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LETTER TO THE EDITOR

A quasielastic light scattering study of the $1q$ to $2q$ transition within the incommensurate phase of $Ba_2NaNb_5O_{15}$

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Abstract. Inelastic light scattering in incommensurate (IC) $Ba_2NaNb_5O_{15}$ reveals a dynamic central mode whose width satisfies $\tau^{-1}(q, T) = D(T)q^2$ with diffusivity $D(T)$ exhibiting a maximum of $0.85\ cm^2\ s^{-1}$ at $T_R \simeq 565$ K, the temperature at which electron microscopy shows an abrupt roughening transition within the antiphase boundaries (APBs). This phase change involves a transition from modulation along one axis ($1q$) to modulation along two orthogonal axes ($2q$). The dynamic central mode is also observed to couple strongly with the [100] longitudinal acoustic (LA) phonon.

In several incommensurate insulators it has recently been observed that within their incommensurate (IC) phases, there are first-order phase transitions from a $1q$ structure with modulation along a single crystallographic axis, to $2q$ or $3q$ structures with equivalent modulations along two or three axes. For example, Manolikas *et al* and Schneck *et al* [1] have shown a $1q$ to $2q$ transition within the higher IC phase (543–582 K) in $Ba_2NaNb_5O_{15}$ and have provided a free-energy theory of that transition; Bastie *et al* [2] have shown a $1q$ to $3q$ transition within the narrow (1.5 K) IC phase of unstressed quartz; and Muralt *et al* [3] have found a $(1 + \delta)a^*/3$ to $(1.0)(a^* \pm b^*)/3$ transition in $(C_3H_7ND_3)_2MnCl_4$ that can be described as $1q$ to $2q$ if the $(a^* \pm b^*)/3$ phase is not exactly commensurate. Xiaoqing and Duan have shown [4] that the $1q$ to $2q$ transition in barium sodium niobate (BSN) is accompanied by depinning and roughening of discommensuration walls, as observed directly via electron microscopy. In the present work we have measured, using optical techniques, the diffusivity associated with this wall roughening, which peaks at $0.85\ cm^2\ s^{-1}$ at the $1q$ to $2q$ transition temperature (565 K in BSN). In agreement with the theoretical calculation of Hassold *et al* [5], this diffusivity is faster than that due to ordinary thermal diffusion of entropy fluctuations in the same material [6] (by approximately 40).

Several optical spectroscopic studies of incommensurate insulators have been made, primarily in the search for phasons [7–11], and although it is apparently well understood that the absence of underdamped propagating phasons for wavevector $q \simeq 0$ results from q-independent damping [12, 13], the interpretation of diffusive light scattering

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(quasielastic scattering from dynamic central modes) has remained controversial [13–16]. This, to a great extent, is because the experimental data do not satisfy the predictions of theory. In particular, the theories generally predict vanishingly small cross sections for scattering from phase modes, within a continuum approximation in which the phasons may be described as propagating modes in the plane-wave regime near T_I, the upper transition temperature of the IC phase, and diffusion of kink-like antiphase boundaries (APBs) near T_L, the lower transition temperature.

These theories generally neglect two important points: (i) the atomic microscopic structure of the APBs, which permits internal diffusive modes ('roughening') in addition to the diffusion of soliton-like walls; such roughening accompanies the recently discovered $1q$ to $2q$ first-order transitions within IC phases; (ii) the possibility of very strong coupling between these diffusive modes and other excitations such as sound waves.

In the present letter we present the results of a quasielastic light scattering study of IC BSN. Our sample came from the same boule as samples on which detailed electron microscopic studies have recently been done [4]. The diffusivity D inferred from our central mode linewidth $\tau^{-1}(T, q) = D(T)q^2$ exhibits a maximum of $\simeq 0.85\ \mathrm{cm^2\ s^{-1}}$ at 565 K, in the middle of the IC phase, where an abrupt roughening of APB walls is observed by electron microscopy [4]. The dynamic central mode was also observed to couple very strongly to the LA phonon propagating along the IC direction ([100] with reference to the room temperature orthorhombic axes); the coupling at 565 K is $\simeq 9.6$ GHz and generates $\simeq 89\%$ of the quasielastic scattering cross section.

To perform the experiments, two samples of BSN were cut from the same parent crystal and then poled and detwinned, so as to be single domain both ferroelectrically and ferroelastically. Laser excitation for the light scattering experiment was provided by a Spectra Physics 165 argon-ion laser operating in a single mode at a wavelength of 5145 Å and a typical power of 200 mW. The scattered light was analysed by a piezoelectrically scanned, five-pass, four-pass tandem Fabry–Perot interferometer [17]. Spectra were recorded between 298 K and 755 K in a right-angle scattering geometry. A few spectra were also recorded in both back-scattering and forward-scattering geometries over approximately the same temperature range. Since the photon count in the central mode part of the spectrum was typically 10^{-2} times that in the phonon region, scan times for a single spectrum were a minimum of two hours, with some as long as eight hours. Representative data are shown in figure 1.

In order to assign the observed mode as due to diffusion it is important to establish the dependence on q^2 of its linewidth, since other microscopic non-diffusive mechanisms produce dynamic central modes in light scattering with widths independent of q or linearly dependent on q [18]. Because of the coupling between the LA phonon and the central mode in the present work, this is a non-trivial demonstration; only the uncoupled central mode is expected to exhibit a $\tau^{-1} = D(T)q^2$ dependence, and even this may be modified by a constant g, dependent upon defect pinning and the consequent energy gap [15] in the excitation spectrum, leading to $\tau^{-1} = D(T)q^2 + g$.

The coupled mode analysis we use is by now fairly standard [19, 20]. The scattering intensity $I(\omega)$ is given by a generalised fluctuation-dissipation theorem

$$I(\omega) = -\frac{k_B T}{\pi \hbar \omega} \sum_{i,j=1}^{2} P_i P_j \operatorname{Im}\{G_{ij}\} + B \tag{1}$$

where the inverse coupled-mode matrix is given by

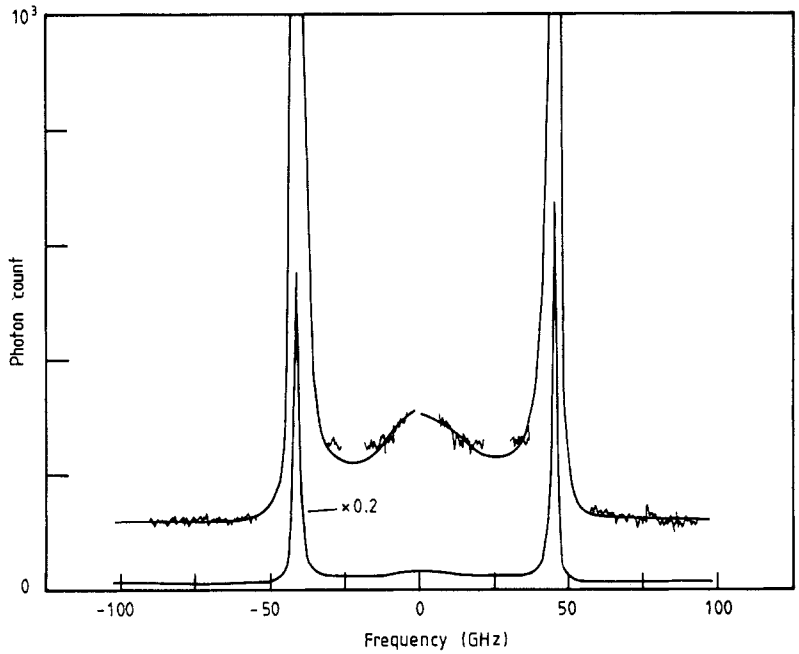

Figure 1. Spectrum of BSN taken at 546 K in a right-angle scattering geometry, showing the asymmetrically broadened LA phonon and the central mode. The small gaps near 25 GHz arise from intentional elimination of a few channels in the multichannel analyser to prevent spectral contamination from the TA phonon, which sometimes 'leaks' through in small amounts for this geometry. The full curve shows a fit to the complete spectrum from equations (1) and (2). The LA peak is shown on a scale reduced in intensity by $\frac{1}{5}$.

$$\{G_{ij}^{-1}(\omega)\} = \begin{bmatrix} \omega_a^2 - \omega^2 + i\omega\Gamma_a & -\omega_a\Gamma_{ac} \\ -\omega_a\Gamma_{ac} & \omega_a^2(1 + i\omega\tau_c) \end{bmatrix} \tag{2}$$

and where the P_i are scattering strengths and B is the background (the data fits showed that B is not correlated with the other fitting parameters, although it is T-dependent). The effect of the coupling Γ_{ac} between the acoustic mode at ω_a and the Debye-like central mode is the renormalisation of both the acoustic mode frequency

$$\omega_a' = [\omega_a^2 - \Gamma_{ac}^2/(1 + \omega^2\tau_c^2)]^{1/2} \tag{3}$$

and width

$$\Gamma_a' = \Gamma_a + \Gamma_{ac}^2\tau_c/(1 + \omega^2\tau_c^2). \tag{4}$$

For our data, $\omega_a \approx 40$ GHz, $\Gamma_{ac} \approx 10$ GHz, and $\Gamma_a \approx 1$ GHz, so this coupling produces about a 1.6% renormalisation in the acoustic mode frequency ω_a at the same time that it more than doubles the width Γ_a, a result qualitatively similar to the observation of ω_a and Γ_a anomalies by Young and Scott [21] and by Errandonéa *et al* [22]. Our results show the existence of a central mode of width τ^{-1} whose coupling with the LA phonon produces 100% of the increase in the LA linewidth and most of the decrease in its frequency. The results of this analysis for $\tau(T)$, coupling constant Γ_{ac}, and integrated intensity are shown

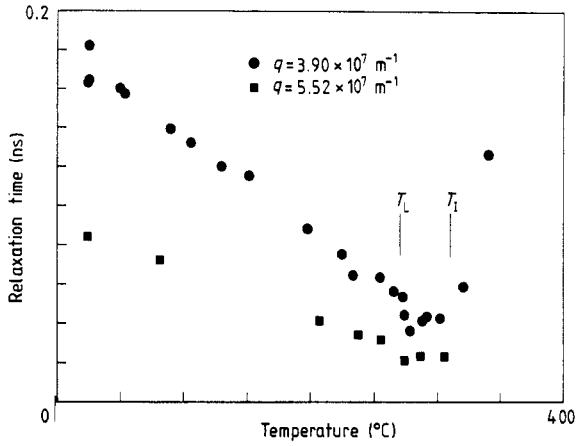

Figure 2. Central mode relaxation time τ_c versus temperature for both right-angle ($q = 3.90 \times 10^7\,m^{-1}$) and back-scattering ($q = 5.52 \times 10^7\,m^{-1}$).

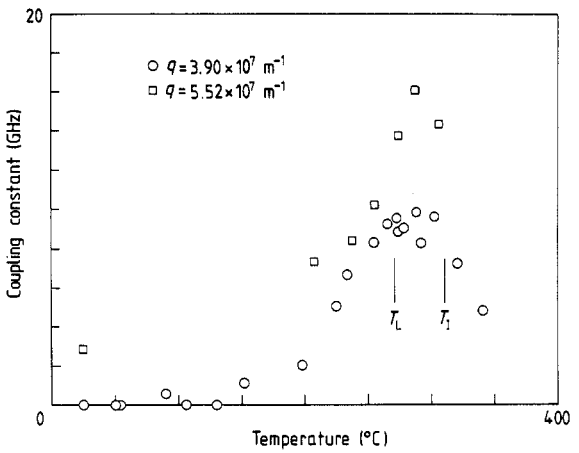

Figure 3. Coupling constant Γ_{ac} versus temperature for both right-angle and back-scattering data.

in figures 2–4. Figure 2 shows a ratio of 1.9 ± 0.2 for τ^{-1} at $q = 3.90 \times 10^7\,m^{-1}$ and $q = 5.52 \times 10^7\,m^{-1}$ (90° and 178° scattering angles, respectively) in good agreement with the ratio 2.0 expected for Dq^2 diffusion.

The coupling constant (figure 3) and integrated intensity (figure 4) exhibit maxima at ≈565 K, which is also the temperature at which the LA linewidth peaks [21, 22]. This is slightly more than midway between the upper and lower bounds of the IC phase ($T_I = 582$ K and $T_L = 543$ K) and identical to the temperature at which the APB wall-roughening transition occurs in our samples (to within an experimental error of ±2 K) as reported in [4]. Note that the APBs in BSN [4] are extremely wavy and will cross any possible phonon propagation direction; they are quite unlike the straight ferroelectric and ferroelastic domain walls also observed in these references. This makes LA phonon interaction with intra-wall relaxation mechanisms geometrically plausible.

Since our central mode scattering appears to arise from intra-wall diffusion in APBs, rather than the soliton-like diffusion of smooth extended structures envisioned in published theories of phason dynamics, we will not try to make detailed contact with

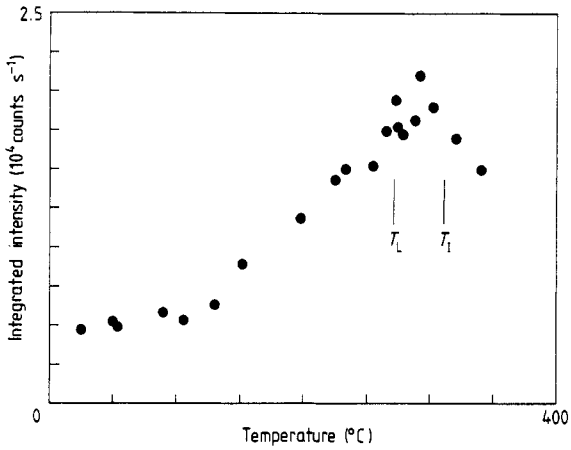

Figure 4. Integrated intensity versus temperature for right-angle scattering data. The maximum intensity occurs at 565 ± 2 K. Within experimental error this is exactly the temperature at which Pan Xiaoqing and Feng Duan [4] report roughening of APB walls in the electron micrographs of specimens cut from the same boule as ours. More recently these authors [26] have confirmed their original report and provided greater details characterising the microdomain growth and inter-phase nucleation near 565 K.

published formalisms. However, it is useful to try to see whether certain relationships are at least qualitatively correct. For example, Lebedev *et al* [15] have proposed that for phason scattering

$$\tau^{-1}(q) = g + Dq^2 \tag{5}$$

where g is proportional to the phason gap energy due to impurity pinning; similarly they obtain for the integrated central mode intensity

$$I(q) \propto \rho^2 q^2 k_B T/(g + \rho^2 Dq^2) \tag{6}$$

where ρ is proportional to the IC modulation amplitude.

From equation (6) above for $I(q)$ we calculate

$$(P_2(178°)/P_1(178°))/(P_2(90°)/P_1(90°))$$

where P_1 and P_2 are the scattering strengths of the acoustic mode and central mode, respectively, and find a ratio that varies from 1.3 to 1.7 using data at different temperatures. This ratio should be 1.0 for zero gap and 2.0 if $g \gg \rho^2 Dq^2$. Thus the intensity data suggest a finite gap. Our $\tau^{-1}(T, q)$ data impose limits on g such that $g \leqslant 0.1\ Dq^2$. Using this limit on g in equation (6) our intensity ratios require $0.10 \leqslant \rho \leqslant 0.15$, i.e. an incommensurate modulation of 10–15%, which may be reasonable†.

Our result that $g/\rho^2 Dq^2$ is of order unity is in sharp contrast to Lebedev and Levanyuk's estimate that it is 10^2–10^3 for typical defect densities of 10^{18} cm^{-3} [15]. This is perhaps reasonable when we recall that their gap is for inter-APB pinning and ours describes intra-APB pinning.

In summary we have observed a dynamic central mode in the IC phase of BSN using Brillouin scattering techniques. This mode was observed to couple strongly with the LA

† See the *Note added in proof.*

phonon along the direction of the IC modulation. Good fits to the spectra were obtained using mode coupling theory. All of the LA mode width divergence and much of its frequency anomaly were found to be due to coupling. In the curve fits, the central mode width was found to satisfy $D(T)q^2$, characteristic of diffusion, with a maximum diffusivity of 0.85 $cm^2\ s^{-1}$ at $\simeq$565 K in the middle of the IC phase. The central mode width, coupling constant, and integrated intensity were all found to reach a maximum at $\simeq$565 K. This is exactly the temperature at which a roughening transition is observed in the APBs by TEM. We assign the central mode to antiphase boundary diffusion. In particular, it is probably due to a diffusive excitation along the APBs corresponding to the observed roughening. It is important to note that we observed strong diffusion optically for $T \geqslant 220$ °C; this is very close to the onset observed via electron microscopy [23, 24]. Van Tendeloo *et al* [25] observe that when the temperature is raised above ambient (but below the nominal lock-in temperature at 543 K), 'the discommensurations become very mobile and their number quickly increases'. Thus, optically observed mobility corresponds with that manifest in electron microscopy.

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Note added in proof. Labbé *et al* [27] have very recently measured the magnitude of the incommensurate modulation in BSN. At 295 K they find, via x-ray crystallography, that the average magnitude of the tilt angle φ for twelve inequivalent NbO_6 octahedra, relative to the commensurate structure, is $\langle|\varphi|\rangle = 6.64°$, corresponding to $\rho = \tan\langle\varphi\rangle = 0.116$. This value agrees very well, perhaps fortuitously, with the estimate $\rho = 0.12 \pm 0.03$ given in the present work from equation (6), using central mode intensities at higher temperatures.

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