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Raman spectroscopy of incommensurate $Ba_2NaNb_5O_{15}$

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We have performed Raman studies of the E-symmetry phonon modes in barium sodium niobate in the tetragonal ferroelectric phase above 582 K and measured carefully their splitting into pairs of B_1 and B_2 symmetry in the incommensurate (IC) phase between 543 and 582 K. For both heating and cooling cycles the data satisfy mean-field predictions with B_1-B_2 frequency splitting proportional to the order parameter. The data show that the incommensurate-incommensurate transition at 565 K (heating) does *not* alter the orthorhombic symmetry; that is, it is *not* a true $1q$-$2q$ transition, and tetragonal symmetry does not set in until the incommensurate-normal transition at 582 K. This is compatible with very recent electron microscopy data (Verweft, Van Tendeloo, and Van Landuyt), which show that the incommmensurate-incommensurate transition near 565 K produces only short-range order in a direction perpendicular to the long-range $1q$ modulation, and with x-ray studies of this transition (Kiat, Toledano, and Schneck). An analogous situation is observed just below the incommensurate-commensurate transition at 105 K: Here the C_{11} and C_{22} elastic coefficients have minima at 105 K, signaling a phase transition, but they do not become equal ($C_{11}=C_{22}$) until approximately 90 K, indicating that there is an incommensurate-incommensurate transition from orthorhombic to tetragonal near 90 K. The 90-K IC-IC transition seems quite analogous to the 565-K IC-IC transition, but electron microscopy shows that these phases are not reentrant.

I. INTRODUCTION

Raman spectroscopy has been successfully used as a tool for studying structural phase transitions in two quantitative ways: In displacive systems there is a "soft" optical phonon whose frequency varies approximately as the order parameter with temperature; and in both order-disorder and displacive systems there is often a frequency splitting induced below the transition temperature of modes which are symmetry degenerate in the high-temperature phase. Perhaps the best examples of the latter technique have been illustrated in triazine, where doubly degenerate modes at 942 and 1412 cm^{-1} split into well separated doublets as the temperature is lowered into the ordered phase.[1-3] It is the latter technique of analysis that we employ in the present study of barium sodium niobate in its incommensurate phase. We shall examine below the splitting of two modes at 47 and 76 cm^{-1} of E symmetry in the tetragonal $P4bm$ phase above 582 K into B_1 and B_2 components in the orthorhombic incommensurate phase(s) between 543 and 582 K. Special attention will be paid to the temperature region near 565 K, where an incommensurate-incommensurate transition occurs.[4-6]

The phase diagram for barium sodium niobate is shown schematically in Fig. 1. A complicated sequence of phases is encountered upon cooling. All of these below $T_c=853$ K are ferroelectric and some are incommensurate. Unlike the situation in many incommensurate insulators, the incommensurate modulation and the ferroelectricity in $BaNaNb_5O_{15}$ are not closely related and in fact occur along orthogonal directions. Considerable controversy exists concerning the incommensurate (IC) phases. Schneck *et al.* have inferred from their studies[7] that the IC phase between 40 and 105 K is a "$2q$" tetragonal structure with identical long-range modulations along two orthogonal directions. This is supported by neutron scattering and Brillouin scattering from our group.[8,9] However, electron microscopy shows, to the contrary,[10] that this IC phase is orthorhombic, with only a $1q$ modulation. A similar discrepancy remains to be reconciled for the high-temperature IC phases(s). The x-ray studies of Kiat[11] give a $2q$ structure between 543 and 565 K. Light scattering and some initial electron microscopy confirm the presence of such an incommensurate-

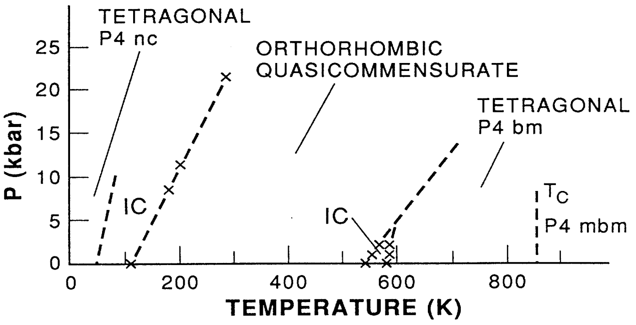

FIG. 1. Schematic phase diagram for barium sodium niobate (heating). From Refs. 14 and 15. The change in the lower commensurate-incommensurate transition (105 K at ambient pressure) is 8.6 K/kbar. That of the lock-in transition (543 K at $P=1$ bar) is 14.2 K/kbar; and that of the normal-incommensurate transition (582 K at $P=1$ bar) is stated, with greater uncertainty, as ≤ 5 K/kbar.

incommensurate transition near 565 K.[12,13] But more recent electron micrographs reveal only a 1q orthorhombic structure throughout the entire high-temperature IC range (543–582 K). It is a primary aim of the present work to reconcile these qualitatively different conclusions.

II. EXPERIMENT

The Raman data presented below were obtained with conventional equipment, consisting of a 1-W argon-ion laser operating at 514.5 or 488.0 nm, a double grating spectrometer with cooled phototube and photon-counting detection, and an on-line computer. Because moderately high resolution measurements of line splitting was required, slit widths had to be kept reasonably small. A 0.25 cm^{-1} spectral resolution was achieved, and the spectrometer drive was set in those increments. The actual splitting measured for two pairs of B_1-B_2 phonon pairs at 46 and 76 cm^{-1} varied from 0.3 to 2.6 cm^{-1}, as shown in Figs. 2 and 3.

The specimens used were two: one from CNET (Bagneux) and one from Nanjing University. Both had low sodium vacancy concentrations, known thermal histories, and were poled and detwinned using established techniques. The poling procedure consisted of depositing 0.5-μm-thick gold layers on the two polar faces by vapor deposition and then current poling at 2 $\mathrm{mA/cm}^2$. The current was kept low to minimize diffusion of gold into the specimens. Then the samples were slowly heated (4 K/min) to 853 K (20 K above the Curie temperatures in these samples), during which time oxygen gas was bubbled through distilled water into the oven containing the crystals. AT 853 K a dc voltage was applied sufficient to produce the specified 2 $\mathrm{mA/cm}^2$ current. The sample was viewed throughout the poling procedure, and a boundary plane was visually observed to form at the anode and move slowly across the specimens. The temperature was maintained at 853 K for an additional 30 minutes and then turned off and permitted to cool slowly to room temperature. After this procedure the samples were detwinned by application of 1.5×10^7 $\mathrm{dyn/cm}^2$ compressive stress along the a or b axis (orthorhombic) at a detwinning temperature of 593 K for 30 minutes. The specimens were finally checked under crossed polarizers through a 100× microscope and verified to be single ferroelastic domains. They were then placed in a tubular alumina furnace in which the temperature could be stabilized to a few hundred mK over a 20-min run sufficient for data collection. The temperature was monitored by a thermocouple in close proximity to the sample but not in thermal contact with it. Because of this, and including laser heating effects, the absolute temperatures quoted in this work are probably accurate to only ±1 K.

These data show two things: first, the observed splittings of the modes that have degenerate E symmetry above 582 K in the tetragonal phase can be accurately fitted to a mean-field theory over the entire IC range of temperatures, for both heating and cooling cycles; second, there is no indication of any tetragonality at $565\leq T\leq580$ K (i.e., the incommensurate-commensurate transition at 565 K cannot be an orthorhombic-tetragonal "1q-2q" transition).

Figure 3 shows the raw phonon frequencies. Somewhat surprisingly, the individual phonon branch energies do not both vary monotonically with T; the B_1 component actually increases in frequency and then decreases as temperature is raised. A similar behavior is exhibited in triazine and presumably arises from the combination of an overall softening as T approaches T_0 plus a splitting that increases the frequency of the upper branch.

Note the large thermal hysteresis of 45 K for cooling versus heating cycles for the incommensurate-normal transition. The normal phase is actually quasicommensurate, with a small residual amount of discommensurations persisting in most specimens due, presumably, to imperfect stoichiometry; in the best specimens the residual incommensurate structure corresponds to a wave vector within 0.02 a^* of commensurate, so we will term this room-temperature phase "commensurate" in the present paper. The incommensurate phase between 543 and 565 K may be the same one as is encountered below 105 K; that is, the IC phase may be reentrant. The phase boundary of the lower normal-incommensurate transition has been studied by both temperature and hydrostatic pressure, with the results shown[14] in Fig. 1. In Fig. 1 we use the values of the pressure shift in transition temperatures given by Savary and Toledano[14] (T_L shifts linearly upward at 14.2 K/kbar, and T_I linearly upward at 5 K/kbar). These linear pressure shifts, if extrapolated, predict that the IC phase will vanish above 4 or 5 kbar, rather than being continuous with that at low temperatures, as we had conjectured in Ref. 8. Our measured transition temperatures on heating (573 K) agrees well with those of Refs. 14 and 15, but for cooling we get a lower value (528 K versus their 548 K), which is probably sample dependent and determined by defect concentra-

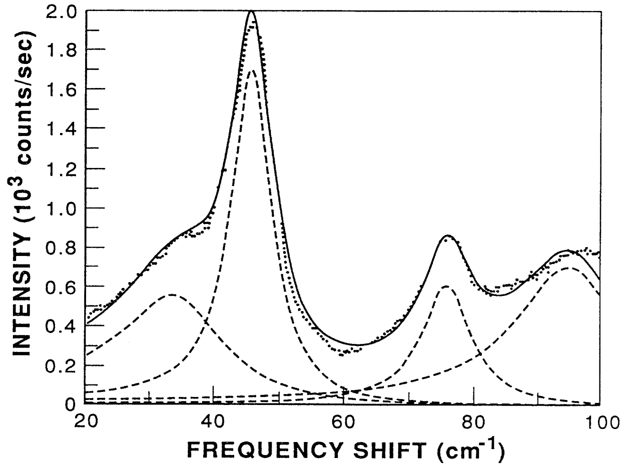

FIG. 2. Phonon spectra in barium sodium niobate at 298 K (heating) in the 20–100 cm^{-1} region. The dots are raw data for $xx+xy$ polarizability components; solid curves, theoretical four-mode computer fits; dashed curves, individual mode profiles.

tions. In a later section of the present paper we discuss whether the incommensurate phase between 40 and 105 K is tetragonal or orthorhombic, and whether there is also an incommensurate-incommensurate transition from $1q$ to $2q$ within this IC phase.

In addition to the phonon energies and splittings discussed above and in Figs. 2 and 3, we have measured the intensities of an important pair of modes at 32 and 86 cm^{-1}. We have proposed that this B_1-B_2 pair also represents an eigenfunction that would be degenerate (E symmetry) above 582 K in the normal tetragonal phase, and that the unusual temperature dependence of the 32 cm^{-1} component reported earlier[15] arises from orthorhombic splitting and not from mode softening associated with a low-temperature phase transition, as proposed in the earlier work.[15] In Fig. 4 we examine the Raman intensities of this pair of modes. Note that both decrease on heating to an extrapolated zero intensity at approximately 573 K, the same temperature at which the splittings go to zero for the other modes, shown in Figs. 2 and 3. This supports the interpretation of this pair of phonon modes as zone boundary in the normal $P4bm$ phase. However, as shown in Fig. 5, this intensity dependence is somewhat sample dependent; moreover, in all our samples the linear decrease in intensity with temperature as T approaches T_0 from below is interrupted by the IC phase. The intensity dependence $I(T)$ flattens out at 543 K and actually exhibits a maximum at 565 K. We interpret

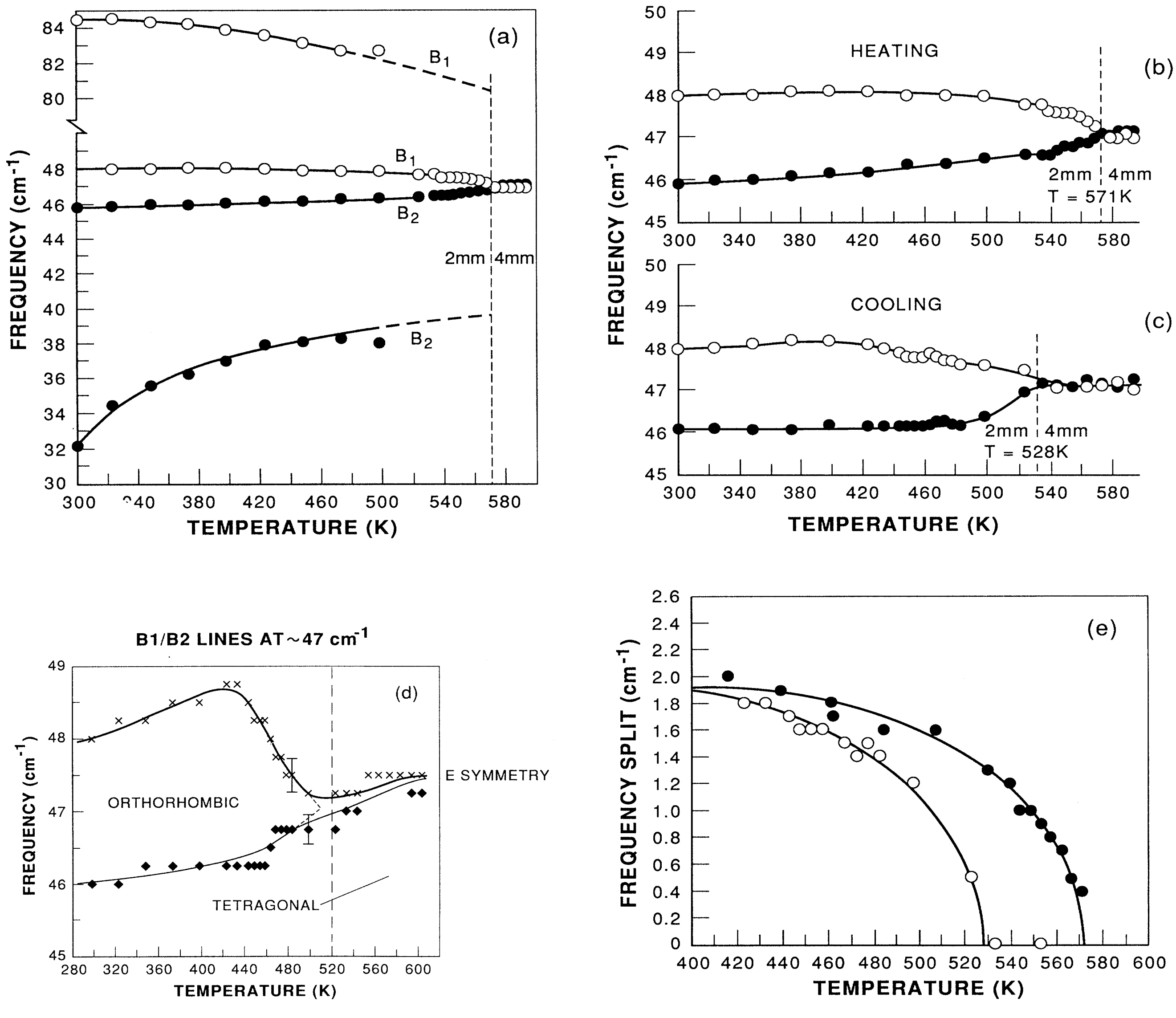

FIG. 3. (a) Phonon frequencies vs temperature near the normal-incommensurate transition TI in barium sodium niobate. (b) $B1$-$B2$ frequency splittings vs temperature near TI (heating). (c) Frequency splitting near TI (cooling) for CNET sample. (d) Frequency splitting near TI (cooling) for Nanjing sample. (e) CNET sample data for phonon frequency splitting compared with mean-field theory (solid lines).

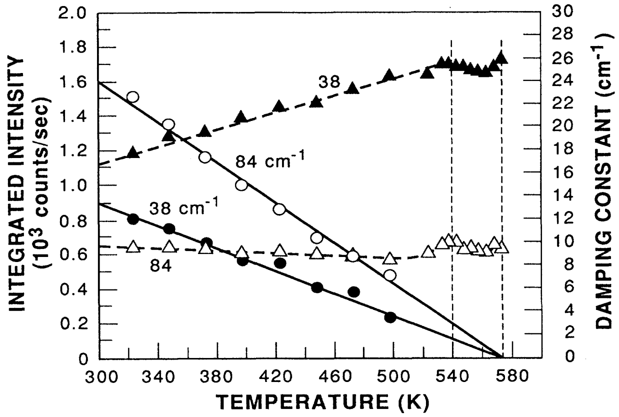

FIG. 4. Raman intensities and linewidths vs temperature for B_1-B_2 symmetry phonon pairs at 32–38 and 86 cm^{-1} near TI in barium sodium niobate. The solid curves are intensities; dashed curves, linewidths. Data are for warming runs.

these data as indicating that the intensities of these two modes would continuously decrease to zero at the orthorhombic-tetragonal phase transition temperature if there were no IC phase(s) between the quasicommensurate room-temperature phase and the tetragonal $P4bm$ phase. The data of Fig. 4 might be expected to fit a power law

$$I(T)=I_0t^{2\beta-\gamma} \tag{1}$$

in the simplest theory, where t is reduced temperature, $(T_I-T)/T_I$ with $T_I=573$ K or so. In mean field[16] this is simply a step discontinuity but when interactions with other modes are included (particularly with acoustic modes),[17] the discontinuity is smoothed out in an approximately linear way. Because of the sample differences found in the data, it is not our aim in the present paper to describe the detailed fitting of these intensities to the theory of Chen and Scott, but we point out that these intensity dependences observed in Fig. 4 are not incompatible with mean-field theory and hence with the frequency splitting data of Figs. 2 and 3. Unlike the frequency data, however, they give a clear indication of a transition at 565 K, within the IC regime, as discussed below.

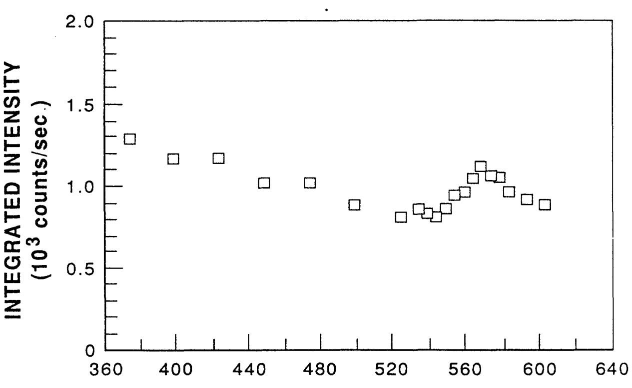

FIG. 5. Raman intensities vs temperature for the mode near 32–38 cm^{-1} in barium sodium niobate (Nanjing sample), showing anomalous peak near 565 K. Compare with Fig. 4.

Note in Fig. 4 that the Raman linewidth of the mode near 32 cm^{-1} has a minimum at 565 K. This is not understood even qualitatively, but it does provide additional evidence for a phase transition at that temperature. Complementary details are given in Fig. 5. Here the Raman intensity $I(T)$ for that mode (at 32–38 cm^{-1}) is carefully measured into the temperature region between the orthorhombic-IC transition at $TL=543$ K and the IC-tetragonal transition TI above 573 K. Rather surprisingly, a nonmonotonic temperature dependence is observed for $I(T)$ with a peak at exactly 565 K, where the "1q-2q" transition occurs. We cannot explain why the linewidth has a minimum and intensity a maximum at 565 K. But if, as proposed above, this mode is intimately related to the orthorhombic distortion from the parent tetragonal phase, a 2q-1q change in average structure at 565 K$=T_0$ should affect both width and cross section for it.

We note that the asymmetric LA (longitudinal acoustic) phonon spectra in the Brillouin scattering[9] near 565 K are quite like those predicted by Mayer and Cowley.[18] Note that these authors predict theoretically a mixing of both phase modes and amplitude modes with LA phonons for phonon propagation along the modulation direction, which is the case here and approximately that in our earlier BaMnF$_4$ studies.[18]

III. COMPARISON WITH ELECTRON MICROGRAPHS

A. High-temperature IC phase(s)

The unpublished electron micrographs of low sodium vacancy, carefully annealed barium sodium niobate specimens do indeed show evidence[19] for an incommensurate-incommensurate phase transition within the IC phase from 543 to 582 K. The exact transition temperature is difficult to ascertain from such studies, due to beam heating of the target specimen, but it is estimated as 10–20 K below the incommensurate-normal transition at 582 K. However, the transition is observed to be different from that of a simple 1q-2q orthorhombic-tetragonal transformation. In particular, the modulation has no well-defined wavelength or long-range ordering and therefore does not permit us to describe the phase between 565 and 582 K as "2q." In the absence of a conventional notation in the literature for such a structure, we shall label it as "q_1+q_2," where it must be understood that the wave vector q_2 has a considerable breadth of values (i.e., its Fourier transform is not at all a δ function).

This interpretation helps reconcile the light scattering data, x-ray data, and electron microscopy. The divergent central mode observed[8,9,12,20] in light scattering experiments does indeed signal a phase transition at 565 K. But it need not be one of 1q-2q character (in fact, it could be simply order disorder). In order to produce an intense central mode in the Raman spectrum, the system need only have very large fluctuations in its dielectric function. These do not need to be of very long range in real space. The idea that the 565 K incommensurate-incommensurate transition corresponds to a roughening of antiphase boundaries (APB's)[18] has already been proposed by us elsewhere.[8,9,12] That description seems at least qualitatively correct, in light of the most recent electron microscopy; however, the topological changes involved are not simple roughening of the $1q$ phase boundaries, but involve perpendicular growth of microstructures out of those initial boundaries. The x-ray data of Kiat are very important in establishing that an additional Bragg peak appears above 565 K on warming. It is somewhat intermediate between the a^* and b^* positions of the orthorhombic $1q$ structure; however, it is not simply the average of a^* and b^*. Toledano has suggested that it arises from a quiltlike superstructure of a and b microdomains having a repeat distance of approximately 100 Å.

Van Tendeloo, Van Landuyt, and Verweft find[19] from their detailed electron microscopy of $Ba_2NaNb_5O_{15}$ that "the high-temperature $2q$ modulated phase" (between 565 and 582 K in our samples) "is a pseudoperiodic occurrence of two-dimensional domains of ferroelastic nature, which domains are described as 'amplitude solitons' by Toledano." By comparison, the low-temperature $2q$ phase (from 40 to about 90 K in our specimens, and discussed further in the section below) "consists of a periodic occurrence of planar defects, where the defects—or antiphase boundaries—are stacked in a disordered manner. If the structure would be perfectly ordered in the two directions, one would have a $2q$ phase soliton modulation." The latter point lets us see why this phase appears to be perfectly tetragonal on the scale of the probe length characteristic of neutron scattering,[8] birefringence,[21] or other optical probes,[22,23] but slightly orthorhombic on the smaller length scale probed by electron microscopy;[19] it is a question of whether the disorder in the defect sites of the low-temperature phase is averaged locally or in a nanometer scale or greater. The main difference between the high-temperature $2q$ phase (565–582 K) and the low-temperature $2q$ phase (40–90 K) is that in the low-temperature phase no "ferroelastic microdomain patchwork is observed" by electron microscopy.[19] This shows that the two phases are not identical and cannot be viewed as reentrant, contrary to the suggestion by the present authors in earlier work.[8]

B. Low-temperature IC phase(s)

Below 105 K barium sodium niobate becomes incommensurate again. On the basis of X-ray and birefringence data, Schneck *et al.* have proposed[21] that this phase is a $2q$ modulation in which the tetragonal structure of higher temperature is restored via the creation of two equivalent modulations along orthogonal directions in the plane perpendicular to the fourfold axis. This is compatible with our neutron scattering data, which establish that the final lock-in phase below 40 K has the $P4nc$ tetragonal space group predicted by Schneck.[21] However, the electron micrographs between 80 and 105 K show unambiguously[10] that the temperature range has a lq orthorhombic structure. Can we reconcile these disparate results? The Brillouin data in this temperature range are extremely helpful. As first shown by Yagi *et al.*[22] and more recently and precisely by Oliver *et al.*,[23] the acoustic phonon data show clearly that the C_{11} and C_{22} elastic coefficients both exhibit sharp dips with minima at 105 K, the signature of a phase transition (in this case, from commensurate-incommensurate). However, as is clear from the figures in Refs. 22 and 23 but not emphasized in the discussions in those papers, C_{11} does not become equal to C_{22} until about 20 K below this 105 K transition. That means that the phase immediately below 105 K cannot be tetragonal, or that at a minimum there is a coexistence of tetragonal and orthorhombic phases between 85 and 105 K. The truly tetragonal phase is apparently reached only below 85 K. This suggests that the low-temperature IC regime actually consists of two IC structures—tetragonal from 40 to 85 K and orthorhombic from 85 to 105 K. That would be consistent with the electron micrographs,[10] and it would provide a mirror image on a P-T phase diagram like that in Fig. 1 of the situation we infer in the high-temperature IC regime (543–582 K). Note, however, that recent electron micrographs show[19] that any distortion from tetragonality is extremely small: Verweft, Van Tendeloo, and Van Landuyt report[10] $a=3.524$ m, and $b=3.518$ nm (less than 0.2% difference). Toledano *et al.* suggest[5] that such residual stabilization of the orthorhombic room-temperature phase may be attributed to defects. Additional electron microscopy between 40 and 85 K might clarify this question, but very stoichiometric specimens would be required.

ACKNOWLEDGMENTS

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