SOFT OPTIC MODES IN BARIUM TITANATE†

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Phonon dispersion relations of $BaTiO_3$ have been measured in the cubic phase by the inelastic neutron scattering technique. The energy of the soft mode, consistent with Cochran's theory, decreases with temperature to 0.8 meV at 230°C.

The existence of the soft ferroelectric mode, predicted by Cochran[1] and Anderson,[2] has been clearly demonstrated for $SrTiO_3$ and $KTaO_3$ by infrared reflectivity measurements[3-5] and by the inelastic neutron scattering technique.[6,7] Above the Curie point the square of the transverse-optic-mode frequency ω_{TO}, measured at $\vec{q}=0$, is in both cases inversely proportional to the dielectric constant. These two crystals do not transform into a well-established ferroelectric phase, however, apparently because of intervening phase transformations before normal Curie points can be reached. The transition in $BaTiO_3$, on the other hand, is usually considered as typical of the perovskite ferroelectrics, but the soft mode behavior for this crystal has been unsettled. Estimates of the ω_{TO} mode from infrared measurements[8,9] have varied considerably, depending upon the particular model adopted; for example, it has been given as either 5.2 meV[10] or 1.6 meV[9] at 200°C and either 4.2 meV[8] or 1.5 meV[9] at room temperature. Recently, Harada and Honjo[11] studied the optic mode at room temperature in an x-ray diffuse scattering study. They reported two points on the dispersion curve (at $q=0.31$ and 0.36 $Å^{-1}$), which are more in line with the low estimate at $\vec{q}=0$. Moreover, their results indicate that the transverse optic (TO) branch lies below the transverse acoustic (TA) branch except for small $\vec{q}$ values.

The present measurements of phonon dispersion relations of $BaTiO_3$ have been carried out on the triple-axis spectrometer at the Brookhaven high-flux beam reactor. A large single crystal, with a volume of 1.7 cm^3, was grown by a technique described previously.[12] The measurements were made in the cubic phase at several temperatures above the Curie temperature of 130°C. The constant-Q technique,[13] with a fixed incoming energy E_0, was employed. Some of the results are shown in Figs. 1 and 2. The measurements were made in the $[hk0]$ zone, mostly around the (200) and (400) reciprocal lattice points. The lowest optic branch, TO, has unusually low excitation energies over the entire range of q values. These optic modes have relatively weak intensities and they are sandwiched between the strong TA modes and a huge incoherent scattering peak due to Ba and Ti. Thus the optic modes were identified clearly only by a proper combination of E_0 and the beam collimation. At $q=0$, the background due to low-energy acoustic phonons was min-

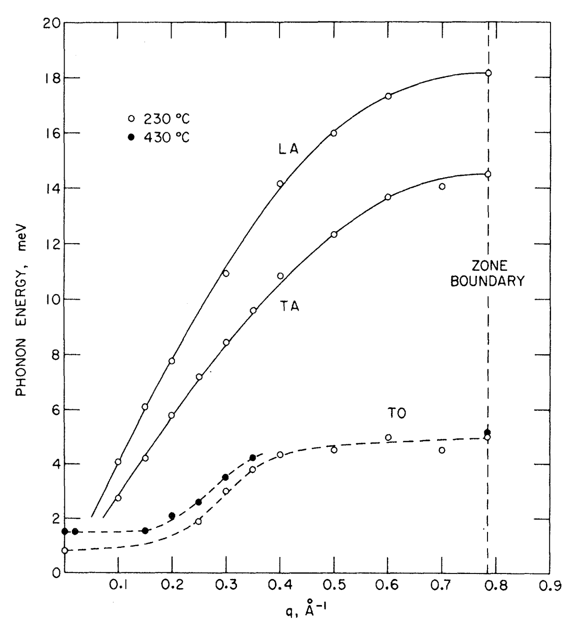

FIG. 1. Phonon dispersion relations of $BaTiO_3$ along [100] direction in the cubic phase. The q at the zone boundary is 0.782 $Å^{-1}$. Conversion factor to the wave number (cm^{-1}) is 8.07 and to the frequency (10^{12} cps) is 0.242.

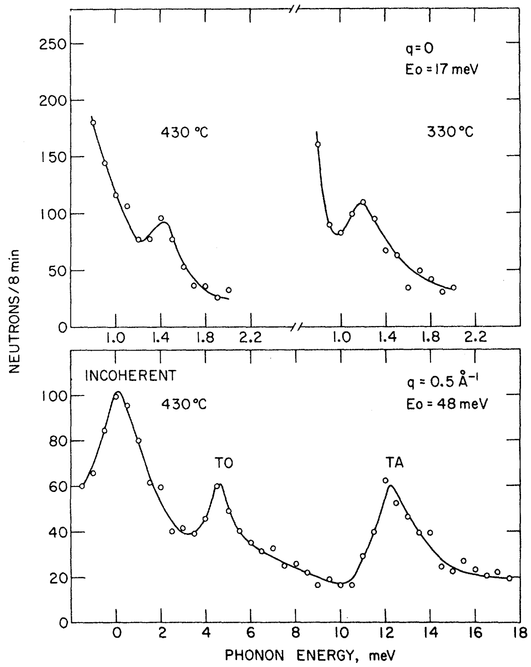

FIG. 2. Some representative neutron groups corresponding to transverse modes in cubic $BaTiO_3$. The $q = 0$ data shown were taken at (300) and the $q = 0.5$ Å^{-1} data from (400). The data points shown are average values of repeated runs at 8 min per point.

imized by using a smaller E_0 and a tighter collimation. This $q = 0$ mode was also studied at the (300) reciprocal lattice point, where the background was further reduced because of weaker acoustic phonons. The measurements for small q values were made for neutron energy gain and loss and gave the identical peak positions.

The energy of the soft mode, ω_{TO}, decreases with temperature, as expected, from 1.4 meV at 430°C to 0.8 meV at 230°C. The latter is the limit of our resolution at present. This behavior is consistent with Cochran's[1] theory according to which

$$\hbar^2\omega_{TO}^2 = A \times 10^4/\epsilon \cong K(T - T_0)$$

where $T_0 = 120$°C is an extrapolated Curie temperature. The constant A for $BaTiO_3$ is estimated as 0.11 meV^2, using the Curie constant $C = 1.55 \times 10^5$ °C. This value should be compared with the much larger values of $A = 3.7$ meV^2 for $SrTiO_3$,[3,6] and $A = 2.8$ meV^2 for $KTaO_3$.[4,5,7]

It has been speculated that the soft mode in $BaTiO_3$ might be "overdamped" so that no neutron group with distinctive energy change would be observable near $q = 0$. This apparently is not the case. However, the intensities of the TO modes are unusually weak for q values between 0.05 and 0.15 Å^{-1}, where TO modes cross over TA modes. A further study of TO modes in this q range and near the Curie temperature is now under way. It is also planned to measure the dispersion relations in the ferroelectric phase.

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