mode $\gamma(\gamma_f)$, defined by

$$\begin{aligned} \gamma_f &\equiv - \left(\frac{\partial \ln \omega_f}{\partial \ln V} \right)_T \\ &= \kappa^{-1} \left(\frac{\partial \ln \omega_f}{\partial P} \right)_T, \end{aligned} \quad (4)$$

can then be readily determined from the pressure derivatives and the compressibility. Figure 4 shows $\gamma_f(T)$, and we note that, unlike normal optic-mode γ 's which are of the order of ~ 2 , γ_f here is large and increases sharply with decreasing T —unique properties of the soft mode.⁹

We have discussed the increase in ω_f with pressure and the large values of γ_f for the perovskites elsewhere.⁹ It suffices to say here that the effects can be qualitatively understood by noting that in the soft mode description ω_f is determined by a balance between short-range and Coulomb forces, and that the short-range forces increase more rapidly with increasing pressure than do the Coulomb forces leading to an increase in ω_f . The effect is most dramatic when the cancellation of the two forces is most nearly complete, which is at the lowest temperatures in KTaO_3 . Thus, for example, $\gamma_f = 460$ at 4°K .

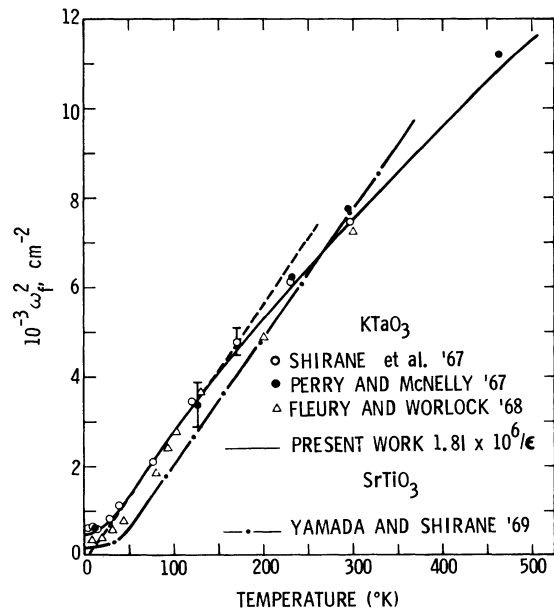


FIG. 5. Temperature dependence of the square of the soft-mode frequency of KTaO_3 at 1 bar comparing directly measured response (symbols) with that deduced from the present dielectric constant data (solid line). Results for SrTiO_3 are shown for comparison.

TABLE I. Values of the static dielectric constant (ϵ) of KTaO_3 and its logarithmic pressure and temperature derivatives at different temperatures. Also listed are values of the volume expansivity β and compressibility κ (see text). The measured isobaric temperature derivatives are separated into their pure-volume and pure-temperature contributions.

T (°K)	ϵ	β ($10^{-5} \text{ }^\circ\text{K}^{-1}$)	κ ($10^{-4} \text{ kbar}^{-1}$)	$\left(\frac{\partial \ln \epsilon}{\partial P}\right)_T$ ($10^{-2} \text{ kbar}^{-1}$)	$\left(\frac{\partial \ln \epsilon}{\partial T}\right)_{P=1 \text{ bar}}$ ($10^{-3} \text{ }^\circ\text{K}^{-1}$)	$= -\frac{\beta}{\kappa} \left(\frac{\partial \ln \epsilon}{\partial P}\right)_T + \left(\frac{\partial \ln \epsilon}{\partial T}\right)_V$ ($10^{-3} \text{ }^\circ\text{K}^{-1}$)	
4.0	3840	~ 0	4.23	-39.0 ± 0.1	~ -2.4	~ 0	-2.40
50.0	1350	0.70	4.28	-11.85 ± 0.1	-21.00 ± 0.50	1.78	-22.78
77.2	825	0.79	4.30	-7.24 ± 0.05	-12.75 ± 0.50	1.33	-14.08
180.3	375	1.20	4.39	-3.17 ± 0.05	-5.19 ± 0.10	0.87	-6.06
248.3	281	1.50	4.45	-2.30 ± 0.05	-3.70 ± 0.10	0.78	-4.48
300.0	239.0	1.76	4.50	-1.83 ± 0.01	-2.70 ± 0.10	0.72	-3.42
375.0	199.5	1.97	4.57	-1.54 ± 0.01	-2.17 ± 0.10	0.66	-2.83
450.0	172.6	2.08	4.63	-1.36 ± 0.02	-1.80 ± 0.10	0.61	-2.41

IV. ANHARMONIC SELF-ENERGY OF SOFT MODE

A. Evaluation of Self-Energy Shifts

The measured temperature dependence of ω_f (or ϵ) at constant pressure for a cubic crystal such as KTaO_3 derives from two contributions: (i) the contribution associated with the change in crystal volume V , i. e., the explicit volume effect, and (ii) the explicit temperature dependence which would occur even if the volume of the sample were to remain fixed. Writing $\omega_f = \omega_f(V, T)$ we then have

$$\begin{aligned} \left(\frac{\partial \ln \omega_f}{\partial T}\right)_P &= \left(\frac{\partial \ln V}{\partial T}\right)_P \left(\frac{\partial \ln \omega_f}{\partial \ln V}\right)_T + \left(\frac{\partial \ln \omega_f}{\partial T}\right)_V \\ &= -\frac{\beta}{\kappa} \left(\frac{\partial \ln \omega_f}{\partial P}\right)_T + \left(\frac{\partial \ln \omega_f}{\partial T}\right)_V. \end{aligned} \quad (5)$$

Thus the constant-volume contribution $(\partial \ln \omega_f / \partial T)_V$ can be evaluated from the known isobaric and isothermal derivatives, which in turn are evaluated from measured quantities via Eqs. (3) and a knowledge of the volume thermal expansivity β and compressibility κ . Table I summarizes some of the measured results at a number of temperatures expressed in terms of ϵ . It can be easily seen from this table and Eqs. (3) that the pure-volume and pure-temperature contributions are opposite in sign and that the pure-temperature effect, $(\partial \ln \omega_f / \partial T)_V$, is the predominant term in determining the isobaric temperature derivative of ω_f at all temperatures covered. The pure-volume contribution is however also substantial in magnitude amounting to 17% (34% in terms of ϵ) of the measured isobaric derivative at 450 °K. That the pure-temperature effect dominates is of course expected as mentioned earlier (Sec. I). The results in Table I just make this fact more quantitative.

The above conclusion is made more explicit by evaluating the pure-volume and pure-temperature

contributions to ω_f at every temperature over the whole temperature range covered by the measurements. To do so we rewrite Eq. (5) in the form (deleting the subscript f in ω_f for convenience)

$$(\Delta \omega_T)_P = -(\Delta \omega_P)_T + (\Delta \omega_T)_V. \quad (6)$$

In this notation $(\Delta \omega_T)_P$ is the measured change in ω_f on raising the temperature from 0 to T °K at constant pressure (1 bar); $(\Delta \omega_T)_V$ is the change in ω_f caused by raising the temperature from 0 to T °K at constant volume, that being the volume of the crystal at 0 °K and 1 bar; $-(\Delta \omega_P)_T$ is the change in ω_f caused by raising the pressure at a constant temperature T from 1 bar to a value P sufficient to produce a volume change equal in magnitude to that caused by raising the temperature from 0 to T °K at 1 bar. It is readily evaluated from $\omega_f(P)$ data and the known β and κ . Obviously this term enters with a negative sign [Eqs. (5) and (6)] since the signs of β and κ of KTaO_3 are normal, i. e., ΔV is positive on heating and negative on compression. From the data presented earlier in this paper we have all the information needed to evaluate $(\Delta \omega_T)_V$ and $(\Delta \omega_P)_T$ as functions of T . The results are given in Fig. 6. These results clearly show the dominance of the pure-temperature effect at all temperatures in determining the isobaric $\omega_f(T)$ dependence. The pure-volume effect produces a negative frequency shift which acts to reduce the magnitude of the pure-temperature effect.

B. Discussion

We now wish to examine the theoretical implications of the above results. As we have seen the frequency shift $(\Delta \omega_P)_T$ is the contribution to the measured frequency (at 1 bar) arising from the thermal expansion of the crystal. In magnitude it amounts to $\sim 7\%$ of the measured frequency at 300 °K and $\sim 10\%$ at 500 °K. Its origin and sign are easily

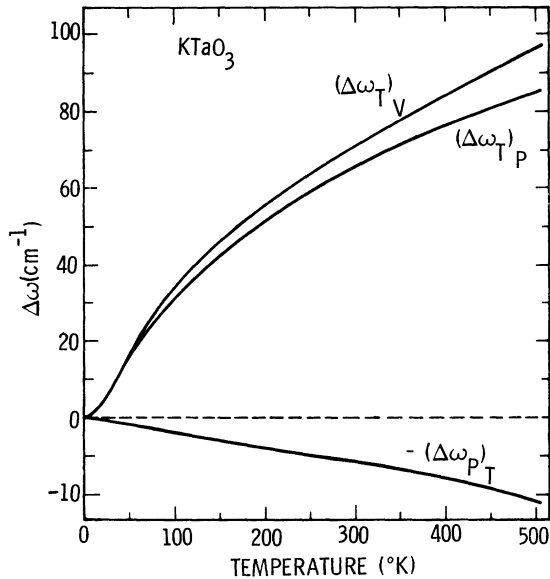


FIG. 6. The pure-volume $-(\Delta\omega_P)_T$ and pure-temperature $(\Delta\omega_T)_V$ contributions to the measured isobaric (1 bar) shift $(\Delta\omega_T)_P$ of the soft-mode frequency of KTaO_3 . At 0°K and 1 bar, $\omega = 21 \pm 4 \text{ cm}^{-1}$. Note the change of scale for the negative ordinate.

understood. As the interatomic distances increase with increasing T , the restoring force for the FE mode, which is primarily a vibration of the Ta ion against the oxygen octahedron, and hence the frequency ω_f , decreases. Although thermal expansion itself results from anharmonic interactions among phonons, the theoretical treatment of this frequency shift is generally (and in most cases satisfactorily) carried out using harmonic lattice dynamics but with the ionic vibrations about new equilibrium positions appropriate to the homogeneously enlarged crystal at the high temperature in question. This is the quasiharmonic treatment and the resulting frequency is the quasiharmonic frequency.

In KTaO_3 the predominant frequency shift at 1 bar arises from the pure-temperature contribution $(\Delta\omega_T)_V$. The origin of this term lies in the anharmonic vibrations of the ions about their equilibrium positions, and to understand it we must resort to the lattice dynamical theory of anharmonic crystals. Unfortunately detailed treatments of anharmonic lattice dynamics of insulators involve many-body theory and are very complex. Only approximate treatments are possible. The conventional approach is to employ a perturbation expansion of the crystal potential around a harmonic basis and assume rapid convergence.^{27,28} This has proven quite satisfactory for weakly anharmonic crystals such as the alkali halides and alkaline earth fluorides and for crystals exhibiting weak-soft-mode

behavior such as the thallos halides and rutile where the anharmonic self-energy shift to the normal-mode frequency is smaller than the strictly harmonic frequency.

The situation is much more complicated for the case of ferroelectrics such as BaTiO_3 and PbTiO_3 or incipient ferroelectrics such as SrTiO_3 and KTaO_3 . In such crystals the soft-mode frequency is expected to be pure imaginary in the harmonic approximation so that a harmonic basis does not exist in principle (i. e., it does not represent a stable equilibrium for the crystal). This was recognized in the original soft-mode treatments of Cochran¹ and Anderson,² where it was assumed that it is the anharmonic interactions which stabilize the soft-mode frequency ω_f by an effective renormalization which makes ω_f real. Many authors^{25,28-30} have since formally shown how this renormalization comes about, and the difficulties with the perturbation treatments were recently re-emphasized by Gillis and Koehler.³⁰ Several approaches have been employed to overcome these difficulties.

Silverman and Joseph²⁵ and Maradudin²⁹ employed canonical transformations and renormalization procedures whereby a large part of the anharmonic contributions is incorporated in the unperturbed Hamiltonian, and this effectively removes the modes with imaginary frequencies from the lattice sums. Cowley,²⁸ on the other hand, performed the perturbation calculations by neglecting all modes with imaginary frequencies on the assumption that the number of such modes is very small compared with the total number of modes in the lattice sums. The soft modes are then treated by an analytic extension of the results into the regime of imaginary frequencies. The above approaches are of course approximations. An inherently more realistic and satisfactory scheme would be to use a self-consistent phonon treatment as recently discussed by Gillis and Koehler.³⁰ Operationally here one deals with a trial harmonic Hamiltonian in which the force constants (or frequencies) are renormalized force constants determined variationally, and they represent the real (physical) constants of the crystal. Though simple in concept, the self-consistent treatment is very involved in practice and its only detailed application to the FE soft-mode problem is that recently given by Gillis and Koehler. They considered a model NaCl lattice invoking several simplifying assumptions.

Our object here is not to go into a detailed discussion of the theoretical results but rather to discuss the experimental results in terms of the qualitative predictions of the theoretical models. Fortunately for this purpose both the perturbation and self-consistent treatments lead to qualitatively

similar results, although there are important fundamental differences between the two as noted above. In lowest order, the perturbation treatment encompasses the cubic anharmonic interactions to second order and the quartic interactions to first order. The result for the zone-center ($\vec{q} = 0$) soft-mode frequency squared ω_f^2 is found to be of the form

$$\omega_f^2 = \omega_0^2 - \phi U^T + \Phi^{(4)}[n(\vec{q}j)] - [\Phi^{(3)}]^2[n(\vec{q}j), \omega(\vec{q}j), \Omega], \quad (7)$$

where ω_0 is the strictly harmonic frequency, and the second term is the contribution of the thermal strain which, as discussed earlier, is negative. The third term is the contribution of the quartic potential and is a function of the phonon occupation number $n(\vec{q}j)$, where \vec{q} is the wave vector and j denotes the optic branch. The last term is the contribution of the cubic potential and is a function of the phonon occupation numbers and frequencies, $\omega(\vec{q}j)$, and the applied frequency Ω . It involves the square of the cubic potential $\Phi^{(3)}$ and is found to be negative at low applied frequencies. The usual soft-mode description depicts $\omega_0^2 < 0$ for a FE crystal with a finite transition temperature (where $\omega_f^2 \rightarrow 0$ at T_0) or ω_0^2 as small and either positive or negative for a crystal which is barely stable at 0°K. In either case, and in view of the signs of the various contributions in Eq. (6) in this approximation ω_f is stabilized by the quartic anharmonicities.

The result of the self-consistent treatment of the model paraelectric crystal employed by Gillis and Koehler³⁰ can be expressed in the form

$$\omega_f^2 = \Omega_f^2 - [\Phi^{(3)}]^2[n(\vec{q}j), \omega(\vec{q}j), \Omega], \quad (8)$$

where Ω_f^2 is the square of the renormalized soft-mode frequency which is determined self-consistently. It incorporates the contributions from the quadratic (harmonic) potential, the quartic anharmonic potential and the thermal strain, and which, in terms of reduced units, is given by

$$\Omega_f^2 = 2[\phi^{(2)} + \frac{2}{3}\epsilon_C - \frac{1}{8} + 12\phi^{(4)}\langle u^2 \rangle + 4\phi^{(4)}\eta^2 + 6\phi^{(3)}e + 12\phi^{(4)}e^2], \quad (9)$$

where the ϕ 's are the force constants, ϵ_C is the Coulomb energy per particle (a negative quantity), u is the dynamic displacement, η is the rigid relative displacement of the two sublattices of the model (NaCl) crystal, and e is the thermal strain. Here the cubic interaction enters as shown in Eq. (8) and via its coupling to the strain in Eq. (9). Again we note that Ω_f , and hence ω_f , is stabilized largely by the quartic interaction.

We now wish to make some observations about the KTaO₃ results. As mentioned earlier pure

KTaO₃ remains paraelectric down to the lowest temperatures. At 4°K, $\omega_f = 21 \pm 4 \text{ cm}^{-1}$ ($6.3 \pm 1.2 \times 10^{11} \text{ sec}^{-1}$), so that if ω_0 were truly imaginary, then one would have to conclude that ω_f is stabilized by anharmonic interactions associated with zero-point motion. For $\omega_0^2 \leq 0$ these zero-point anharmonicities would have to contribute a frequency shift $\Delta\omega \geq 21 \pm 4 \text{ cm}^{-1}$. A possible approximate way of estimating this anharmonic zero-point frequency shift comes from the results of the perturbation treatment. In the high-temperature classical limit the phonon occupation numbers and the volume (or thermal strain) are expected to vary linearly with T (see, e.g., Fig. 1) so that all the terms on the right-hand side of Eq. (7) except ω_0^2 should be linear in T , and we can write

$$\omega_f^2 = \omega_0^2 + \alpha T, \quad (10)$$

where α is a positive constant, the positive sign deriving from the dominance of the quartic anharmonicities. Note that Eq. (10) applies *only* to the linear portion of the $\omega_f^2(T)$ response, so that ω_0^2 is *not* the measured value of ω_f^2 at 0°K. Thus extrapolation of the linear $\omega_f^2(T)$ response back to 0°K should yield ω_0^2 .

One of the interesting features of the soft FE mode in the perovskites is the long recognized observation that for many members of this family $\omega_f^2(T)$ is found to be linear over a wide T range well below the Debye temperature Θ_D . This is well illustrated by the behavior of SrTiO₃ ($\Theta_D \approx 1000^\circ\text{K}$) in Fig. 5 which shows the linear region extending down to $\sim 50^\circ\text{K}$. This feature is not explained by the perturbation-theory results but arises in a somewhat natural way in the self-consistent treatment. Gillis and Koehler³⁰ find that by treating all modes self-consistently, the density of soft modes with $\hbar\omega \ll kT$ is weighted more heavily at low temperatures than if the contribution from soft optic branches of long wavelength had been neglected (as done in perturbation schemes). These authors have also observed that the temperature range over which the linear $\omega_f^2(T)$ response obtains decreases with decreasing quartic anharmonicity. We should also note that the linear $\omega_f^2(T)$ response obtains in lowest order (as represented by the above models). When higher-order anharmonic interactions are included (and their effects become felt at high T) the linear response no longer obtains.

Examination of Fig. 5 shows that in contrast to SrTiO₃, the $\omega_f^2(T)$ response of KTaO₃ is rather non-linear. An approximately linear region, denoted by the dotted line, extends over a relatively small region from ~ 30 to $\sim 125^\circ\text{K}$. Extrapolation of this linear response back to 0°K yields an intercept³¹ $\equiv \omega_0^2 = -200 \pm 200 \text{ cm}^{-2}$. Although this approach to evaluate ω_0^2 may be somewhat doubtful, the con-

clusion that $\omega_0^2 \approx 0$ or slightly negative on the scale of things in Fig. 5 is probably not too far wrong. All the stabilization of ω_f at 0°K is thus provided by the zero-point anharmonicities which contribute a frequency shift of something over $21 \pm 4 \text{ cm}^{-1}$. Unfortunately it does not appear possible to evaluate ω_0^2 from the experimental data via the self-consistent phonon treatment. Interpreted in terms of the Gillis and Koehler results,³⁰ the fact that the linear $\omega_f^2(T)$ region in KTaO_3 is so much smaller than that in SrTiO_3 probably implies that the quartic anharmonicities play a less dominant role in KTaO_3 . The nonlinear $\omega_f^2(T)$ response at high temperatures suggests that lowest-order anharmonic treatments are not adequate for KTaO_3 .

In conclusion, the results of the present work allow us to separate the isobaric (1-bar) temperature dependence of the soft-mode frequency ω_f of KTaO_3 into its two contributions: the one arising from the thermal strain and the other arising from the pure-temperature higher-order anharmonic effects. The thermal-strain contribution, though small, is not negligible and amounts to 7% of the measured frequency at 300°K and 10% at 500°K . It also acts to reduce the influence of the pure-temperature anharmonicities. A rough estimate suggests that the strictly harmonic frequency of

the soft mode ω_0 is ≈ 0 or just barely imaginary, and thus all of the stabilization of ω_f at 0°K is provided by zero-point anharmonicities. Interpreted in terms of both the perturbation and self-consistent phonon treatments, the high-temperature stabilization of ω_f is dominated by the quartic anharmonicities. Unfortunately, however, these treatments do not give us any indication about the microscopic origin of the various anharmonicities and the cancellation between the short-range and Coloumb forces so important in the soft-mode picture. The answers to these are the important remaining questions. The very large increase in ω_f with pressure at low temperature (19.5% kbar^{-1} at 4°K) for a low compressibility crystal such as KTaO_3 —a unique property of the soft mode—serves to beautifully illustrate the delicate balance that exists between the short- and long-range forces in this crystal. The strictly harmonic frequency becomes real at high pressure.

ACKNOWLEDGMENTS

The expert technical assistance of B. E. Hammons and R. A. Trudo are gratefully acknowledged. We are also grateful to N. S. Gillis for many informative and helpful discussions.

*Work supported by the U. S. Atomic Energy Commission.

- ¹W. Cochran, *Adv. Phys.* **9**, 387 (1960); *Adv. Phys.* **18**, 157 (1969).
- ²P. W. Anderson, in *Fizika Dielektrikov*, edited by G. I. Shanavi (Akad. Nauk SSSR, Moscow, 1960).
- ³R. A. Cowley, *Phys. Rev.* **134**, A981 (1964).
- ⁴G. Shirane, R. Nathans, and V. J. Minkiewicz, *Phys. Rev.* **157**, 396 (1967). See also, Shirane *et al.*, *Phys. Rev.* **177**, 848 (1969); *Phys. Rev.* **177**, 859 (1969); *Phys. Rev. Lett.* **19**, 234 (1967); *Phys. Rev. B* **1**, 1227 (1970).
- ⁵P. A. Fleury and J. M. Worlock, *Phys. Rev.* **174**, 613 (1968).
- ⁶G. Shirane, J. D. Axe, J. Harada, and J. P. Remeika, *Phys. Rev. B* **2**, 155 (1970).
- ⁷H. H. Barrett, *Phys. Rev.* **178**, 743 (1969); *Phys. Lett. A* **26**, 217 (1968); R. E. Nettleton, *Phys. Rev.* **140**, A1453 (1965).
- ⁸See, e.g., A. J. Bosman and E. E. Havinga, *Phys. Rev.* **129**, 1593 (1963); B. D. Silverman, *Phys. Rev.* **135**, A1596 (1964).
- ⁹G. A. Samara, *Ferroelectrics* **2**, 177 (1971).
- ¹⁰W. R. Abel, *Phys. Rev. B* **4**, 2696 (1971).
- ¹¹The earliest work (Ref. 14) and some recent work (Ref. 16) have given some definite evidence for a phase transition at $\sim 10^\circ\text{K}$ as evidenced by a peak in the static dielectric constant. We do not believe that this peak (transition) is an intrinsic property of the *pure* crystal which is optically clear, i.e., no transition related to the soft mode at zone center occurs at any temperature for pure KTaO_3 . No evidence for a transition was seen in the work of Refs. 5, 10, and 15 or in the present work. The neutron scattering work (Ref. 4) indicated

- anomalies in some of the phonon modes near 10°K , and it was speculated that these were due to an interaction between the soft (TO) mode and the longitudinal-acoustic (LA) mode at finite wave vector ($\vec{q} \approx 0, 2$).
- ¹²R. C. Miller and W. G. Spitzer, *Phys. Rev.* **129**, 94 (1963).
- ¹³C. H. Perry and T. F. McNelly, *Phys. Rev.* **154**, 456 (1967).
- ¹⁴J. K. Hulm, B. T. Matthias, and E. A. Long, *Phys. Rev.* **79**, 885 (1949).
- ¹⁵S. H. Wemple, *Phys. Rev.* **137**, A1575 (1965).
- ¹⁶D. G. Demurov and Yu. N. Venevitsev, *Fiz. Tverd. Tela* **13**, 669 (1971) [*Sov. Phys.-Solid State* **13**, 553 (1971)].
- ¹⁷R. W. Lynch and B. Morosin, *J. Appl. Cryst.* **4**, 352 (1971).
- ¹⁸P. Vousden, *Acta Cryst.* **4**, 373 (1951).
- ¹⁹B. Morosin and J. E. Schirber, *Phys. Lett. A* **30**, 512 (1969).
- ²⁰H. H. Barrett, *Phys. Lett. A* **26**, 217 (1968). The constants c_{11} and c_{12} are needed to calculate κ for a cubic crystal, but the temperature dependences of c_{12} and c_{44} should be similar.
- ²¹Purchased from Electro-Optical Division, Sanders Associates, 95 Canal St., Nashua, N. H.
- ²²G. A. Samara and P. S. Peercy, *Phys. Rev. B* (to be published).
- ²³G. A. Samara, *J. Phys. Chem. Solids* **26**, 121 (1965); *Ferroelectrics* **2**, 277 (1971).
- ²⁴J. H. Barrett, *Phys. Rev.* **86**, 118 (1952).
- ²⁵B. D. Silverman and R. I. Joseph, *Phys. Rev.* **129**, 2062 (1963).
- ²⁶Y. Yamada and G. Shirane, *J. Phys. Soc. Jap.* **26**, 396

(1969).

²⁷A. A. Maradudin and A. E. Fein, *Phys. Rev.* 128, 2589 (1962).

²⁸R. A. Cowley, *Adv. Phys.* 12, 421 (1963); *Philos. Mag.* 11, 673 (1965).

²⁹A. A. Maradudin, in *Ferroelectricity*, edited by E. F.

Weller (Elsevier, Amsterdam, 1967), p. 72.

³⁰N. S. Gillis and T. R. Koehler, *Phys. Rev. B* 4, 3971 (1971); see also, N. S. Gillis (unpublished).

³¹A somewhat larger negative value is obtained if one emphasizes Fleury and Worlock's data in Fig. 5.