# Temperature Dependence of the Soft Ferroelectric Mode in $KTaO_3$†

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(Received 21 December 1966)

The lattice dynamics of the perovskite-type ferroelectric $KTaO_3$ has been studied by inelastic neutron-scattering techniques. In particular, the temperature dependence of the soft ferroelectric mode, namely a transverse optical mode at $q=0$, has been studied between 4 and 295°K. At 295°K, the phonon energy of this mode is $10.7\pm0.3$ meV ($86.3\pm2.5$ cm$^{-1}$), in excellent agreement with the optical measurement of Miller and Spitzer. The square of the energy of the soft mode follows closely the temperature dependence of $1/\epsilon$ down to 15°K (the extrapolated Curie temperature is 2–4°K). The deviation of the dielectric constant $\epsilon$ from a Curie-Weiss law, at the high- and low-temperature extremes, is faithfully reflected in the temperature dependence of the soft mode. Anomalous behavior was observed at 4.3°K in this mode as well as in other modes. A tentative explanation for this anomalous behavior is that a phase transition has set in at approximately 10°K.

## I. INTRODUCTION

THE lattice dynamics of the perovskite-type ferroelectrics has received considerable attention in recent years.[1–3] Anderson[1] and Cochran[2] have developed a theory of ferroelectricity in which the existence of the ferroelectric state and the onset of a lattice instability are related to one another. The central prediction of the theory is that the energy of a transverse optical (TO) mode at $q=0$ vanishes at the Curie temperature, causing a crystal instability, which in turn leads to the ferroelectric state. The energy of this mode $\hbar\omega_{TO}$ is expected to have a temperature dependence of the form

$$(\hbar\omega)^2 \propto (T-T_0), \qquad (1)$$

where $T_0$ is the extrapolated (paraelectric) Curie temperature. This $T_0$ agrees with the ferroelectric Curie temperature $T_c$, if the phase change is truly of the second order. This mode has been called the "soft" or the ferroelectric mode.

The energy of this soft mode can be extracted from reflectivity measurements in the infrared region or measured directly by inelastic neutron scattering. The temperature dependence of this mode in $SrTiO_3$ has been studied by Cowley[3] using neutron spectroscopy. Between 400 and 90°K, $\omega^2$ was found to follow a Curie-Weiss law with an extrapolated Curie temperature of 32°K.

This paper gives the results of neutron measurements on $KTaO_3$ between 295 and 4°K. $KTaO_3$ has the cubic perovskite structure with a lattice constant of 3.989 Å at room temperature. The Curie temperature was reported to be 13°K by Hulm, Matthias, and Long.[4] More recent measurements by Wemple[5] indicate that the crystal remains paraelectric down to 1.6°K. Infrared measurements were made by Miller and Spitzer[6] and the soft mode was estimated to be 85.1 cm$^{-1}$ at room temperature. Theoretical considerations by Joseph and Silverman[7] have led them to identify this mode as the mode proposed by Slater.[8] The emphasis of the present measurement is on the behavior of the ferroelectric mode close to the Curie temperature, where, to date, no neutron measurements have been reported. An excellent single crystal of $KTaO_3$ was kindly provided for the present study by Dr. S. H. Wemple and Dr. R. C. Miller of Bell Telephone Laboratories.

## II. EXPERIMENTAL

This single crystal of $KTaO_3$ was grown by Wemple[5] by a modified Kyropolis method, and was the same crystal used by Miller and Spitzer[6] for their infrared measurements. It contains 200-ppm Fe which was added for paramagnetic resonance studies. The crystal has the dimensions $8\times8\times5$ mm. The relatively small size of the crystal, for inelastic neutron scattering, has somewhat limited the accuracy and scope of the present investigation. On the other hand, this crystal has the very narrow mosaic spread of 0.3′ (measured against a perfect Ge crystal). Thus the lower limit of phonon measurements is determined by the collimation of the neutron beams and not by the mosaic spread of the sample.

The measurements were carried out at the triple-axis spectrometer at the Brookhaven high-flux beam reactor. The constant $Q$ scan[9] was used with an incoming neutron energy of 45 meV. The majority of the measurements were done with the effective beam collimation of 20′ both before and after the sample.

† Work performed under the auspices of the U.S. Atomic Energy Commission.

[1] P. W. Anderson, in Proceedings of the All-Union Conference on the Physics of Dielectrics of the Academy of Sciences of the U.S.S.R., 1958, p. 290 (unpublished).
[2] W. Cochran, Advan. Phys. **9**, 387 (1960).
[3] R. A. Cowley, Phys. Rev. **134**, A981 (1964).
[4] J. K. Hulm, B. T. Matthias, and E. A. Long, Phys. Rev. **79**, 885 (1950).
[5] S. H. Wemple, Phys. Rev. **137**, A1575 (1964).
[6] R. C. Miller and W. G. Spitzer, Phys. Rev. **129**, 94 (1963).
[7] R. I. Joseph and B. D. Silverman, J. Phys. Chem. Solids **25**, 1125 (1964).
[8] J. C. Slater, Phys. Rev. **78**, 748 (1950).
[9] B. N. Brockhouse, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 113.

## III. TRANSVERSE OPTICAL MODE

The transverse optical mode with the momentum transfer $q$ along the [001] direction has been measured as a function of temperature with the results shown in Fig. 1 and Table I. At 295°K, the phonon energy of the $q=0$ mode is $10.7\pm0.3$ meV, which corresponds to $86.3\pm2.5$ cm$^{-1}$ in wave number, in excellent agreement with the optical measurement of Miller and Spitzer.[6]

The data were obtained around the (2,0,0) reciprocal-lattice point; the zone-boundary value of $q$ is 0.788 Å$^{-1}$. Examples of neutron groups corresponding to $q=0$ are shown in Fig. 2. In order to reduce the background at the low-energy side, the data at 15°K were obtained by using a tighter collimation of 10′ for the neutron beam before the scattering. It is interesting to note that the background below 2 meV is not due to the tail of the Bragg reflection, but to the low-energy phonons of the transverse acoustic (TA) mode. This point was proved by studying the temperature dependence of the background. The lack of an elastic component in the background is due to the extremely narrow mosaic spread of the crystal.

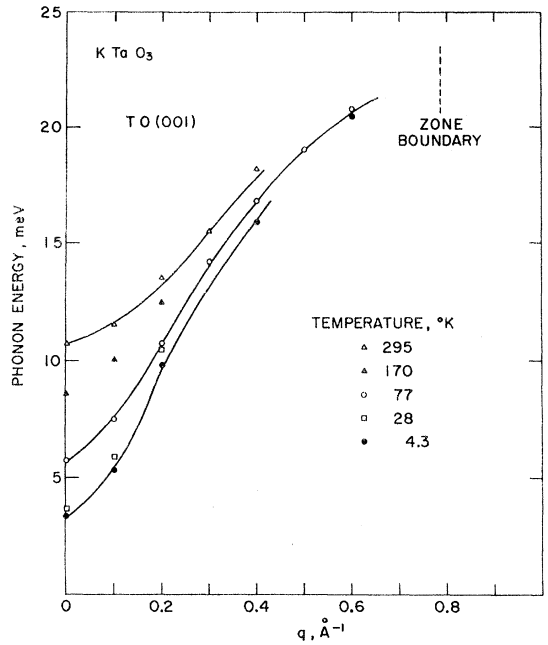


FIG. 1. Temperature dependence of the TO branch in $KTaO_3$.

The neutron groups are well defined even at low temperatures very close to the extrapolated Curie point. The different profiles of the data shown in Fig. 2 are mainly due to effects associated with the finite resolution of the spectrometer. A slight, but noticeable, broadening in the peak profile was observed at 4°K; the broadening is probably the result of a phase transition at 10°K. This conjecture will be elaborated on more thoroughly in Sec. V.

TABLE I. Phonon energies of the [001] transverse optical mode in $KTaO_3$ in units of meV. Conversion factor to the optical wave number (cm$^{-1}$) is 8.07 and to the frequency ($10^{12}$ cps) is 0.242. Estimated errors of phonon energies are 0.2–0.3 meV. The $q$ at the zone boundary is 0.788 Å$^{-1}$.

| $T$ (°K) | $q$ (Å$^{-1}$) | Phonon energy (meV) 0 | 0.1 | 0.2 |
|---|---|---|---|---|
| 295 | | 10.7 | 11.5 | 13.5 |
| 230 | | 9.7 | | |
| 170 | | 8.6 | 10.0 | 12.5 |
| 120 | | 7.3 | | |
| 77 | | 5.7 | 7.5 | 10.7 |
| 40 | | 4.2 | 6.0 | |
| 28 | | 3.6 | 5.9 | 10.5 |
| 15 | | 3.0 | 5.3 | |
| 10 | | 3.2 | 5.2 | |
| 4 | | 3.1 | 5.3 | 9.8 |

The temperature dependence of the ferroelectric mode is shown in Fig. 3. Here the square of phonon energies $(\hbar\omega)^2$ is plotted against the temperature. As in the case of $SrTiO_3$,[3] this quantity follows approximately the Curie-Weiss law. However, a definite deviation from the straight line is noted at the high- as well as at the low-temperature extremes of the data. Since $(\hbar\omega)^2$ is expected to be proportional to the reciprocal of the dielectric constant $\epsilon$ (for which the Curie-Weiss law is only an approximation), a direct comparison is made against the observed dielectric constant.

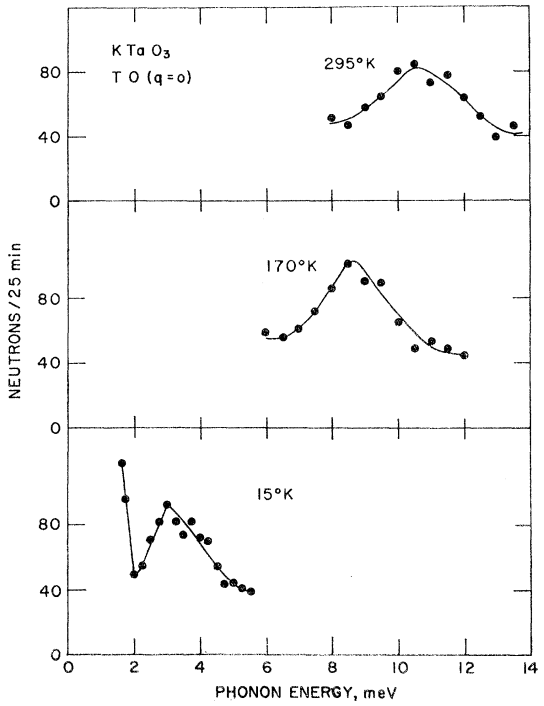


FIG. 2. Neutron groups corresponding to the TO mode at $q=0$ at various temperatures.

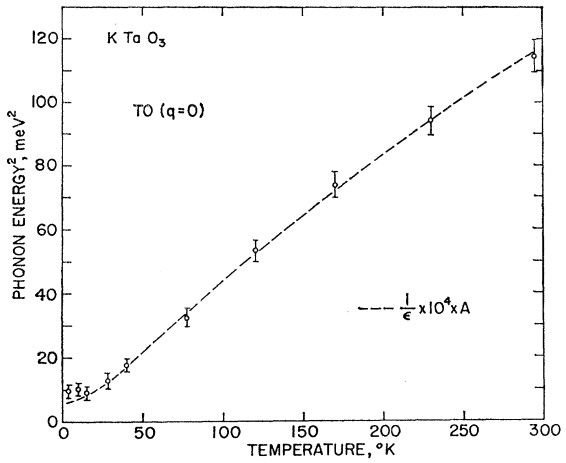


FIG. 3. Temperature dependence of the TO mode at $q=0$. The square of the phonon energy is compared with the reciprocal of the dielectric constant, as explained in the text.

Wemple[5] has measured the dielectric constant of a $KTaO_3$ crystal grown under conditions similar to the present sample. The dielectric constant $\epsilon$ above 30°K can be fitted to the expression

$$\epsilon=48+[5.7\times10^4/(T-4)]. \quad (2)$$

A similar expression was given by Rupprecht and Bell[10] with slightly different constants. The temperature-independent term produces a significant deviation from a Curie-Weiss law at high temperatures. Below 30°K, a roundoff of $\epsilon$ was observed; this is probably due to the quantum effect discussed by Barrett.[11]

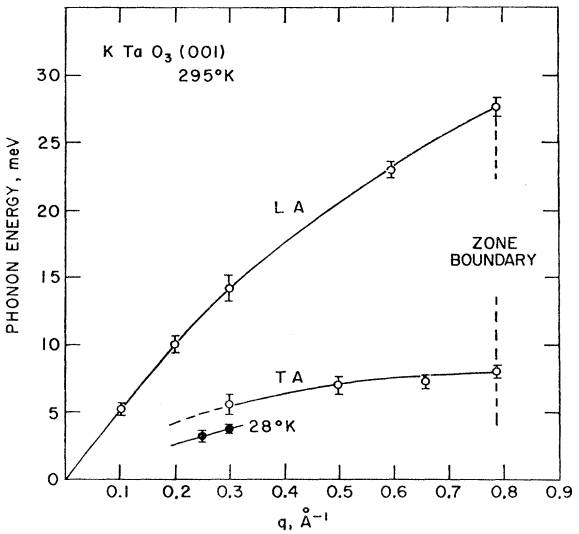


FIG. 4. Longitudinal acoustic (LA) mode and transverse acoustic (TA) mode in $KTaO_3$, along the [001] direction.

[10] G. Rupprecht and R. O. Bell, Phys. Rev. **135**, A748 (1952).
[11] J. H. Barrett, Phys. Rev. **86**, 118 (1952).

The comparison of our observed $(\hbar\omega)^2$ between 40 and 295°K with the expression of Eq. (2) gives

$$(\hbar\omega)^2=A\times(1/\epsilon)\times10^4,$$

$$A=2.825\ (\text{meV})^2. \quad (3)$$

At temperatures lower than 40°K, the observed values of $\epsilon$ were inserted in Eq. (3) to get the calculated $(\hbar\omega)^2$. The curve calculated with Eq. (3) is shown in Fig. 3 with a broken line. The over-all agreement between the present measurements and the phonon energies calculated from $\epsilon$ is excellent. The only disagreement is in the temperature region from 4 to 10°K.

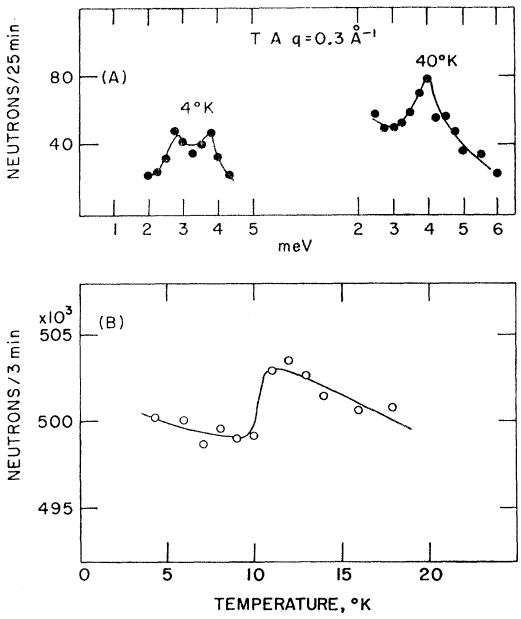


FIG. 5. (a) TA mode with $q=0.3$ Å$^{-1}$ at 40 and 4°K. (b) Temperature dependence of the (200) Bragg reflection of $KTaO_3$.

A possible cause for this disagreement will be discussed in Sec. V. The lowest energy we have measured for the soft mode is 3.0 meV at 15°K, and, from Eq. (3), it would correspond to a value for the dielectric constant of 3140.

The dispersion relation of this TO branch near the zone boundary was not determined accurately. At the zone boundary, we observed a broad neutron group corresponding to 24 meV. This, however, probably belongs to the next highest transverse branch. The $q=0$ mode of this branch is given as 24.7 meV by Miller and Spitzer.[6] The zone-boundary phonon of lowest TO mode is probably around 21–22 meV, where a weak and ill-defined neutron group seems to exist.

## IV. ACOUSTIC MODES

Only a very brief study was carried out on the acoustic phonon branches along [001]; the results are shown in Fig. 4. The longitudinal acoustic (LA) branch was investigated only at room temperature. The transverse acoustic modes with $q=0.25$ and 0.30 Å$^{-1}$ were measured at 40 and 28°K; the data at the latter temperature are shown in Fig. 4. The values at 40°K are approximately 10% higher than those of corresponding values at 28°K. The measurements by Cowley[3] on $SrTiO_3$ have shown a similar decrease of the TA modes with decreasing temperature, in contrast to a much weaker temperature dependence of the LA modes.

## V. PHASE TRANSITION AT 10°K

We have already mentioned the noticeable line broadening of the TO mode at 4°K. A much more pronounced anomaly was observed for the TA modes with $q=0.25$ and 0.30 Å$^{-1}$. These modes were well defined at 40 and 28°K, as shown in Fig. 5(a). At 4.3°K, however, these are so broad that a definite assignment of the phonon energy is quite difficult. This fact strongly suggests a phase transition somewhat above 4°K.

In order to determine the temperature of this transition, the following experiment was carried out. The spectrometer angles were set at the positions corresponding to the half-height of the (200) Bragg reflection, and neutron intensities were measured as a function of temperature. As seen in Fig. 5(b), a small but definite step was observed in both the heating and cooling curves around 10°K. One can make a very crude estimate of lattice distortion at this temperature if one assumes that the observed step is entirely due to a change of lattice constant through the transition. The rocking curve of this crystal has a full width at half-maximum of 0.15°, which is, in fact, the mosaic spread of the monochromator. The observed step would correspond to approximately $3\times10^{-5}$ in $\Delta a/a$, which is extremely small when compared with lattice distortions at the transitions in many other perovskite-type oxides.

The evidence we have presented for this phase change is by no means conclusive and further study is needed to clarify this question. Nevertheless, this phase change may be the cause of the anomalous behavior in the TO and TA modes at 4°K. It is interesting to note the observation made by Geusic *et al.*[12] in their study of nonlinear dielectric properties of $KTaO_3$ at 4°K. They reported that some of the dielectric properties could not be explained if the crystal retained a center of symmetry at this temperature. If the crystal is not cubic below 10°K, our measurements at 4.3°K do, of course, depend upon the domain or twin configurations. This could create a broadening and a splitting, as well as nonreproducibility of the phonon groups as was observed in the present study.

One striking similarity does exist between this phase transition and the 110°K transition in $SrTiO_3$. In the latter, Cowley[3] observed that the transverse optical mode is almost degenerate with the logitudinal acoustic mode over a considerable region of $q$ space in the temperature range around 110°K. We find that an exactly identical degeneracy prevails in $KTaO_3$ in the 4–15°K range. Since the LA mode is only weakly temperature-dependent, one can compare the TO mode in Fig. 1 with the LA mode in Fig. 4. Around 10°K, the TO mode between $q=0.1$ and 0.2 is completely degenerate with the corresponding LA mode.

We may note that the 110°K transition in $SrTiO_3$ does *not* reflect itself in the behavior of the dielectric constant. In $KTaO_3$, no anomaly was reported in the temperature dependence of the dielectric constant[5] around 10°K. It is tempting to speculate that the interaction of the temperature-dependent TO mode with the LA mode may be the cause of "small" phase transitions, without dielectric anomaly, frequently observed in perovskite-type compounds *near* their ferroelectric or antiferroelectric Curie temperatures.

## ACKNOWLEDGMENTS

The authors are very grateful to Dr. R. C. Miller and Dr. S. H. Wemple for the excellent single crystal and many illuminating discussions.

[12] J. E. Guesic, S. K. Kurtz, T. J. Nelson, and S. H. Wemple, Appl. Phys. Letters **2**, 185 (1963).