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Raman spectroscopy of submicron KNO_3 films

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We have obtained Raman spectra of phase-I, -II, and -III KNO_3 films 0.26 μm thick. The primary aim was to establish the physical mechanism for stabilization of the ferroelectric phase III in thin films. In bulk, phase III exists only as a reentrant phase stable from ~113 °C to 120 °C. However, application of hydrostatic or uniaxial pressure greatly enlarges the temperature range over which phase III is stable. This has led to the conjecture that stress (e.g., from differential thermal expansion of film and substrate) stabilizes phase III in thin films. Our vibrational spectroscopy shows that this is not likely to be the dominant effect. The dominant effect appears to be surface electric fields. This is shown in the shift and splitting of low-energy odd-parity modes from an unresolved broad peak at 120 cm^{-1} in bulk crystals to resolved TO-LO pairs at 92 and 97 cm^{-1} and 107 and 113 cm^{-1}. The Raman data show that the KNO_3 thin films are more highly ordered than in bulk. This is compatible with spontaneous polarization values, which are 50% or more greater in the films, and with much higher T_C values in the thinner films. The values of T_C as a function of thickness d are compatible with the theory of Tilley and Zeks [Solid State Commun. **49**, 823 (1984)] as well as with similar experimental results by Hadni and Thomas [Thin Solid Films **81**, 247 (1981); Ferroelectrics **59**, 221 (1989)] on triglycine sulfate.

I. INTRODUCTION

Ferroelectric potassium nitrate films offer one of the most promising raw materials[1] for random-access memory devices (RAM's). Such films have address voltages between 2 and 6 V, depending upon thickness, nonvolatile memories, and switching times as fast as 20 ns.[2] However, some aspects of their physics are not well understood. In particular, it is not known why the ferroelectric phase III is stable over a wide temperature range (typically +130 °C to below 0 °C in thin films,[3] whereas this phase is a reentrant phase encountered only upon cooling in bulk, and stable over only a few degrees (~113–120 °C) in such single-crystal specimens.[4] Several mechanisms have been proposed for the stability of ferroelectric KNO_3 thin films. Based upon Bridgman's early phase diagram,[4] which showed that hydrostatic pressure greatly increased the temperature range for phase III, as shown in Fig. 1, it was suggested[3,5] that hydrostatic or uniaxial stress, perhaps induced by differential contraction of film and substrate upon cooling after deposition, might be the cause of phase-III stability. We shall attempt to show in this paper that this is probably a "red herring;" the actual mechanism for phase-III stability appears to be due to large surface electric fields.

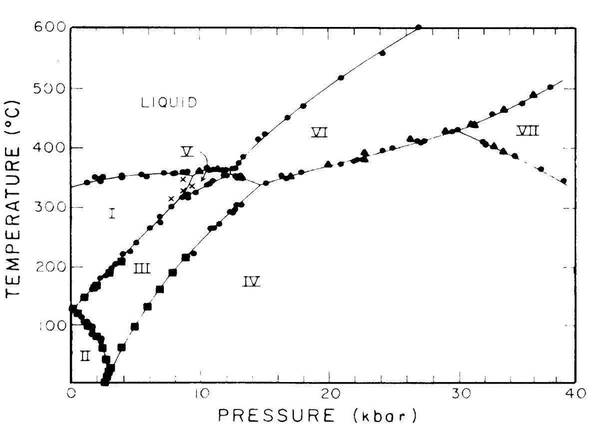

FIG. 1. Phase diagram of bulk KNO_3 (after Refs. 4 and 14).

II. EXPERIMENT

The films studied here were prepared by vapor transport deposition on glass substrates at 400 °C. Growth rates were 30 Å/min. Film thicknesses of 250–265 nm were determined both optically and mechanically. The spectra were obtained with an argon-ion laser emitting 400 mW at 514.5 or 488 nm and an 0.85-m double-grating spectrometer. Because the scattering volume in a 0.25-μm film is small, the laser beam was focused to a line image with a cylindrical lens, and this image was then focused onto the spectrometer entrance slit. With this arrangement, intensities of order 100 counts/sec could be obtained for the phase-II vibrational line at 50 cm^{-1} using spectral slit widths of 3 cm^{-1}, as shown in Fig. 2.

III. THEORY

Below we consider briefly a group-theoretical analysis of KNO_3 phases. This is done because our results

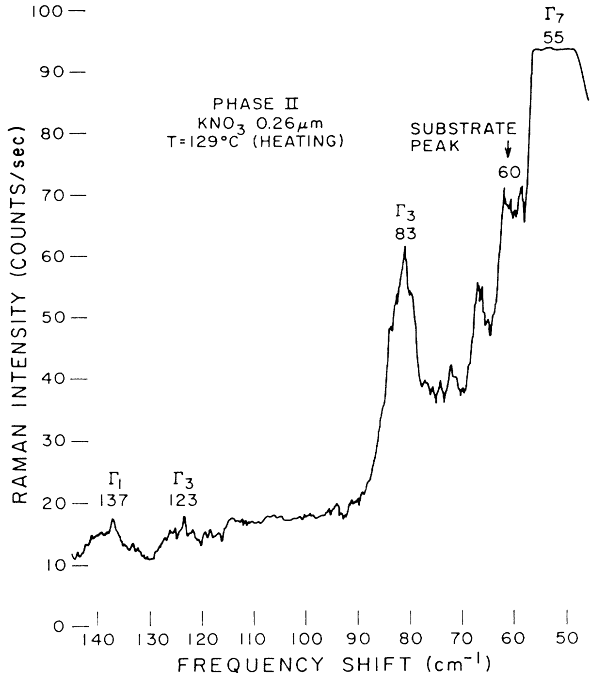

FIG. 2. Raman spectra of phase-II KNO$_3$ 0.26-μm film. Temperature: 129 °C (heating). The spectra agree with those of bulk single crystals (Refs. 5 and 6).

disagree for phase I with other published theories, but are in agreement with experiment. This analysis also allows us to point out the specific predictions for the number and symmetry of low-energy phonon branches in phase-III KNO$_3$ and then to compare those predictions with our data.

A. Phase-III group theory

In the ferroelectric phase the structure is ordered, with space-group symmetry C_{3v}^5 ($R3m$). In this structure, both K and N ions lie at a sites of the International Table for X-Ray Crystallography (C_{3v} point-group symmetry sites). Each of these two atoms therefore contributes $1A+1E$ vibrational modes (often labeled $1\Gamma_1+1\Gamma_3$). In addition, the oxygen ions are at three b sites and therefore contribute a total of $2A_1+1A_2+3E$ modes (i.e. $2\Gamma_1+1\Gamma_2+3\Gamma_3$).

The sum therefore is $4A_1+1A_2+5E$. Of these, $1A_1+1E$ are acoustic (sound waves); the remaining $3A_1+1A_2+4E$ are optic modes. Of these eight optic modes, $2A_1+2E$ are "ionic" and involve out-of-phase motion of K^+ against rigid NO$_3$ ions. Two (A_2+E) correspond to NO$_3$-ion rotations (A_2 is about the ferroelectric axis and is "silent"—forbidden in both infrared and Raman spectra; E is about either of the two axes perpendicular to the ferroelectric axis). The remaining four ($2A_1+2E$) are covalent vibrations within the NO$_3$ ion. Noteworthy in this analysis is the fact[5] that of the $4E$ modes, two are predicted on the basis of lattice dynamical models[5] to lie near 100 cm^{-1}, each of which must be split into a TO+LO (transverse optical and longitudinal optical) pair of spectral lines. Of these four predicted polar mode components, only one broad feature centered at 120 cm^{-1} has been observed in bulk single crystals.

B. Phase II

The aragonite D_{2h}^{18} ($Pnma$) structure is unambiguous for phase II. Several authors (e.g., Ref. 5) give the correct group-theoretical analysis of this phase, which has four formula groups per primitive cell.

C. Phase I

Traditionally there has been a controversy concerning the structure of phase I of KNO$_3$. Tahvonen[6] assigned it to D_{3d}^5 with one formula group per primitive cell. Unfortunately, that structure predicts no allowed vibrations in the Raman effect; since all ions sit at centers of symmetry, all long-wavelength vibrations are of odd parity: The modes are divided as $4\Gamma_4+4\Gamma_6$. This disagrees with ex-

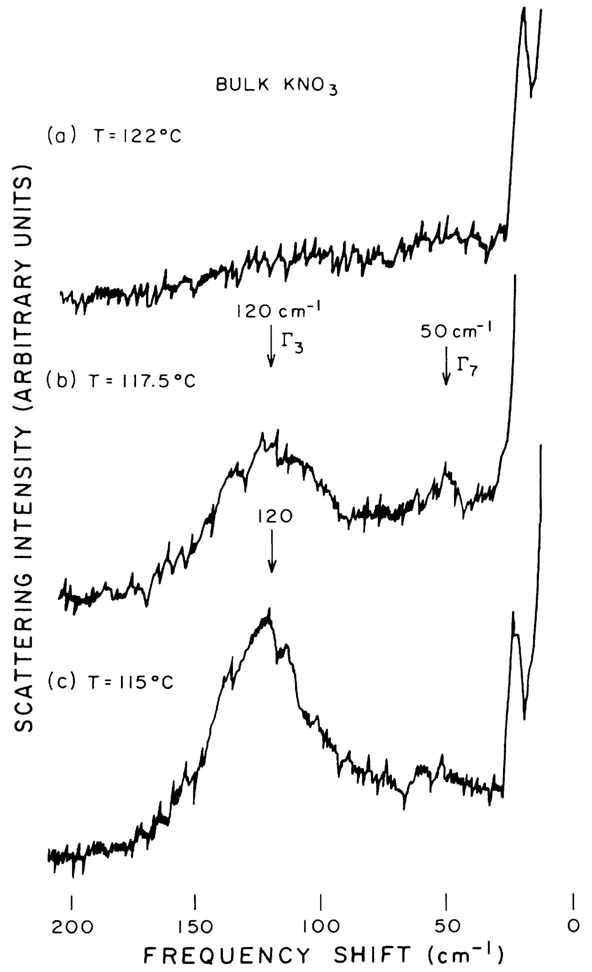

FIG. 3. Raman spectra of phase-III bulk KNO$_3$ (Refs. 5 and 6).

periment. Shinnaka[7] assigned it to space group D_{3d}^{6} with two formula groups per primitive cell. This predicts

$$1\Gamma_1+3\Gamma_2+4\Gamma_3+3\Gamma_4+2\Gamma_5+5\Gamma_6$$

optic modes, which is far more than have been observed experimentally. In addition, it is quite certain that both KNO_3 and $NaNO_3$ (under pressure) are simple, proper ferroelectrics that do not alter the size of their primitive crystallographic cells in the phase-I to phase-III transition. This means that there must be one formula group per primitive cell in both phase I and phase III. What then is the structure of phase-I KNO_3 and what is the proper group-theoretical analysis of its vibrations?

We interpret our data as evidence that phase-I of KNO_3 has a disordered structure that is *locally* of C_3 point-group symmetry, with $Z=1$ formula group per primitive cell. Because of the disorder in oxygen positions in the NO_3 ions, there is no net polarization, and the *spatial average* is that of a D_{3d} point group. The same effect of zero polarization and D_{3d} symmetry could, in principle, be produced by a cell-doubling (antiferroelectric) phase transition; this would yield the ordered D_{3d}^{6} space group hypothesized by Shinnaka. However, that hypothesis disagrees with the experimental data in the present study and elsewhere. The fact that the actual structure in phase-I KNO_3 appears to be locally C_3 with $Z=1$ but spatially averages to D_{3d}^{6}, is not incompatible with *short-range* antiferroelectric ordering; in fact, out-of-phase rotations of adjacent NO_3 ions may occur *without* doubling the primitive cell, since the oxygen positions are disordered. This disorder is demonstrated both by x-ray studies and by dielectric measurements, which yield 50—70 in phase I, compared with 17 in phase III.

With this interpretation the correct group-theoretical analysis of phonon branches is as follows:

Phase III	Phase I
$4\Gamma_1$	$\Gamma_1+2\Gamma_4$ optic $+1\Gamma_4$ acoustic
$1\Gamma_2$	Γ_2
$5\Gamma_3$	$3\Gamma_3+1\Gamma_6$ optic $+1\Gamma_6$ acoustic

In other words, the number of modes is exactly the same in phases I and III. We note parenthetically that the "soft" optical mode observed by Lettieri *et al.*[8] under hydrostatic pressure in $NaNO_3$ is Γ_1 in phase III and Γ_4 in phase I. Since KNO_3 is more order-disorder and less displacive (i.e., less "martensitic") in character than $NaNO_3$, such a soft mode is not observed in KNO_3.

We emphasize three things about the above analysis. First, it agrees perfectly with all experiments. It predicts $\Gamma_1+\Gamma_2+3\Gamma_3+2\Gamma_4+\Gamma_6$ modes for optical phonons in phase I. Experimentally $\Gamma_1+3\Gamma_3+\Gamma_4+\Gamma_6$ have been observed.[5] The predicted Γ_2 mode is forbidden by symmetry in both the infrared and Raman spectra; and one of the two Γ_4 modes is predicted to lie near 100 cm^{-1} in the infrared spectrum, where no studies have yet been reported on KNO_3. Second, the analysis shows that both Tahvonen's D_{3d}^{5} ($Z=1$) structure and Shinnaka's D_{3d}^{6} ($Z=2$) structure are incorrect. The correct structure is a disordered one that averages to D_{3d} but locally is C_3 with $Z=1$. (If the adjacent cell ordered in phase, the structure would be C_{3v}; if exactly out of phase, D_{3d}; if random, C_3.) Third, the proper number and symmetry of vibrational modes cannot easily be made using standard tables,[9] because such tables are not intended for disordered structures.

IV. ANALYSIS

The Γ_3 symmetry spectra of phase-III bulk KNO_3 is shown in Fig. 3, reproduced from Balkanski *et al.*[5] What is observed is a broad, structureless feature extending from 100 cm^{-1} to 140 cm^{-1}, and centered at 120 cm^{-1}. We do not interpret this as a defect-induced or disordered-induced one-phonon density-of-states spectrum. Its selection rules and rather Gaussian shape suggest instead that it is one or more Γ_3 symmetry modes, inhomogeneously broadened. By comparison, we show in Fig 4 a spectrum of KNO_3 0.25-μm film at 123 °C which displays both phase-II and phase-III features. The phase-II features become more intense at low temperatures and

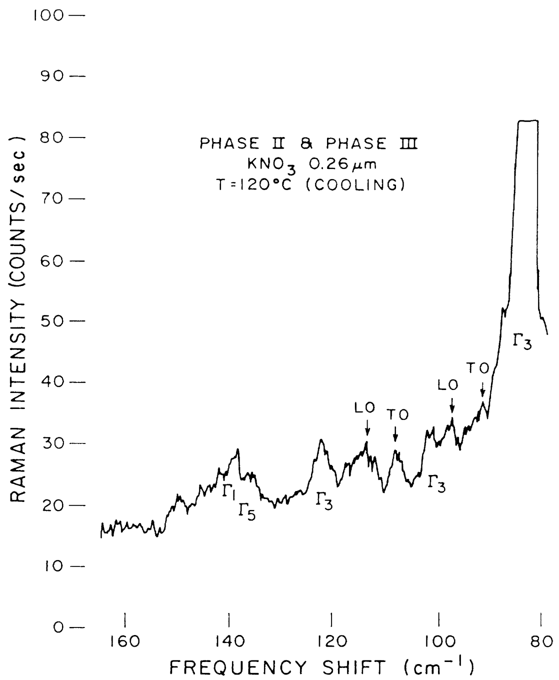

FIG. 4. Raman spectra of phase II plus phase-III KNO_3 0.26 μm. The lines at 92, 97, 107, and 113 cm^{-1} marked with arrows disappear upon cooling below ambient temperature or upon exposure to moisture at higher temperatures. They are interpreted as Γ_3 TO-LO pairs of phase III. The other lines marked with their symmetry labels under them are phase-II modes at 83 cm^{-1} (Γ_3), 103 cm^{-1} (Γ_3), 122 cm^{-1} (Γ_3), 133 cm^{-1} (Γ_5), and 138 cm^{-1}(Γ_1). The narrow linewidths in these spectra show that the surface-to-volume ratio for this film is low (Ref. 15), i.e., the film is very smooth. The coexistence of phase-II and phase-III domains in thin films is well known (Ref. 11) from earlier x-ray work. The range of temperature stability for phase III in thin films such as this is discussed in Refs. 3 and 33.

are attributed in this spectrum to nucleation of phase-II domains due to water vapor in the atmosphere; the spectrum in Fig. 4 was from an unpassivated film in which moisture is known to produce phase-III to -II conversion at the surface. This is discussed in the caption of Fig. 4 and is compatible with earlier x-ray studies of KNO_3 films by Morlin *et al.*,[10] which consistently showed the coexistence of phases II and III in thin films.

The important spectral features in Fig. 4 are at 92, 97, 107, and 113 cm^{-1}. These features are not observed in bulk,[5] and they disappear at low temperatures in our films. They correspond well in number and frequencies with those predicted for phase III. We assign them as Γ_3 TO—LO pairs (TO at 92 and 107 cm^{-1}; LO at 97 and 113 cm^{-1}).

It is important that these lines are well resolved and that their center is shifted from the 120 cm^{-1} of bulk KNO_3 in Fig. 3. We believe that the only mechanism that will shift the odd-parity mode frequencies while leaving the even-parity phase-II modes unaffected is electric field, and that the difference between the Γ_3 spectra of bulk and film illustrated in Figs. 3 and 4 is due to surface electric fields. As we discuss more quantitatively in the following section, it is therefore more likely that the stabilization of phase III in thin films is due to surface electric fields than to pressure. This surface electric field need not arise from impurities or defects, but simply from the increase in spontaneous polarization near the surface. Such an increase in spontaneous polarization is equivalent to an increase in internal electric field $E = 4\pi P$ which will generate a uniaxial stress through electrostriction, but such stress is to be distinguished here from extrinsic stresses at film-substrate interfaces or at grain boundaries; the latter will anneal out, whereas the electrostrictive stress will not.

In order to confirm that the lines in Fig. 4 are indeed longitudinal and transverse components we use the cross-section anisotropy discussed by Hayes and Loudon and by Dawson.[11] By slightly varying the propagation angle of the phonons in the films (either by directly changing the angle of laser incidence or, through the film birefringence, the laser polarization) one can enhance the TO scattering and reduce the LO scattering, as shown in Fig. 5, or vice versa.

What requires some explanation is not why we see $2\Gamma_3(TO)+2\Gamma_3(LO)$ in the low-frequency region of our spectra—since that agrees exactly with theoretical prediction—but why Balkanski *et al.*[5] did not see them in bulk. First we note that in addition to shifting phonon frequencies, large surface electric fields will generally greatly increase the intensity of LO phonons,[12] through the electrooptic contribution to the Raman tensor.[12] Indeed, Balkanski *et al.* report no observation of LO modes at all in bulk. As to why the low-frequency Γ_3 mode(s) was much broader in bulk than are the lines we observe, we can only speculate. Modes which involve BO_3 rotations in ABO_3 structure oxides are known to be very sensitive to oxygen vacancies;[3] see, for example, Ref. 13. It seems likely to us that lack of oxygen stoichiometry could lead to spectra such as those in Fig. 3 for KNO_3. By comparison thin-film vapor deposition processes for ferroelectric oxides are known to be remarkably self-healing. In fact, a comparison of Figs. 3 and 4 suggests that our 0.25-μm films may be more stoichiometric than the earlier bulk samples grown from slow evaporation of aqueous solutions. This conclusion is also supported by Rutherford backscattering (RBS) data made available to us from Hamdi.[14]

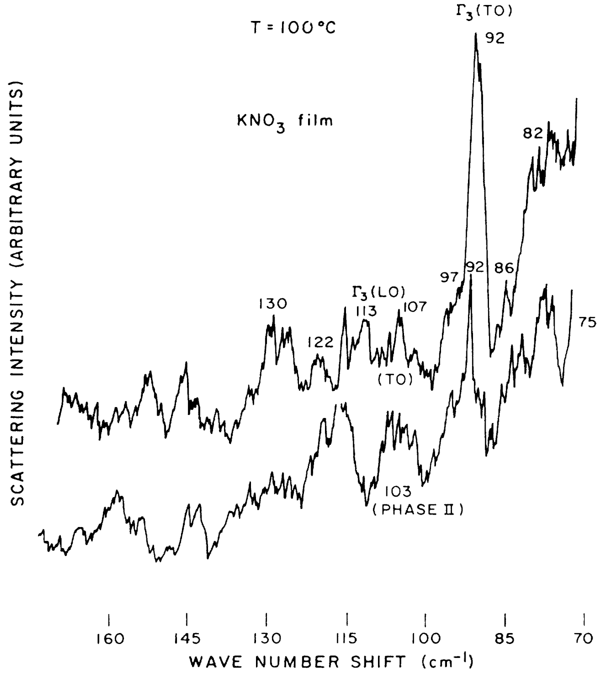

FIG. 5. Raman spectra of KNO_3 film, as in Fig. 4, but with phonon propagation rotated to enhance Γ_3 (TO) modes and decrease cross sections for Γ_3 (LO) modes.

Our specific interpretation of the data in Fig. 4 is that the pair of modes at 92 and 97 cm^{-1} and the pair at 107 and 113 cm^{-1} shift upwards by 20 cm^{-1} and broaden in bulk specimens. The narrow linewidth in the films imply low surface-to-volume ratios,[15] i.e., good smoothness.

V. DISCUSSION

In order to rule out pressure stabilization of the ferroelectric phase in thin-film KNO_3, it is useful to make quantitative arguments. A hydrostatic pressure of 1 kbar is known to stabilize the ferroelectric phase 20 °C above the bulk Curie temperature.[16] Most relatively soft crystals have pressure derivatives of their optical-phonon energies of order 1.0 cm^{-1}/kbar.[17] This suggests that any pressure in our KNO_3 films is less than 1 kbar, since all of the phase-II phonon frequencies agree within ± 1 cm^{-1} with bulk values. Use of the 20 °C/kbar shift mentioned above, yields a maximum shift of 20 °C in the transition temperature due to pressure. By comparison, Nolta *et al.*[3] report shifts of 55 °C in the phase-II to-III transition temperature as film thickness is decreased from 100 to 0.25 μm. Hence, it would appear that less than half of this change in transition temperature can be accounted for by pressure in the film.

We have other ways of eliminating pressure, particularly uniaxial stress, as a major cause of film stabilization. Such stress has been conjectured to arise from grain boundaries. However, our film Curie temperatures, spontaneous polarizations, and Raman spectra are quite independent of grain size, from large (micron) grains down to the normally smooth films with grain size of order 500 Å. Equally important, the film properties mentioned are unaffected by annealing. These make stress an unlikely cause of film stabilization. No spectral shifts are observed in the Raman spectra of our films which can be attributed to hydrostatic pressure, nor splittings of degenerate modes which can be attributed to uniaxial stress. As mentioned in an earlier section of this paper, some uniaxial stress must occur near the surface of the film due to the surface fields discussed below, through the electrostrictive effect. The relationship between the hydrostatic and uniaxial stress dependence of T_C in KNO_3 is given[18] in terms of the electrostriction coefficients Q_{133} and Q_{333} by $dT_C/dp = -(Q_{333}+2Q_{133})/C = +1.5\times 10^{-8}$ K cm^2/ dyn, where $Q_{333} = -6.05\times 10^{-11}$ and $Q_{133} = +1.33\times 10^{-11}$ cm^2/dyn. These numbers show that the effect of uniaxial stress along the c axis in KNO_3 will be to increase T_C about twice as fast as hydrostatic pressure, for a given value of dyn/cm^2.

We can also estimate the effects of electric fields. In other ABO_3 ferroelectrics we find that the field dependence of polar phonons can be as large as[19] 0.5—2.0 cm^{-1} per kV/cm of field for very-low-energy phonons (10 to 40 cm^{-1}) and somewhat less (about 0.2 cm^{-1} per kV/cm) for higher-energy modes (100—200 cm^{-1}). In addition, the temperature change in T_c is of order[20] 1.5 °C per kV/cm. Thus, our inferred shift of 20 cm^{-1} from 120 cm^{-1} in bulk to 100 cm^{-1} (TO + LO average) in 0.25-μm film corresponds to a 150 °C shift in transition temperature, using the 0.2 cm^{-1} per kV/cm value mentioned above. Thus, surface fields can account for all of the shift in transition temperature measured by Nolta *et al.*[3]

Note that our inferred internal field can be calculated by using the 55 °C shift measured by Nolta *et al.* and reversing the calculation above. This yields a 30-kV/cm surface field in our films, which will be measured as 30 kV/cm times 0.25 μm = 0.75 V bias voltage. Such a small bias voltage is not incompatible with the experimental switching data,[1,2] as shown in Fig. 6. Here switching occurs at +4.1 and −1.7 V implying a bias voltage of +1.2 V: our theoretical estimate is ~40% lower.

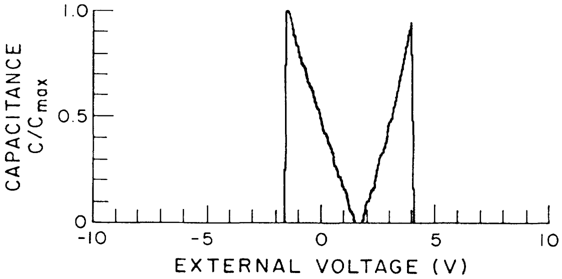

FIG. 6. Capacitance versus voltage (C/V) data in a KNO_3 film, showing switching at +4.1 V and −1.7 V, and thus implying a +1.2-V intrinsic bias. In most of our films the bias voltages from the two surfaces cancel exactly. However, if top and bottom electrodes differ slightly, a net bias results.

Oxygen deficiency is a possible direct cause of phase-III stabilization. In $LiTaO_3$ it is known[21] that a 0.6% oxygen deficiency causes a 6.5 °C shift in T_C. In $SrTiO_3$ a 10^{20} cm^{-3} oxygen deficiency shifts[13] the transition temperature 25.5 °C. Residual gas analysis (RGA) of our KNO_3 film deposition shows that oxygen nonstoichiometry is greater than these values. Therefore a transition temperature shift of order 40 °C might be caused in this way. We note in passing that our films are far too thick for true two-dimensional effects.[22]

The KNO_3 films are reminiscent of "type-B" surface layers studied carefully in $BaTiO_3$ by Chynoweth[23] which remain polarized well above T_c (bulk). These layers have[24] a dielectric constant much less than that of the bulk. Similar superpolarized surface layers have been reported in TGS.[25] Like TGS films, our KNO_3 films have[1,2] spontaneous polarization values which are *greater* than those in bulk single crystals. (This was not true of KNO_3 films prepared by Nolta *et al.*,[3] which we believe had damaged surface layers.) These charge layers are similar to those studied in thicker $BaTiO_3$ films by Callaby,[26] and in TGS by Pulvari and Kuebler and by Kay and Dunn.[27] It is interesting to note that KDP does not exhibit such layers, nor is it ever semiconducting, unlike the oxide ferroelectrics; this suggests the role of oxygen vacancies and resulting surface fields in the ABO_3 ferroelectric oxides.

One thing that the thin-film Raman data do establish is that the film structure is the same as that in single crystals. Since subtle phase transitions have recently been reported in nominally isomorphic $NaNO_3$,[28] there was a possibility of slightly different structures in film and bulk, analogous to those discussed in the preceding paragraph for $BaTiO_3$ surface layers.

All of the stabilization effects discussed above are summarized in Table I: These are not all independent effects. For example the surface electric fields may be intrinsic or may be related to oxygen nonstoichiometry. In Fig. 7 we compare our measured Curie temperatures for bulk and for 75- and 260-nm films with the theory of Tilley and Zeks. Their theory,[30] based upon earlier work by Luben-

TABLE I. Estimated change in phase II to phase III transition temperature in KNO_3 encountered in going from bulk to thin film.

Total change (bulk to 0.2 μm)	55 °C	Ref. 3
Pressure (hydrostatic and/or uniaxial)	0 to 20 °C	present work
Surface electric fields	30 to 150 °C	present work
True two-dimensional effects	0	Ref. 22
Oxygen deficiency	10 to 40 °C	Refs. 13, 21
Nonelectric surface layer effects	10 to 20 °C	Refs. 29—33

sky and Rubin,[31] predicts that ferroelectric films with T_c higher than bulk will also have higher P_s and that T_C will vary as $1/d$. This is compatible with our data, as shown in Fig. 7. The solid curve is a theoretical fit to the data; its slope is given, in the notation of Ref. 30, by $\xi_0^2/\delta=0.615$ nm. Note that for thinner films than considered here depolarization effects analyzed by Binder[32] will cause the curve in Fig. 7 to level off and then drop to zero as $1/d$ continues to increase, i.e., as the film thickness decreases to zero. Although the theory of Tilley and Zeks provides a reasonable format for the analysis of $T_C(d)$ in our films, it cannot readily give us $P_S(d)$; the reason is that $P_S(d)$ is related to $T_C(d)$ through a complicated elliptic integral relationship, and this has not been made explicit for first-order phase transitions, as in KNO_3. The theory of Tilley and Zeks gives no information at all for the lower-temperature transition between phases III and II; in their theory this transition is completely accidental. Our limited data for the temperature dependence of the lower transition temperature $T_{\text{III-II}}$ show that it is $-55\,^\circ$C (218 K) at $d=75$ nm, 20 °C (293 K) at $d=800$ nm, and 117 °C (390 K) in bulk ($d=\infty$).

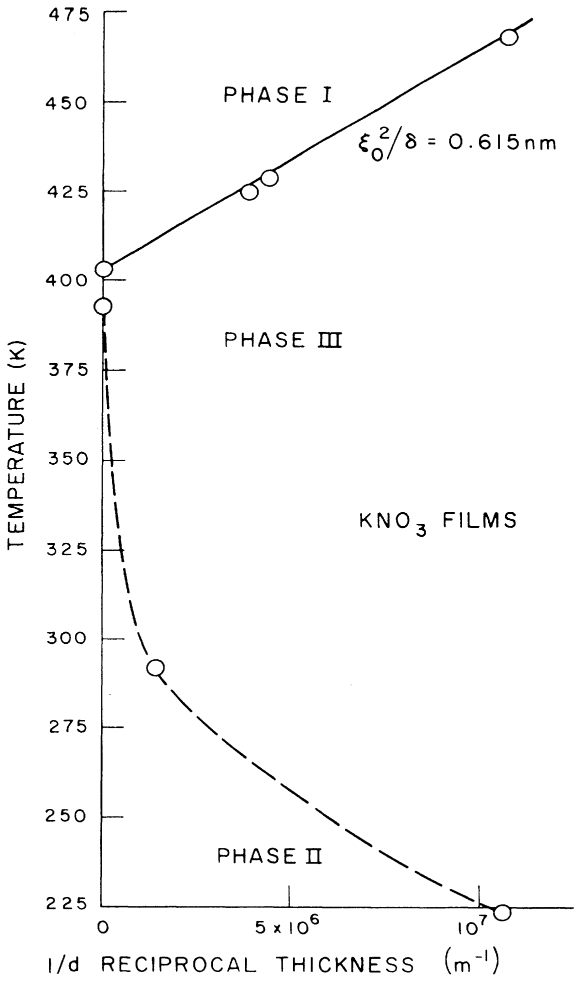

FIG. 7. Thickness dependence of the Curie temperature in KNO_3 films. Solid line is the $1/d$ dependence predicted by the theory of Tilley and Zeks. The dashed curve for the lower-temperature phase boundary is only a guide to the eye; it is not yet available from the published theory and requires extension of the results of Tilley and Zeks to first-order transitions; the curves are related through elliptic integrals.

Our conclusion from these considerations and from the data in Figs. 1—3 is that pressure provides less than half of the observed shift in the phase-II to -III transition temperature in KNO_3 thin films, compared with bulk single crystals, and that what pressure effects exist probably arise from electrostriction associated with surface electric fields. The spectral data show our films to be very smooth, with low surface-to-volume ratios.[14]

In summary, surface effects[29—33] and in particular, surface electric fields in KNO_3 appear to be of paramount importance in the stability of the ferroelectric phase in thin films. The preliminary data on $T_C(d)$ are compatible with the intrinsic theory of Tilley and Zeks, although oxygen vacancies may play a role in the surface electric fields. The Raman data are compatible with the higher T_C and higher P_S in the films, compared with bulk, in that each confirms that the films are more ordered than the bulk single crystals. Although such highly ordered films seem

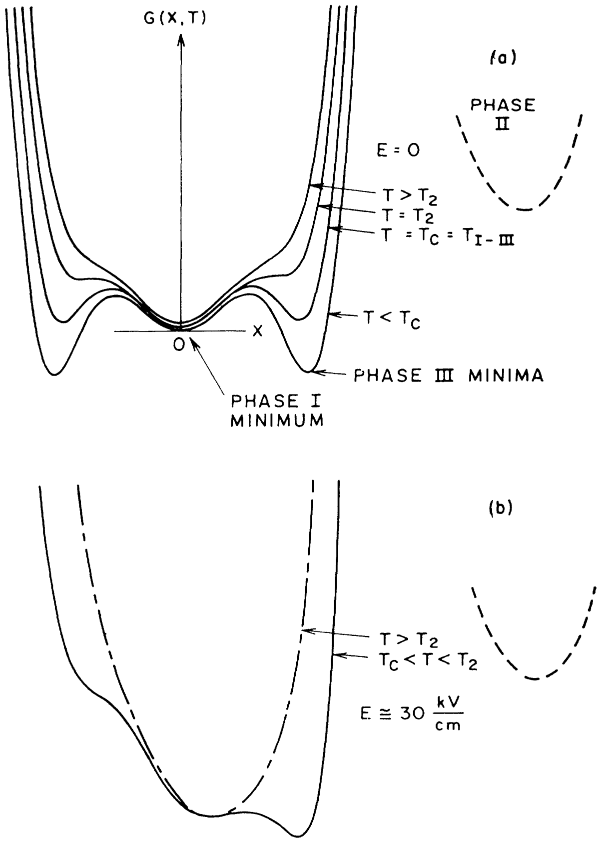

FIG. 8. (a) Free energy of phases I and III (solid curves) versus displacement parameter x at different temperatures in zero field near $T_C=T_{\text{I-III}}$. The dashed curve is for phase II. (b) In an applied field of order 30 kV/cm along $+x$ (i.e., along the $+c$ crystal axis).

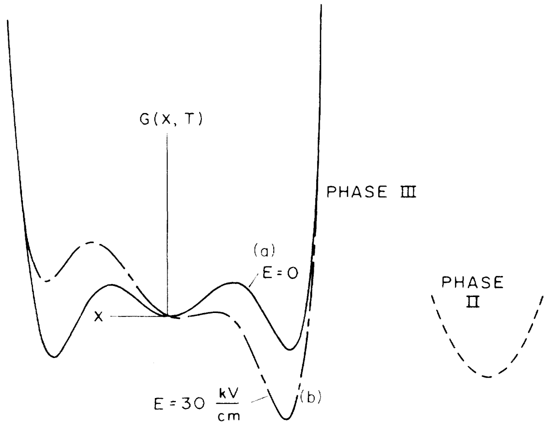

FIG. 9. (a) Free energies of phase III (solid curve) and phase I (dashed curve) versus displacement parameter x near the lower transition $T_{\text{II-II}}$ in zero field. (b) In an applied field of order 30 kV/cm along $+x$.

incompatible with our intuition and conventional wisdom in ferroelectricity, they agree with the theories of Tilley and Zeks and Lubensky and Rubin.

Of paramount importance is the conclusion that the ferroelectric phase III is the stable phase in thin films of KNO_3 at ambient temperatures; prior to the present work it had been assumed that this was only a metastable phase. The importance of this conclusion in the commercialization of KNO_3 thin-film memories cannot be overemphasized.

ACKNOWLEDGMENT

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APPENDIX

In this appendix we will show why the transition temperature $T_{\text{I-III}}$ between phases I and III in KNO_3 increases only a few degrees in most KNO_3 thin films (the maximum measured upward shift is 66 K in the thinnest 75-nm films), whereas the lower transition temperature $T_{\text{II-III}}$ between phases II and III decreases approximately 180 °C. It will be shown that this asymmetry is strong support of the surface electric field model of phase-III stabilization and against a pressure stabilization mechanism. Some clarification of the transition kinetics for the reentrant phase is also given.

The free energy for both phases I and III is shown in Fig. 8 as curves corresponding to different temperatures. The horizontal axis is the magnitude of the normal coordinate x that corresponds to the displacement vector required to transform phase I into phase III. This distortion is a flexing of the NO_3 ion, which is planar in phase I, plus a displacement of the K^+ ion along the c axis. The phase I-III phase transition in KNO_3 is somewhat displacive and slightly first order. The free energy for such a system is known to develop[34,35] a metastable state a few degrees above the actual transition temperature; we shall denote this state as T_2, in accord with Ref. 34. At temperatures above $T_C = T_{\text{I-III}}$ ferroelectricity can be induced by an applied electric field; at temperatures above T_2 ferroelectricity cannot be induced by an applied field, however strong, as shown in Fig. 8(b). In $BaTiO_3$ T_2 lies 10 °C above T_C.[34] In KNO_3 our data and those of Ref. 3 show that T_2 lies approximately 65 °C above $T_c = T_{\text{I-III}}$. Theoretically, $T_2 - T_C = \gamma^2/5\beta\delta$, where β, γ, and δ are the leading coefficients of the free-energy expansion in terms of the spontaneous polarization P.

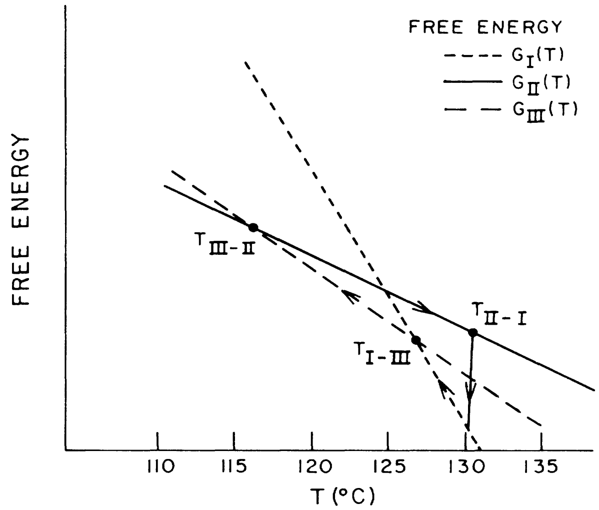

FIG. 10. Free energies of KNO_3 phases versus temperature, showing hysteresis and the reentrant nature of phase III. See also, S. Swaminathan and S. Srinivasan, Acta Crystallogr. Sect. A 31, 628 (1976); H. F. Fischmeister, J. Inorg. Nucl. Chem. 3, 182 (1956).

Figure 8 also shows the free energy for phase II. This aragonite structure has an equilibrium value of the normal coordinate x that is very different from that of phase I or phase III. At temperatures near $T_{\text{I-III}}$ the free energy of phase II is much higher than those of I or III. Hence, this phase plays no role in the I→III transition dynamics. The situation is quite different, however, near the lower transition temperature $T_{\text{II-III}}$ as shown in Fig. 9. As shown in this figure, the application of a sufficiently large external electric field will *always* make phase III the stable phase, no matter how low the temperature is, since the double-well potential exists for all $T < T_C$. Thus, the surface electric field model explains why the stable temperature range of phase III extends in thin films only 66 °C higher than that in bulk but ~180 °C lower. By comparison, the pressure dependence shown in the phase diagram in Fig. 1 of the main text is nearly symmetric with respect to the upper and lower transition temperatures; it does *not* predict such an asymmetric spread of temperature range for the stability of phase III as a function of pressure. This should be regarded as supporting evidence for the surface electric model of phase III stabilization in KNO_3 thin films.

It might be hoped that these figures would also give some qualitative insight into the kinetics at $T_{\text{I-III}}$ and

$T_{\text{II-III}}$ and in particular why phase III is only a reentrant phase. The important thing in this regard in Figs. 8 and 9 is that the discontinuity in displacement parameter x is much smaller between phases I and III than between II and I or II and III. What happens is shown schematically in Fig. 10. If we temporarily ignore the existence of phase I, the hysteresis in the phase-II to phase-III transition is about 15 °C (Ref. 36). This is larger than the width of phase III in bulk. Consequently, upon heating, phase II overshoots phase III and goes directly into phase I. Upon cooling, however, phase I transforms almost continuously to phase III, as shown in the figure. It is important to note in this figure that the slopes of the lines drawn (free energies versus temperature) are given by $-S$, where S is the entropy of each state. Since phase I is disordered, as discussed in the theoretical section of this paper, it has a much larger entropy than that of phase II or III, as shown.

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