PHYSICAL REVIEW B VOLUME 49, NUMBER 2 1 JANUARY 1994-II

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Inelastic-neutron-scattering study of the cubic-to-tetragonal transition in $K_{0.965}Li_{0.035}TaO_3$

J. Toulouse
Physics Department, Lehigh University, Bethlehem, Pennsylvania 18015

B. Hennion
Laboratoire Léon Brillouin, Centre d'Etudes Nucleáires Saclay, 91191 Gif-sur-Yvette, France

(Received 16 February 1993; revised manuscript received 16 June 1993)

For over ten years the existence of a ferroelectric phase transition in $K_{1-x}Li_xTaO_3$ has been the object of a strong controversy despite early Raman results which revealed a splitting of the soft TO_1 mode at low temperature. We report here the results of an inelastic-neutron-scattering study of a 3.5 at. % Li crystal which show, for $q \neq 0$, a corresponding splitting of the TA branch between *a*-polarized and *c*-polarized phonons and no condensation of the TA mode. The phonon assignment is based on measurements made in the presence of a bias electric field. These results confirm the existence of a cubic-to-tetragonal transition in $K_{1-x}Li_xTaO_3$ even for relatively low concentrations. They reveal the order-disorder nature of this transition and the strong coupling of *c*-polarized TA phonons to the spontaneous polarization. A strong anisotropy of the dispersion surface is also shown to explain the asymmetric shape of the phonon peaks.

INTRODUCTION

The vibrational properties or lattice dynamics of pure $KTaO_3$ have been well studied in the past by Raman[1] and inelastic scattering.[2] In particular, these studies have revealed that, although no phase transition is observed, the TO_1 optic mode nevertheless softens significantly, its energy decreasing continuously from above 10 meV at 295 K down to approximately 3 meV at 6 K. Concurrently, the transverse acoustic (TA) branch exhibits softening at finite q. This anomalous acoustic dispersion in a centrosymmetric crystal was shown to arise from the quasiharmonic coupling of optic- and acousticlike excitations.[2]

In lithium-doped $KTaO_3$, $K_{1-x}Li_xTaO_3$, two detailed Raman studies[3,4] have revealed new features. In a study of the soft optic mode, Prater, Chase, and Boatner[3] found that Li induces a transition which is manifested, at sufficiently high concentration, by the splitting of the related Raman line. The polarization of the two resulting lines showed that these were, respectively, the A_1 mode (high frequency) and the E mode (low frequency) found in the tetragonal symmetry. Below the transition, at about 50 K, the A_1 mode stiffens while the E mode continues to soften. Similar results have also been obtained in our laboratory. Despite this normal behavior, the transition in Li-doped $KTaO_3$ is quite uncommon in that it is preceded by the appearance, many degrees above, of polar nanoregions. These give rise to otherwise forbidden first-order Raman lines, starting at approximately 250 K. In a detailed study[4] of the two hard optic modes, the polar TO_2 and the nonpolar TO_3 modes, DiAntonio *et al.* showed that large structurally ordered domains (≥ 6000 Å) formed at the transition but that the size of the ferroelectric or polar domains remained considerably smaller (≤ 100 Å). This confirms the earlier Raman results of Prater, Chase, and Boatner and is also in agreement with birefringence and second harmonic generation results.[5]

Although the occurrence of a transition in $K_{1-x}Li_xTaO_3$ (KLT) is now beyond doubt,[6,7] at least for high enough concentrations ($\geq 2\%$), the precise nature of the transition is not entirely clear. While the TO_1 optic mode is clearly soft, as shown by Raman and neutron scattering, it does not condense at the transition,[8] contrary to what would normally be expected for a displacive phase transition. Instead, the soft mode splits when still at a relatively high frequency and one which increases with concentration.[3] There exists two possible interpretations of these facts. First, due to the existence of precursor polar nanoregions, the transition may exhibit an order-disorder character in which case the soft mode would not condense. Alternatively, considering the TO-TA coupling and the anomalous acoustic dispersion, the transition may be driven by the condensation of the TA mode. It is to examine these two possible explanations that we undertook an inelastic-neutron-scattering study of the transverse acoustic branch in KLT. As is shown below, the neutron results reveal a splitting of the TA phonon below the transition, very similar to the TO_1

0163-1829/94/49(2)/1503(4)/$06.00

splitting mentioned previously. The TA phonon is also not seen to condense at the transition, a fact that clearly points to the order-disorder character of the transition.

RESULTS AND DISCUSSION

The measurements of the transverse acoustic (TA) branch were made on a KLT crystal with approximately 3.5 at. % Li (nominal 4%). This same crystal had previously been used for Raman,[4] dielectric,[6] and ultrasonic measurements[7] and showed a transition at $T_c = 52 \pm 2$ K upon heating in all three experiments. The inelastic-neutron-scattering experiment was performed on the spectrometer 4f2, installed on a cold source of the reactor Orphee at the Laboratoire Leon Brillouin. Constant-Q scans were carried out with fixed final wave vectors of the neutrons $k_f = 1.64$ or 2.662 Å^{-1}, higher-order contaminations being prevented by a graphite filter. A PG 002 was used for monochromator and analyzer and the first of the two parallel monochromators was vertically bent. Only Soller slits collimators of 40′ were set before and after the analyzer, which corresponded to effective collimations $-/27'/40'/40'$ and yielded a frequency resolution (full width at half maximum) of 0.05 THz ($k_f = 1.64$ Å^{-1}) or 0.2 THz ($k_f = 2.662$ Å^{-1}).

The sample was oriented with a [010] vertical axis and mounted in a cryostat. The scattering plane was defined by the (100) and (001) directions. In this plane, the TA phonon propagated along one of these two directions and was polarized along the other, therefore probing the C_{44} elastic constant at small q. The measurements were performed about the (200) point for reduced wave vectors, q, between 0.025 and 0.16 and at several temperatures upon heating.

In the field experiment, a 2 kV/cm dc electric field was applied along the (001) direction. Measurements were then successively performed at (2,0,q), (q,0,2), and (2,q,0) for q equal to 0.12 and 0.16. The latter measurement was performed by tilting the scattering plane around the (001) direction. These three positions corresponded, respectively, to c-a, a-c, and a-a phonons. Here, the first letter indicates the direction of propagation, the second letter indicates the direction of polarization and the c direction is taken to be the direction of the **E** field, labeled (001) in the experiment.

The data analysis was complicated by the significant anisotropy of the dispersion surface in $KTaO_3$.[8] This anisotropy was also investigated in KLT and the results will be reported in a later publication. The phonon frequencies were found to increase linearly with q along the cubic directions and quadratically away from them. It is a well-known fact that, due to the finite size of the resolution ellipsoid of the instrument, one accumulates some contribution from the phonon branches perpendicular to the main direction of propagation. Consequently, for a phonon propagating in the cubic x direction, the phonon frequency was written

$$\omega^2 = [(\omega_0 + C(q_x - q_{x0})]^2 + D(q_y^2 + q_z^2) , \quad (1)$$

where q_{x0} designates the reference point in reciprocal space and ω_0 the phonon frequency at this point, and C and D are constant coefficients. The linear q dependence of the frequency in the direction of the measurement is normal for acoustic branches at small q.

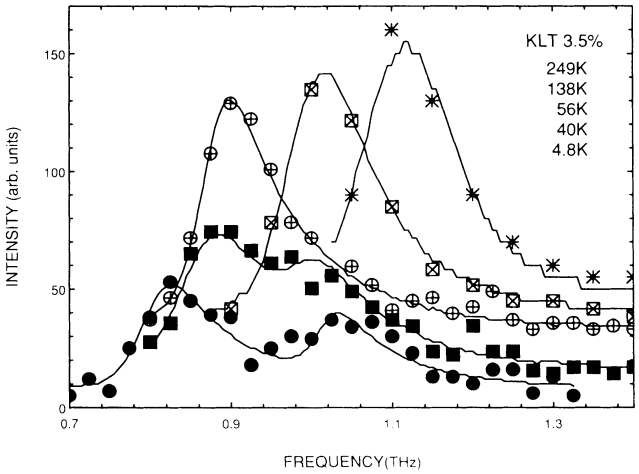

FIG. 1. Scattered intensity from the TA mode vs energy, at $q = 0.16$, for increasing temperatures, 4.8 K (bottom), 40 K, 56 K, 138 K, and 249 K (top). The curves have been shifted for clarity. Solid curves are the result of the fit (see text).

The neutron spectra were fitted by a theoretical scattering cross section convoluted with the resolution function of the spectrometer. The theoretical cross section contained the response of one or two damped harmonic oscillators for the phonon modes plus a constant background, and included the effect of the dispersion anisotropy noted above.

The general results are presented in Fig. 1 where the TA phonon is shown for $q = 0.16$ at five different temperatures. In order to facilitate the comparison of the scattered intensities, these have been corrected for the Bose factor. The solid lines are the result of the fits and are further discussed below. At the three highest temperatures, the phonon are slightly asymmetric, and broader on the high-frequency side. At 40 K the TA phonon appears to split into two components and at 4.8 K these are clearly resolved. It is worth noting that, as previously determined by Raman studies, the transition temperature in this 3.5 at. % Li–KLT crystal is approximately 50 K. The splitting of the TA phonon thus sets in at the transition and parallels the splitting of the soft TO_1 phonon reported earlier. The observation of two components reflects the formation of domains as discussed below. The magnitude of the splitting is unexpectedly large ($\Delta\omega/\omega \sim 25\%$ for $q = 0.16$) when compared with the corresponding change in lattice parameter [$(c-1)/a \sim 0.2\%$]. It also increases with q, as can be seen in Fig. 2 where the split phonon is shown at 4.8 K for $0.05 \leq q \leq 0.16$.

In order to test the validity of the domain hypothesis in explaining the splitting, we carried out measurements of the TA phonon in the presence of a dc bias electric field. This field was applied along a cubic direction hereafter labeled c, the two perpendicular directions being labeled a. As indicated in the experimental section, three scattering configurations were successively selected, to create (c-a),

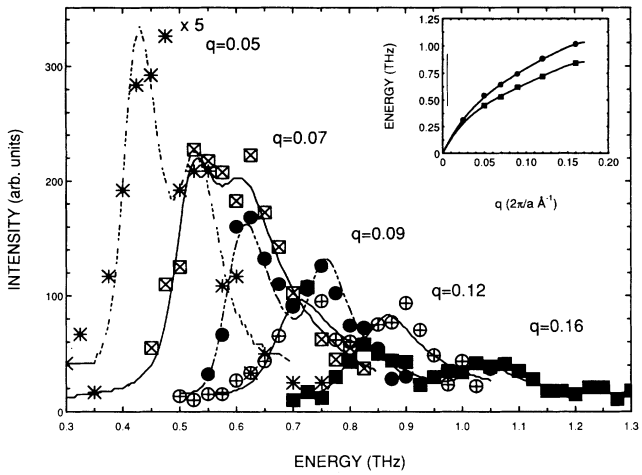

FIG. 2. Scattered intensity from the TA mode vs energy, at $T=4.8$ K, for different wave vectors, q. Inset: TA split dispersion branch, energy vs wave vector q in the (100) direction.

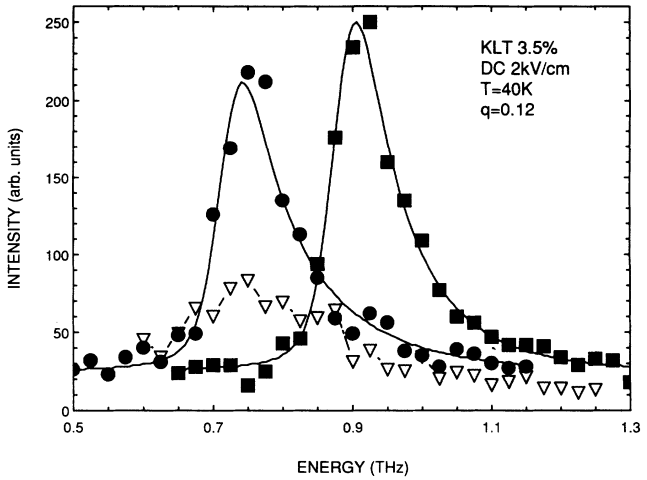

FIG. 3. Scattered intensity from the TA phonons in the presence of a 2 KV/cm dc field: ● (c-a), ■ (a-c), ▽ (a-a) phonon. Solid lines are the results of a fit as indicated in the text.

(a-a), and (a-c) phonons, respectively. Thus, for example, the (c-a) phonon was one propagating in the direction of the electric field and polarized perpendicular to it. Typical results are presented in Fig. 3. The two large peaks correspond to the (c-a) (low frequency) and the (a-c) (high frequency) phonons, respectively, and the very broad and low-amplitude peak corresponds to the (a-a) phonon. The comparatively low amplitude of the latter is due to a much tighter collimation and its large width to the particular scattering configuration used (tilted scattering plane). There is, however, little doubt that its position coincides with the low-frequency position of the (c-a) phonon peak. Thus we see that the determining factor in the frequency location of the phonon is its polarization. Also shown are calculated curves incorporating the anisotropy of the dispersion surfaces [Eq. (1)]. It is clear from the fits that this anisotropy accounts satisfactorily for the asymmetry of the peaks. A comparison of the frequency separation of the two high-intensity phonons in Fig. 3 with that of the two components in Fig. 1 at the same temperature, 40 K, clearly confirms the validity of the domain hypothesis as well as the phonon assignment. Figures 1 and 3 are for $l=0.16$ and 0.12, respectively, but frequency separation is not too different between these two q values as can be seen in the inset of Fig. 2. In Fig. 2, as expected from a multidomain microstructure, all three phonon types are simultaneously present, the (c-a) and (a-a) both contributing to the low-frequency peak. In this case, the theoretical curve was calculated including two damped harmonic oscillators in the scattering cross section and assuming a 2/1 ratio of their strengths consistent with a random distribution of domain orientations. It also incorporated the anisotropy of the dispersion surface. It is interesting to note the particularly strong stiffening effect of the bias electric field on the (a-c) phonon which, because it is polarized in the direction of the field, can couple to the induced electric polarization.

The above neutron results, obtained with and without a dc bias electric field, can be well explained by a single domain and a multidomain microstructure, respectively. The experiment with field, which revealed three phonons, with two of them appearing at the same lower frequency, clearly indicates a cubic-to-tetragonal transition. In such a transition, the high-temperature doubly degenerate phonon should split into an A_1-like phonon and an E-like phonon. This is indeed what is observed. The A_1-like phonon is polarized along the tetragonal c axis and, being coupled to the spontaneous polarization, is expected to stiffen below the transition. This is also what we observe. In the absence of a field, and for a random distribution of domains, the weight of the E-like phonon is expected to be twice that of the A_1-like phonon, as borne out by the fitted curves. The "A_1-like" and "E-like" labels are used to emphasize the parallelism between the previous results on the optic mode and the present results on the acoustic mode even though, strictly speaking, these labels are only valid at $q=0$, where in fact the acoustic modes no longer represent internal modes of vibration.

The present neutron results are also in perfect agreement with the earlier Raman results mentioned in the Introduction.[3,4] In particular, they show that the behavior of the TA phonon parallels precisely that of the soft TO_1 mode which was also shown to split into A_1- and E-symmetry phonons at the transition. An important conclusion can then be drawn from the two combined sets of results. Because neither the frequency of the TO_1 mode nor that of the TA mode approaches zero, the transition itself is not displacive, i.e., soft-mode driven, but rather order-disorder in character. This is consistent with a process in which polar nanoregions, present above the transition, reorient to form structural macrodomains below the transition. This does not negate in any way the importance of the soft mode both in the lattice dynamics far above the transition and in the formation of the polar nanoregions.

In conclusion, the present neutron-scattering results confirm that a ferroelectric cubic-to-tetragonal transition occurs in KLT with $x = 3.5\%$. Moreover, these results show that, in the end, the transition is not driven by the condensation of the TA mode, and thus presents an order-disorder character, most likely due to the ordering of the polar nanoregions. The behavior of the TA mode parallels that of the TO_1 mode and, below the transition, the high-temperature phonon splits into *a*- and *c*-polarized phonons. The large frequency separation of the two phonons at low temperature suggests a strong electrostrictive effect.

ACKNOWLEDGMENTS

Special thanks are given to L. A. Boatner for providing high-quality crystals and to P. DiAntonio for useful discussions. Partial support for this work was provided by the Office of Naval Research under Grant No. N00014-90-J-4098.

[1]P. A. Fleury and J. M. Worlock, Phys. Rev. Lett. **18**, 665 (1967).

[2]J. D. Axe, J. Harada, and G. Shirane, Phys. Rev. B **1**, 1227 (1970); R. Comes and G. Shirane, *ibid.* **5**, 1886 (1972).

[3]R. L. Prater, L. L. Chase, and L. A. Boatner, Phys. Rev. B **23**, 5904 (1981).

[4]J. Toulouse, P. DiAntonio, B. E. Vugmeister, X. M. Wang, and L. A. Knauss, Phys. Rev. Lett. **68**, 232 (1992); P. DiAntonio, B. E. Vugmeister, J. Toulouse, and L. A. Boatner, Phys. Rev. B **47**, 5629 (1993).

[5]G. A. Azzini, G. P. Banfi, E. Giulotto, and V. T. Hochli, Phys. Rev. B **43**, 7473 (1991).

[6]P. Doussineau, Y. Farssi, C. Fresnois, A. Levelut, K. McEnaney, J. Toulouse, and S. Ziolkiewicz, Europhys. Lett. **21**, 323 (1993).

[7]P. Doussineau, Y. Farssi, C. Fresnois, A. Levelut, K. McEnaney, J. Toulouse, and S. Ziolkiewicz, Europhys. Lett. (to be published).

[8]G. Zaccai and A. W. Hewat, J. Phys. C **7**, 15 (1974).