Lattice dynamics of NaI studied by inelastic neutron scattering: Absence of thermally induced discrete breathers

M. Kempa,[1] P. Ondrejkovic,[1] P. Bourges,[2] P. Marton,[1] and J. Hlinka[1,*]

[1]*Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague 8, Czech Republic*

[2]*Laboratoire Léon Brillouin, C.E.A./C.N.R.S., F-91191 Gif-sur-Yvette CEDEX, France*

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The paper presents an inelastic neutron scattering study of lattice dynamics of the NaI alkali halide crystal, aimed to check the previously reported signatures of intrinsic localized modes, so-called discrete breathers. It is shown that three unusual spectral features, previously interpreted as an evidence for thermally induced discrete breathers (an anomalous spectral band in the phononic gap, longitudinal acoustic Λ_1 phonon branch overbending, and fragmentation of the X-point transverse optic mode response) are all absent in the independent experiments reported here.

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I. INTRODUCTION

Discrete breathers, also known as intrinsic localized modes, are well-established vibrational excitations inherent to many types of nonlinear periodic lattices [1,2]. These modes are highly localized in space, similarly as, e.g., the localized modes associated with force-constant defects [1]. Their formation typically requires either a large displacement or a large impulse moment concentrated at one or few atoms only. Below a certain formation energy threshold, the locally absorbed energy is spread over the lattice merely via phononlike vibrations, while above such threshold, the anharmonic shift of the local vibrational frequency prohibits/suppresses the spreading of the energy to the neighboring lattice sites, and the long-lived discrete breather is formed (see Fig. 1). Numerous theoretical and experimental studies of such excitations in various nonlinear systems have been performed in the past [4–17].

In the seminal paper of Sievers and Takeno [1], they theoretically argued that these breather modes might be also thermally generated at cryogenic temperatures in strongly anharmonic crystal lattices of quantum crystals as well as in ordinary solids. However, these thermally excited intrinsic localized lattice vibrations are possibly quite rare, so that it seemed very difficult to discern them experimentally from the usual quasiharmonic phonons. Interestingly, a recent inelastic neutron scattering (INS) study (Ref. [18], hereafter denoted as paper I) did indicate the appearance, at temperatures around 570 K, of a localized vibrational excitation with frequency at about 2 meV above the bottom of the phononic gap of the NaI crystal [18]. Observation of this gap excitation thus really appeared to be the expected evidence for the formation of the originally predicted [1,6] breather mode [18].

Such a challenging claim has obviously triggered several follow-up experimental [19–21] and theoretical [22–26] studies. However, the conclusions of these works are rather conflicting. In particular, the inelastic neutron scattering study of Ref. [21] failed to confirm the original observation [18] of the extraneous band in phonon spectra taken at $\mathbf{Q} = (2.5\ 2.5\ 1.5)$. At the same time, the authors of paper I reported also a set of additional time-of-flight measurements (in Ref. [19], hereafter denoted as paper II), suggesting that the anomalous mode might actually appear only in a rather narrow temperature interval. In addition, even more peculiar anomalies were reported to take place above the phononic gap, in the range of the transverse optic (TO) phonon band. Here, we report a set of new inelastic neutron scattering data of NaI single crystals. Present experiments allow to conclude that neither paper I nor II provide a sufficiently reliable evidence in favor of the thermally activated discrete breathers.

II. EXPERIMENTAL

The experiments were carried out on the 1T thermal neutron three-axis spectrometer (TAS) at the ORPHÉE reactor of the Laboratoire Léon Brillouin, CEA Saclay. The instrument was operated in its standard configuration, using horizontally and vertically focusing monochromator and analyzer crystals of PG(002) together with a natural collimation. The energy of scattered neutrons was fixed to 14.7 meV with a pyrolytic graphite filter in front of the analyzer. A typical full width at half maximum (FWHM) energy resolution was 1 meV. The distances source-monochromator-sample-analyzer-detector were 480, 210, 80, and 80 cm, respectively. The horizontal and vertical dimensions of both monochromator and analyzer were 10 and 8 cm. Both of them were horizontally and vertically in focusing condition in order to obtain the optimal flux.

The crystals of ≈ 4 cm^3 (pellets of diameter 1 inch, mosaicity less than 1°) were grown from melt by the Envinet company [27] (Czech Republic). As in our previous study, both high-purity and slightly Tl-doped NaI single crystals were used [21]. It should be noted that NaI is highly hygroscopic. During the experiment, however, the sample was kept in vacuum, and so it could absorb water vapors only in a limited time when manipulating with the crystal (a few minutes).

The sample, placed in a Nb pocket, was mounted into a furnace with the $[1\bar{1}0]$ axis vertical. For a better notion, the part of the reciprocal plane, explored in this study, is visualized in Fig. 2. The constant-$\mathbf{Q}$ scans were fit to the sum of uncoupled damped harmonic oscillator (DHO) response functions. Observed phonon modes were labeled according to Ref. [28].

*hlinka@fzu.cz

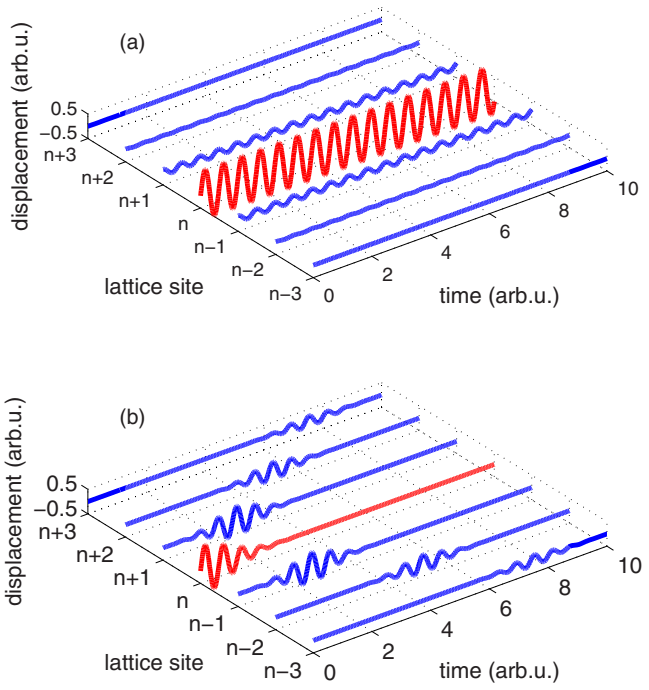

FIG. 1. (Color online) Schematic illustration elucidating the concept of a discrete breather (inspired by molecular dynamics calculations of Ref. [3]). The panels display temporal evolution of atomic displacements in a segment of a defect-free infinite one-dimensional diatomic chain (for clarity, only the displacements of lighter atoms are shown). (a) Strongly anharmonic lattice limit: energy dissipation to the neighboring atoms might be blocked and the vibrational energy, forming a breather, could stay localized over a long period of time. (b) Weakly anharmonic lattice limit: the vibrational energy is quickly spread to the adjacent lattice sites. In both (a) and (b), the same initial displacement pattern, highly localized around a selected atom n, was introduced at time $t = 0$.

III. RESULTS

Our arguments are based on experimental reinvestigation of the three most striking spectral features described in papers I and II: the anomalous spectral band in the phononic gap, the longitudinal acoustic LA(Λ_1) phonon branch overbending, and the fragmentation of the X-point TO mode response. We shall discuss them one by one.

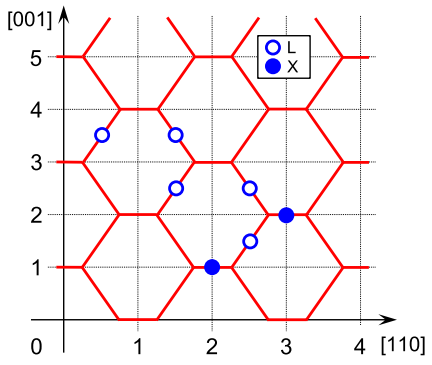

FIG. 2. (Color online) Schematic representation of the part of the reciprocal plane, studied in this paper, with sketched Brillouin zones and marked L and X points, where signatures of intrinsic localized modes have been searched in this work (see Figs. 4 and 6).

A. The gap mode

The most impressive experimental evidence for a thermally activated local phonon mode in the phononic gap is perhaps the set of INS spectra taken at several temperatures in the $\mathbf{Q} = (2.5\ 2.5\ 1.5)$ reciprocal point (Fig. 2 of paper I). All the spectra, measured on the TAS bt7 instrument, show the expected transverse acoustic (TA), LA and TO zone boundary modes, but the spectrum taken at the highest temperature [29] ($T_{\text{th}} \approx 575$ K) clearly suggests an additional spectral band, in agreement with the simple expectations for a thermally activated phenomenon. This new feature is absent in our INS spectra [21], even though these were taken at $T > T_{\text{th}}$ (at 600 and 700 K). For an easier comparison, spectra of these independent experiments are superposed here in Fig. 3. The nicely matching TA mode profiles suggest that the energy resolution in both experiments was very similar. It is also apparent that both experiments yielded similar signal to noise ratio. Moreover, one can see that the Brillouin zone (BZ) boundary TA and TO modes have quite similar relative intensities as well as positions in both measurements. Let us note that the gap mode of paper I is remarkably strong—its intensity is comparable to that of the adjacent TO mode. Actually, the comparison suggests that the intensity of the extraneous gap mode intensity is taken out from the intensity of the LA mode. If this intensity transfer from the LA mode to the gap mode is taken for granted, this observation could indicate some kind of coupling between the two modes.

The LA mode probed in the measurements of Fig. 3 is polarized along the [11$\bar{1}$] direction, and since the $\mathbf{Q} = (2.5\ 2.5\ 1.5)$ reciprocal vector is not parallel to it, this BZ is far from being optimal for LA mode observation. Based on the

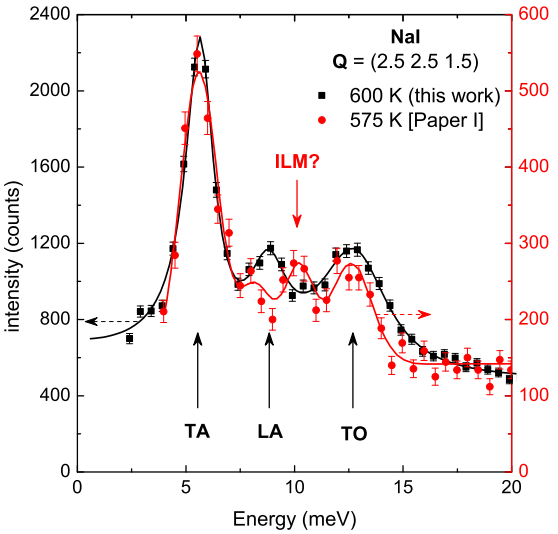

FIG. 3. (Color online) Comparison of inelastic neutron scattering spectra of this work and of paper I (Ref. [18]), measured on 1T and bt7 three-axis spectrometers, respectively. Both spectra are taken at the $\mathbf{Q} = (2.5\ 2.5\ 1.5)$ L point at temperatures close to $T_{\text{th}} = 575$ K. TA, LA, and TO stand for zone-boundary L'_3, L'_2, and L_3 modes, ILM is the extraneous band assigned in paper I to the discrete breather.

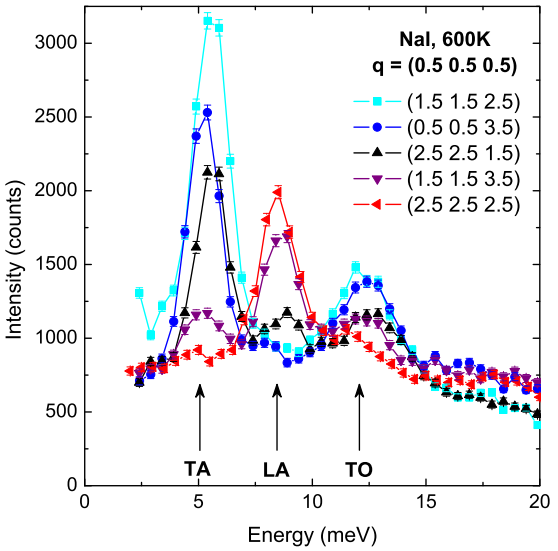

FIG. 4. (Color online) Selected L-point spectra of NaI at 600 K showing zone boundary TA(L'_3), LA(L'_2) and TO(L_3) modes. Different Brillouin zones allow to vary the scattering geometry from an almost transverse [$\mathbf{Q} = (1.5\ 1.5\ 2.5)$] to a purely longitudinal one [$\mathbf{Q} = (2.5\ 2.5\ 2.5)$].

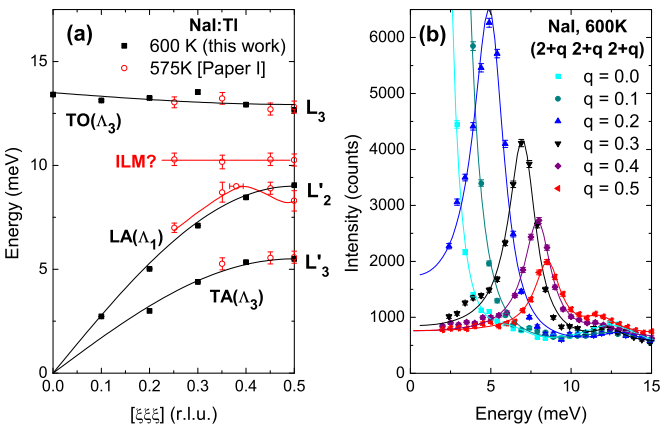

FIG. 5. (Color online) Phonon dispersion in the Λ reciprocal direction in the 575–600 K temperature range. (a) Dispersion curves of Λ_1 and Λ_3 branches in NaI:Tl (this work and Ref. [18]). The alleged dispersion of the intrinsic localized mode from Ref. [18] is also depicted. (b) Phonon spectra at several wave vectors in the longitudinal direction in pure NaI at 600 K.

invoked possibility of the LA intensity transfer, one could expect that the intensity of the gap mode should scale with the LA mode intensity [30]. Therefore we inspected L-point spectra in several different accessible BZs. As can be seen in Fig. 4, the relative intensities of TA and LA zone boundary modes vary as expected, for example, the LA mode intensity is maximal in the purely longitudinal geometry at $\mathbf{Q} = (2.5\ 2.5\ 2.5)$, while the TA mode intensity attains its maximum in the almost purely transverse geometry at $\mathbf{Q} = (1.5\ 1.5\ 2.5)$. Note that the gap mode itself did not appear in any of these spectra.

B. Overbending of the LA branch

Paper I contains also set of data suggesting that the gap mode is forming a flat branch along the Λ (Γ-L) reciprocal direction, and also that the adjacent Λ_1 phonon dispersion of the LA mode at 575 K is anomalously bent down at around $\mathbf{q} = (0.4\ 0.4\ 0.4)$, as if repelled by the gap mode branch. Other authors [31,32] measured this LA branch and did not see any such bending. Nevertheless, these early measurements were all taken at low temperatures. In principle, one can speculate that the phonon dispersion bending might occur around 600 K independently of the gap mode formation. Therefore we have also carefully investigated the Λ_1 LA phonon dispersion curves of both pure NaI and NaI:Tl single crystal specimens at 600 K. Comparison of our dispersion and that of paper I is shown in Fig. 5(a). No LA branch bending is present in our measurements. The monotonous nature of the LA mode dispersion near the BZ boundary is actually apparent directly from the recorded phonon spectra shown in Fig. 5(b).

C. Fragmented TO branch

Let us note that our data shown in Figs. 3–5 are taken at a slightly higher temperature than in paper I. Originally, we expected that this should not make any difference for a process with critical formation energy, but paper II reported that the intensity of the L-point gap mode feature shown here in Fig. 3 has apparently quite strong temperature dependence: it appears to be strong in the 575 and 614 K measurements but disappears completely again at 636 K. At this temperature of 636 K, in parallel, another gap-mode-like feature was noticed in paper II in several BZs near the X reciprocal points of the BZ. In addition, the appearance of this X-point gap feature (ILM*) was associated with a "fragmentation" of the X-point TO zone boundary mode into several sharp peaks (see the open point data in Fig. 6 reproduced from paper II).

For this reason, we have also carried out new measurements at several X points at the very same temperature of 636 K (see the full symbols in Fig. 6). The comparison of the two sets of spectra is much less straightforward than in the case of Fig. 3 because the spectra of paper II are in fact obtained by integration over a large portion of the reciprocal space in all three reciprocal directions around the X point. For example, in the case of the data of Fig. 6(a), the integration involved $\pm 0.2\sqrt{2}$ r.l.u. along the [110] direction, ± 0.4 r.l.u. along the [001] direction, and $\pm 0.25\sqrt{2}$ r.l.u. along the [1$\bar{1}$0] direction. Such a large integration volume obviously influences the line shape, the intensity, and the position of the observed spectral bands [33]. In addition, the TO spectral band recorded in these Brillouin zones is in fact composed of two modes of X'_4 and X'_5 symmetry, and, on the top of that, each of these modes can couple to its lower frequency partner of the same symmetry. Nevertheless, in this case, we actually do see in our sample a small intensity peak or a shoulder at the same frequency (perhaps broadened by a coarser resolution of our setup). Therefore our spectra were tentatively fitted to the spectral function of four uncoupled DHOs representing TA, LA, TO and the anticipated ILM* mode.

Nevertheless, can we really consider this correspondence of the independently recorded data shown in Fig. 6 as an evidence for the intrinsic localized mode in NaI? Unfortunately, the intensity of the assumed ILM* peak (Fig. 6) represents only

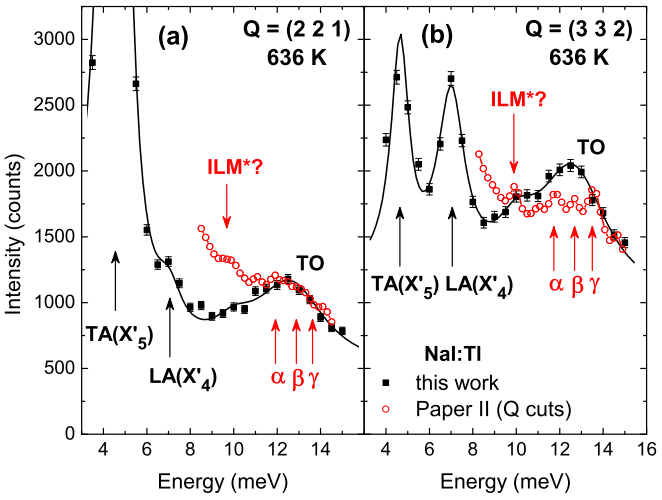

FIG. 6. (Color online) Inelastic neutron scattering spectra of X-point phonon modes collected in the (a) (221) and (b) (332) reciprocal lattice vectors at $T = 636$ K. Both panels show data from two independent experiments using NaI:Tl crystals. The full symbols are TAS data from this work, the open symbol data are reproduced from Figs. 3(c) and 3(d) of paper II and measured on the ARCS time-of-flight spectrometer. Labels α,β,γ, and ILM* stand for the components of the "fragmented TO mode" and the X-point intrinsic localized mode. The latter was included also in the tentative fit to the present data [34].

10% of the full intensity at this point of the spectrum. Although it is larger than the experimental error bars [34], the ILM* peak is visibly less pronounced than the L-point ILM of Fig. 3. In fact, Figs. 2 and 4 of paper II show that comparable intensity fluctuations span over all the q-ω range of the recorded intensity in this experiment, except perhaps for the area of highly populated acoustic branches (below 8 meV) [35]. More importantly, all the spectra displayed in Fig. 6 certainly show a considerable background due to inelastic incoherent scattering. The ratio of coherent to incoherent scattering cross sections of sodium is close to one and it was noticed already in early studies of NaI that the incoherent background might seriously complicate the interpretation of the phonon spectra of NaI in certain scattering geometries [32]. At 600 K, this incoherent scattering certainly involves a number of multiphonon contributions, so it may well contain peaks within the phononic gap. Therefore it is far from clear whether such small intensity variations can warrant justification of a new phenomenon. For the same reason, the α, β, and γ intensity maxima are perhaps simply too small to justify interpretation as a "fragmented TO mode."

IV. CONCLUSION

In summary, no evidence for the thermally activated localized mode in NaI has been found in our experiments. Although the comparison of our data with previous studies confirms a very small peak within the gap, it has so small intensity in comparison to the unfavorably high inelastic incoherent scattering background that one can hardly disentangle whether the peak is part of this background or a genuine first order coherent scattering process by a localized mode within the gap. At the same time, we did not observe the exotic splitting of the X-point zone boundary TO mode. Our experiments suggest that the observation of the L-point ILM seems indeed to be correlated with the anomalous LA mode dispersion, since either both effects are simultaneously present (as in paper I) or both effects are simultaneously absent (as in our experiments, on two distinct samples). However, the presented comparisons strongly suggest that such anomalous observations do not represent intrinsic response of the NaI crystal. Perhaps, they are caused by spurious instrumental signals [36–39] or by extrinsic impurities in the sample [40,41].

We have been aware of the fact that the experimental results of paper I seem to be partly supported by several subsequent theoretical studies [22–24]. Nevertheless, others have shown recently [25] that these theoretical calculations do not justify the interpretation of the observation of papers I and II in terms of thermal formation of ILMs.

To conclude, there are recent experiments suggesting thermally induced intrinsic localized modes in NaI as well as experiments where no indications for these phenomena are found. Based on these accumulated experimental counterexamples, we now have to admit that the experimental evidence for the thermally induced intrinsic localized mode in NaI is, unfortunately, not justified.

ACKNOWLEDGMENTS

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[34] The error bars of the paper II spectra in our Fig. 6 [not shown here, see Figs. 3(c) and 3(d) therein] are slightly larger than those of the present experiment.
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