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Investigations of the NaCl-to-CsCl phase transition in RbI by elastic diffuse and inelastic neutron scattering

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Two groups of measurements were performed: In the first group elastic diffuse neutron scattering measurements were done in two pressure cycles, up to 4.2 and 4.6 kbar, respectively. Above 4 kbar Debye-Scherrer intensities indicate CsCl phase inclusions in the NaCl phase matrix. In the first cycle a very pronounced orientation relationship, together with a more broad one, is observed; in the second cycle the sharp relationship becomes broadened. Although already 75% of the NaCl phase matrix have been transformed the original single-crystal orientation is recovered upon pressure release ("memory effect"). An elastic diffuse intensity discovered in a previous measurement and ascribed to an "intermediate structure" has been confirmed. In the second group of measurements phonons of the TA(00ζ) branch show anomalies in frequency and intensity between 3 and 4 kbar for the smaller q values. These anomalies indicate that changes in the imperfection structure start already at 3 kbar, i.e., below thermodynamic equilibrium. Based on these findings a sequence of steps for the NaCl-to-CsCl phase transition is put forward.

I. INTRODUCTION

RbI, like many other alkali halides transforms under application of hydrostatic pressure from the NaCl to the CsCl structure.[1] The transformation is of first order, with a large volume jump of about 14%.[2]

Second order, or continuous solid-to-solid phase transitions have been in recent years the subject of numerous theoretical and experimental investigations. In contrast, little is known about the mechanism of first order or discontinuous, solid-to-solid transitions despite their more frequent occurrence in nature. The transition in RbI provides an opportunity to investigate a first-order solid-to-solid phase transition in alkali halides, a simple and well-studied class of solids.

In a first-order solid-to-solid phase transition there are regions in the phase diagram where either one or the other of two phases—or both simultaneously—can exist, depending on the history of the sample. In RbI the thermodynamic equilibrium pressure (the conventional "phase boundary") between the low-pressure NaCl and the high-pressure CsCl phase is 3.56 ± 0.02 kbar.[2] The NaCl phase may however be retained to about 4.9 kbar[3] where the transition occurs explosively, with an audible "click". The region from 3.56 to 4.9 kbar is the metastable pressure range of the NaCl phase.

Generally it is agreed that deviations from the perfect phase (either surface or lattice imperfections) play an important role in first-order solid-to-solid phase transitions. Some previous investigations on this subject have shown up changes of the imperfection structure in the metastable pressure region of RbI. Measurements of the mosaic structure over the whole metastable range[3] showed narrowing of the mosaic distribution and a decrease of the integrated intensity. Upon release of pressure a mosaic distribution much broader than the original one has been obtained. This behavior has been ascribed, as discussed in Ref. 3, to the presence of partly coherent nuclei of the CsCl phase in the NaCl matrix.

In a measurement of elastic diffuse scattering performed in the lower part of the metastable region[4] a relatively well-defined scattering intensity around the (0.08, 0.08, 0.55) reciprocal-lattice point of the NaCl phase matrix has been found and has been attributed to an "intermediate structure" with a period larger than the basic lattice.

The role of collective modes in the mechanism of first-order transitions is a subject of some controversy and information on it is of considerable interest. Intuitively one would expect that a softer lattice favors the phase change. RbI (and many other alkali halides undergoing the NaCl-to-CsCl transition) does have some phonon modes with frequencies becoming lower with increasing pressure (negative mode Grüneisen parameters) whereas other modes show the usual pressure behavior of increasing frequency with pressure (positive Grüneisen parameters).[5]

However the frequency decrease at pressure where the transition takes place is in the order of 10–15%[5] and therefore the "soft-mode" mechanism of the second-order phase transitions certainly does not apply to phase transitions like that of RbI. In a previous investigation[6] the frequencies of some phonons in RbI were observed up to about 3.6 kbar. The phonon frequencies proved to be a linear function of pressure up to 3 kbar but the results indicated a possible deviation from linearity when approaching 3.6 kbar. As a cause of this deviation changes of the imperfection structure were conjectured.

In Secs. II and III we report on two groups of measurements undertaken to substantiate further the hypothesis of the intermediate structure, the existence of CsCl phase inclusions in the NaCl phase matrix and the anomalous phonon behavior. Section IV brings an overall picture of the different stages of the transformation that arises from the results of the measurements.

II. DIFFUSE ELASTIC NEUTRON SCATTERING IN THE PRESSURE REGION 4 TO 4.6 KBAR

A. Experimental

The measurements were done on the spectrometer *D*-10, a conventional crystal spectrometer with high resolution, at the High Flux reactor of the Institute Laue-Langevin. The spectrometer was operated partly in its elastic triple-axis mode and partly in the two-axis mode. The wavelength employed was 1.4 Å.

The sample was a cylindrical single crystal (1×1 cm) with the $[1\bar{1}0]$ axis perpendicular to the scattering plane. The crystal was mounted in a high-pressure aluminum cell, described elsewhere.[7] A perfluorated cyclic ether was used as a pressure transmitting liquid. The pressure cycles applied in this experiment are depicted in Fig. 1.

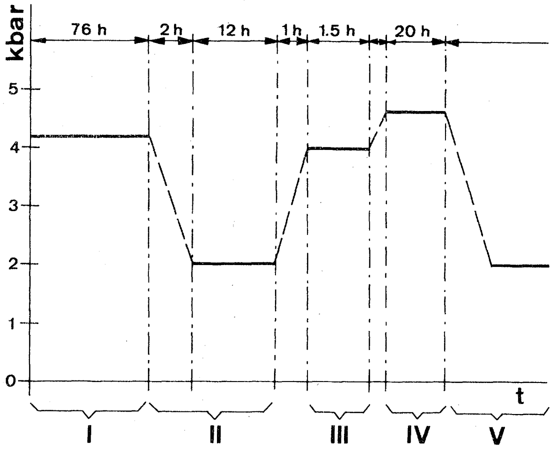

FIG. 1. Pressure vs time relationship in the experiment.

B. Results

1. Region I (4.2 kbar)

The elastic diffuse scattering around the (0.08, 0.08, 0.55) position has been detected though with a considerably lower intensity than in the previous work.[4] At the second-order position, (0.16, 0.16, 1.1), the measurements were not conclusive, i.e., within the errors no enhancement of the diffuse intensity has been found.

Enhancement of the elastic scattering has been found on a circle in the $(1\bar{1}0)$ reciprocal-lattice plane of the NaCl matrix, corresponding to Debye-Scherrer intensity of the (110) reflection of the CsCl structure. The intensity on this circle is not uniform, a strong and narrow peak has been found at (0, 0, 2.35) and a broad distribution has been found in the [111] direction. {The peak intensity in the [111] direction is lower by a factor 4 than at (0, 0, 2.35) (Fig. 2).} This modulation of the (110) CsCl Debye-Scherrer intensity indicated a preferred orientation of the CsCl nuclei in the NaCl matrix, but only in the [001] NaCl direction is the orientation strong. A measurement at right angles to the [001] NaCl direction showed the existence of (002) CsCl intensity in the [110] NaCl direction, comparable to the intensity of the (0, 0, 2.35) pole. Therefore, a preferred orientation exists between the NaCl matrix and the CsCl nuclei {[001](NaCl) $\parallel$ [110](CsCl) and [110](NaCl) $\parallel$ [001](CsCl)}.

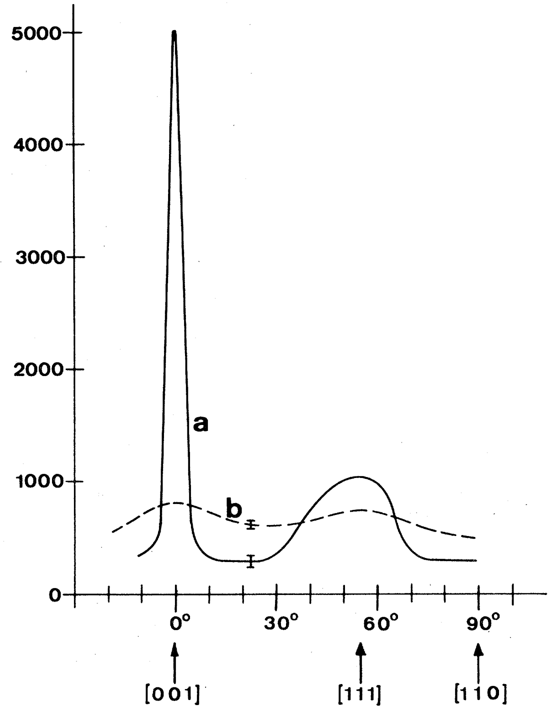

FIG. 2. Intensity distribution along the (110) CsCl Debye-Scherrer circle vs angle; curve *a* at 4.2 kbar during the first pressure cycle, curve *b* at 4.6 kbar during the second pressure cycle.

2. *Region II (4.2–2 kbar)*

The intensities of two points of the (110) CsCl Debye-Scherrer circle, i.e., (0, 0, 2.35) ∥ (002)(NaCl) and (1.4, 1.4, 1.3) in the [111] direction, were monitored during the pressure release to 2 kbar. Generally the CsCl phase intensities decrease strongly from 3 to 2 kbar; from 4.2 to 3 kbar the intensity of the (0, 0, 2.35) point shows a small decrease, whereas the intensity for the (1.4, 1.4, 1.3) point shows even a small increase from 4.2 to 3.7 kbar (Fig. 3).

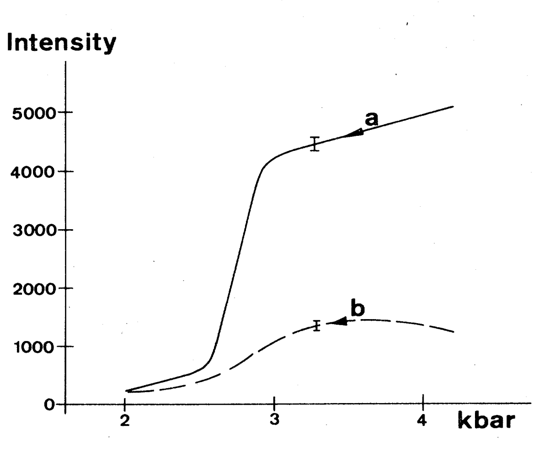

FIG. 3. Intensity of the (0, 0, 2.35) pole *a*, and of the (1.4, 1.4, 1.3) pole *b* of the (110) CsCl reflection, when the pressure is released (first pressure cycle).

At 2 kbar the CsCl intensities have disappeared, and some polycrystalline NaCl phase has been built up, as Debye-Scherrer intensity from the (002) NaCl reflection has indicated.

The elastic diffuse intensity around the (0.08, 0.08, 0.55) point has completely disappeared at 2 kbar.

3. *Region III (4 kbar)*

The polycrystalline NaCl material produced in region II was still present in the NaCl matrix as monitored by the measurement of (002) NaCl Debye-Scherrer intensity on the (1.4, 1.4, 0) point.

The CsCl intensities reappeared with some time lag, e.g., two subsequent measurements within a time interval of about 20 minutes showed an intensity gain of about 20%.

The (110) CsCl Debye-Scherrer intensity appears earlier in the [111] direction and stronger than in the [001] NaCl direction. The intensity ratio between the (0, 0, 2.35) and (1.4, 1.4, 1.3) is nearly unity. (In region I this ratio was nearly 4.)

4. *Region IV (4.6 kbar)*

The application of a still higher pressure induced an immediate CsCl intensity increase of a few percent. Two hours after the pressure had been applied an intensity increase of nearly 25% of the CsCl reflection has appeared. At 4.6 kbar the intensity at the (0, 0, 2.35) point increased stronger than for the (1.4, 1.4, 1.3) point, so that the final intensity ratio is near 1.1.

Curve *b* in Fig. 2 shows the resulting intensity distribution on the (110) CsCl Debye-Scherrer circle. The distribution is more uniform than in region I, and only a small intensity modulation indicates the strong poles that were seen in region I; moreover, the intensity is lower.

Three hours after the pressure has been applied the intensities of the CsCl structure remained unchanged, whereas the NaCl (002) powder intensity disappeared only 12 hours later.

A measurement of the diffuse elastic scattering around the (0.08, 0.08, 0.55) point, where in region I intensity has been found, showed a considerably weaker effect.

The NaCl matrix Bragg reflections (002) and (220) declined in intensity to nearly 25% of the initial value.

5. *Region V (4.6–2 kbar)*

When pressure was released to 3 kbar the CsCl intensities showed a small intensity decrease (Fig. 4). At 2 kbar the CsCl intensities have disappeared and

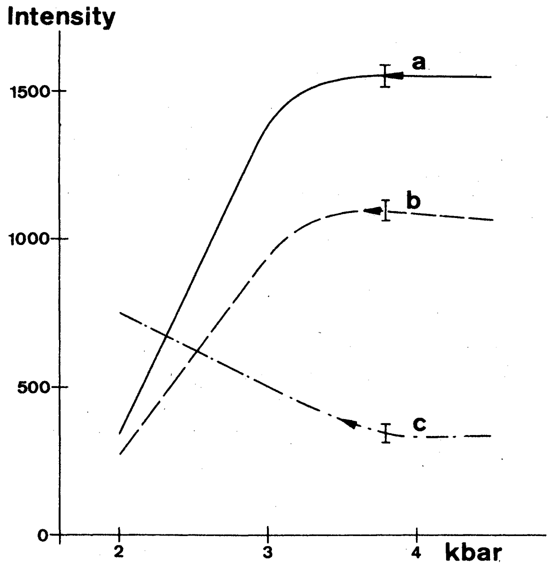

FIG. 4. Intensity of the (0, 0, 2.35) pole *a*, of the (1.4, 1.4, 1.3) pole *b* of the (110) CsCl reflection, and of the (002) NaCl Debye-Scherrer circle at (1.4, 1.4, 0) *c*, when the pressure is released (second pressure cycle).

some NaCl powder has been built up [monitored by some points on the (002) NaCl Debye-Scherrer circle].

An investigation of the (002) and (220) NaCl matrix Bragg reflections at 2 kbar revealed an intensity recovery of nearly 100% (Fig. 5).

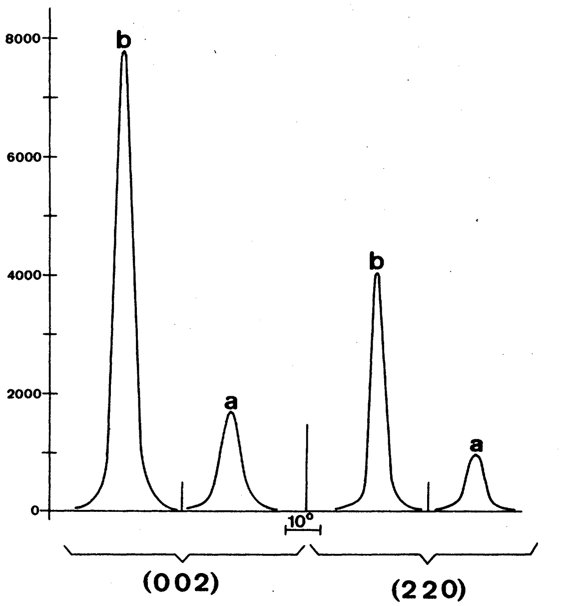

FIG. 5. Rocking curves of the (002) and (220) NaCl Bragg reflection; *a* at 4.6 kbar, *b* after release of the pressure to 2 kbar.

C. Discussion

We have found CsCl intensities in a pressure region where the NaCl structure is still present. The Bragg peaks of the NaCl matrix have lost intensity, but remained in the same order of magnitude and their widths were the same as without pressure; so that strong distortions of the NaCl lattice have not been observed. The shape of the CsCl intensities indicate that the CsCl inclusions are fairly perfect and also relatively large. This is evidenced by the sharpness of the CsCl phase distributions in the radial and also the tangential directions, e.g., at the (0, 0, 2.35) point. The volume change of the transition can be calculated to be 14.7% which agrees well with the value known from the literature for free phases of RbI.[2]

No measurements of orientation relationships in the pressure-induced NaCl-to-CsCl transformations in alkali halides have been reported in the literature. Nor is there an agreed opinion whether there is one discrete orientation relationship, several of them, or a more or less continuous distribution. The present investigation shows that there are peaks in the distribution of the CsCl phase, at (0, 0, 2.35) and (2.35, 2.35, 0). If it is assumed that the same inclusions constitute the two peaks, this would imply the simple relation.

$$[110](\mathrm{NaCl}) \parallel [001](\mathrm{CsCl}) \,,$$

$$[001](\mathrm{NaCl}) \parallel [110](\mathrm{CsCl}) \,.$$

On the other hand, there is a broad distribution of (110) planes around the [111] NaCl direction. It is also that the sharply defined orientation relationship deteriorates after a single pressure cycle (i.e.), the intensity distribution attained in the second cycle is much more uniform.

The sharpness of the above orientation relationship may indicate the existence of a "transformation channel" from one phase to the other. It seems that in the second pressure cycle this well-defined "transformation channel" was closed, so that the transformation, which occurred at higher pressure in the second cycle, had to follow other ways. To this deterioration of easier distinct transition possibilities corresponds the weakly modulated uniform distribution in the second cycle.

In the second cycle the measurement of the NaCl Bragg reflections showed a remarkable intensity decrease—down to 25% which has nearly completely been recovered upon return to 2 kbar (in the first pressure cycle the Bragg intensity changes were smaller than 5%). This intensity regain after the pressure has been released, which means a return to the original single crystal, can not be expected from purely crystallographic considerations. Incoherent CsCl inclusions have a multiplicity of orientations during the back transformation. It can be concluded that the inclusions are at least partially coherent with the matrix and that mechanisms similar to those considered in the "memory effect" in metallic alloys are at work here. A small part of the inclusions, however, looses the coherent connection and appears as polycrystalline inclusions after return to low pressure.

The well-defined elastic diffuse scattering intensity around (0.08, 0.08, 0.55) which had been found in the previous investigation[4] has again been found, however, with a considerably lower intensity, which further declined in the second cycle. In the previous paper, we have ascribed these intensity effects to an "intermediate structure", with a period larger than the basic lattice, possibly a sandwich of alternating variants.

In the present investigation the lower intensity of the diffuse elastic scattering effect around (0.08, 0.08, 0.55) is connected with the finding of well-developed Debye-Scherrer CsCl intensity. This lowered intensity may indicate less of the "intermediate structure", when the CsCl structure begins to appear. It should be noted that in the first pressure cycle of this investigation, where a definite orientation relationship appears, the diffuse scattering around (0.08, 0.08, 0.55) was more pronounced than in the second cycle, where the narrow orientation relationship has disappeared and the diffuse intensity is considerably lower.

III. PHONON FREQUENCY SHIFTS OF THE TA [00ζ] BRANCH FOR PRESSURES FROM 3 TO 4 KBAR

A. Experimental

The measurements were performed on a conventional triple-axis spectrometer on the cold source at the *EI*3-reactor at Saclay. Pyrolithic graphite was used as a monochromator and analyzer (with mosaic widths 0.014 and 0.01 radians, respectively). The collimations in radians, beginning with the in-pile collimator, were 0.09, 0.01, 0.03, and 0.015.

The measurements were made with fixed monochromator wavelength 3 Å. As sample a cylindrical single crystal of RbI (diameter 2 cm and height 5 cm) was mounted in the aluminum high-pressure cell.[7]

Phonons of the transverse-acoustic branch TA [00ζ] were measured at different pressures up to 4.1 kbar. The phonon frequency shifts were measured several times up to 3 kbar, where the whole system behaves linearly.

The peak position and shifts of the phonons were determined by a simultaneous Gaussian fit. The data evaluation method was similar to the method described in Ref. 5. The measured widths of the phonon groups were within a 10% margin equal to calculated values.

B. Results

Figures 6 and 7 show the relative phonon frequency shifts versus pressure for transverse phonons in the [00ζ] direction, with ζ values from 0.3 to 1.

The phonon frequency shifts behave linearly in the whole pressure range up to 3 kbar.

However, the phonon frequency shifts show a significant deviation from linearity towards higher frequencies in the pressure range from 3 to 4 kbar. At the end of this interval, at 4 kbar, it seems that the phonons reapproach the linear curve.

The amplitude of the deviation from linearity seems to increase with decreasing *q* values so that smaller *q* phonons show the effect more strongly. No changes of the linewidths were observed.

Figure 8 shows the intensity of the phonons versus pressure. In the pressure region where the deviation from linearity occurs for phonons with $\zeta \leq 0.6$, the intensity shows a small *increase* (the slow linear increase of intensity can readily be explained by the change of the phonon population factor with diminishing frequency and is thus a "normal" effect).

Finally, we have observed a strictly linear behavior of the lattice constant—as derived from the positions of the Bragg peaks—over the whole pressure region considered.

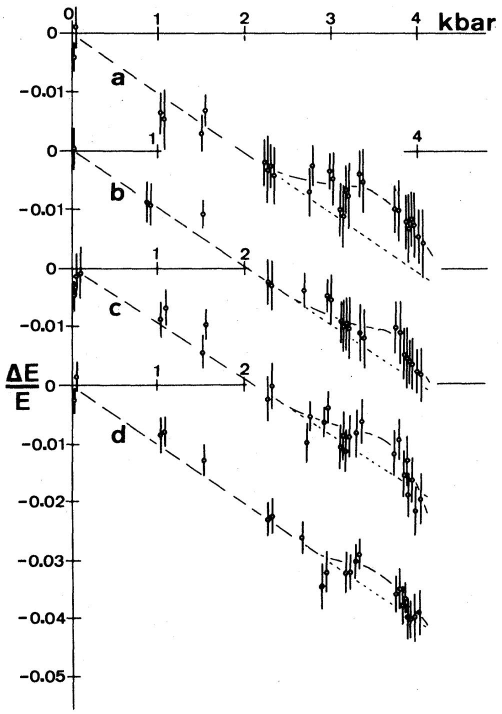

FIG. 6. Relative phonon frequency shifts vs pressure for transverse-acoustic phonons in the [00ζ] direction, for phonons with $\zeta \leq 0.6$: *a* $\zeta = 0.3$, *b* $\zeta = 0.4$, *c* $\zeta = 0.5$, *d* $\zeta = 0.6$.

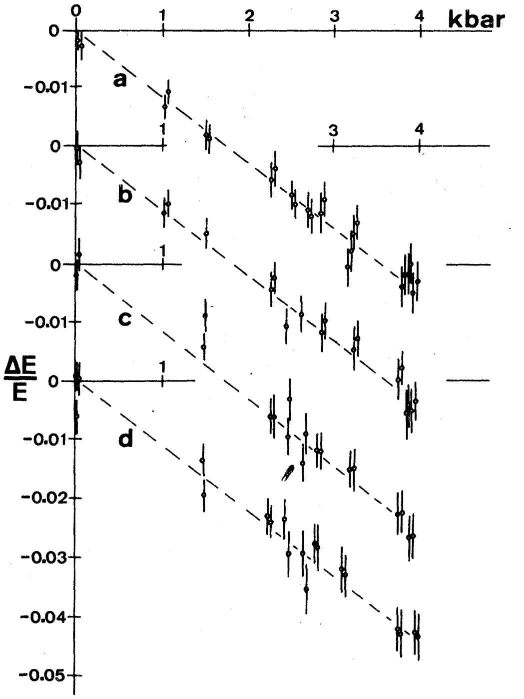

FIG. 7. Relative phonon frequency shifts vs pressure for transverse-acoustic phonons in the [00ζ] direction, for phonons with $\zeta > 0.6$: *a* $\zeta = 0.7$, *b* $\zeta = 0.8$, *c* $\zeta = 0.9$, and *d* $\zeta = 1.0$.

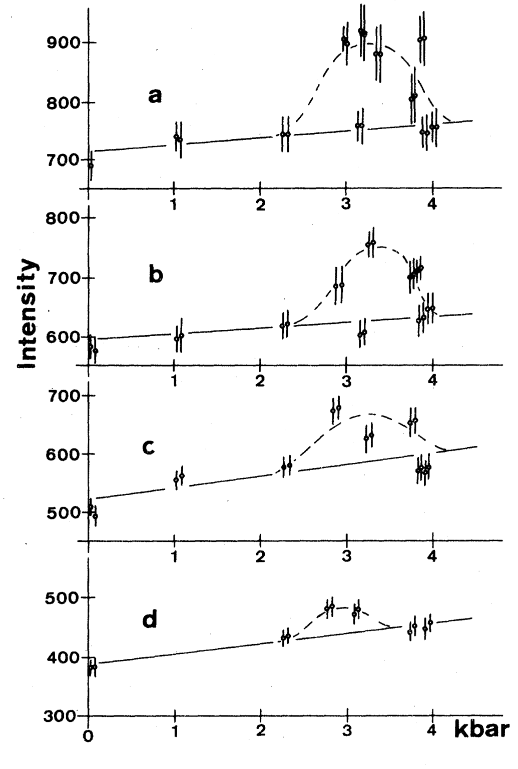

FIG. 8. Intensity changes of some phonons vs pressure: *a* $\zeta = 0.4$, *b* $\zeta = 0.6$, *c* $\zeta = 0.8$, and *d* $\zeta = 1.0$.

C. Discussion

The results of this experiment show a significant deviation from the linear behavior of phonon frequency shifts for all phonons with smaller q values in the [00ζ] direction. This deviation seems to be localized in a pressure interval from 3 to 4 kbar (i.e., to both sides of the thermodynamic equilibrium pressure of 3.56 kbar). At higher pressures the measured phonon shifts again approach the linear behavior.

Classically phonons have been conceived as collective excitations in an ideal lattice; in more recent years the idea of phonons in perturbed crystal lattices became familiar.[8]

Our hypothesis for the present experiment is that changes of the lattice imperfection structure, also observed by the diffuse scattering experiment of Sec. II, cause the anomalies of phonon frequency shifts and phonon intensities in the low-q TA [00ζ] branch. The results show that this atomic regrouping begins already at 3 kbar, i.e., even below thermodynamic equilibrium, and seems to develop at a somewhat higher pressure of 3.5–3.6 kbar into the intermediate structure detectable by elastic diffuse scattering. The smaller-q phonon anomalies are thus sensitive to atomic regroupings not yet "seen" by the elastic diffuse scattering.

It should be noted that the frequency shifts of the higher-q phonons behave linearly up to the higher pressures.

IV. SUMMARY: STAGES OF THE NaCl-TO-CsCl PHASE TRANSFORMATION

Based on the results of Secs. II and III, together with the results of other papers[3,4,6] the following overall picture of the different stages of the transformation arises: Somewhat below thermodynamic equilibrium, at 3 kbar, a rearrangement of imperfections starts, showing up first in the phonon anomalies of Sec. III and later also in the elastic diffuse scattering intensity due to the "intermediate structure" (Ref. 4 and Sec. II of the present paper). At about 4 kbar well-defined CsCl phase inclusions appear, first with rather well-defined orientations relative to the matrix. At about 4.6 kbar the orientations have become rather isotropic, and about 75% of the NaCl phase matrix have transformed (however it is not yet clear whether the smoothing out of the orientations is an effect of the higher pressure alone or whether there is an additional history effect due to a partial pressure release in region II). At a still higher pressure of about 4.9 kbar the "click" completes the transformation. Considering the results above an interesting analogy arises with the stages in first-order transitions in metallic alloys, as discussed by H. E. Cook.[9,10] The phase diagram of ordering reactions (of first order) shows different regions (see, e.g., Fig. 3 in Ref. 9 or Fig. 9 in Ref. 10):

(a) The region between the equilibrium phase boundary and the coherent phase boundary. In this region no ordering reaction occurs, but near the coherent phase boundary "quasistatic fluctuations" may occur, corresponding to the "intermediate structure" in our case, appearing below 4 kbar.

(b) The region between the coherent phase boundary and the coherent instability boundary. Ordered domains coherently connected with the matrix are observed in this region. In our case the appearance of CsCl inclusions above 4 kbar, with a definite orientation relationship with the NaCl matrix, indicates the existence of a pressure region where CsCl inclusions are coherently bound to the NaCl matrix (at lattice imperfections).

(c) The region beyond the coherent instability. In this region "continuous ordering" takes place. In our case the "click" indicates a transformation mechanism working homogeneously over the whole volume of the NaCl matrix. The approach to a more isotropic orientation relation in the second pressure cycle at 4.6 kbar may prepare the appearance of this new transformation mechanism.

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[1] P. W. Bridgman, Z. Kristallogra. Kristallgeom. Krystallphys. Kristallchem. 67, 363 (1928).

[2] A. Lacam and J. Peyronneau, Rev. Phys. Appl. 10, 293 (1975).

[3] O. Blaschko, G. Ernst and J. R. Schneider, J. Phys. (Paris) 38, 407 (1977).

[4] O. Blaschko, G. Ernst, G. Quittner, W. Just, and C. Zeyen, Solid State Commun. 26, 323 (1978).

[5] O. Blaschko, G. Ernst, G. Quittner, W. Kress, and R. E. Lechner, Phys. Rev. B 11, 3960 (1975).

[6] O. Blaschko, G. Ernst, G. Quittner, and J. R. D. Copley, Solid State Commun. 21, 1043 (1977).

[7] O. Blaschko and G. Ernst, Rev. Sci. Instrum. 45, 526 (1974).

[8] R. F. Wood and M. Mostoller, Phys. Rev. Lett. 35, 45 (1975); S. J. Chui, Phys. Rev. B 11, 3457 (1975); H. R. Schober, V. K. Tewary, and P. H. Dederichs, Z. Phys. B 21, 255 (1975).

[9] H. E. Cook, Mater. Sci. Eng. 25, 127 (1976).

[10] H. E. Cook, J. Appl. Crystallogr. 8, 132 (1975).