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Phonon anomalies in RbI transforming from the NaCl to the CsCl phase and a model for the nucleation of the CsCl phase

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A search for phonon frequency anomalies in RbI during the early stages of the NaCl-to-CsCl phase transition has been undertaken for the TA ($\zeta\zeta 0$) branch. The phonon frequencies behave linearly with pressure, but the data suggest possible deviations from linearity at small q values similar to those found for the TA (00ζ) in a previous work. In an aging experiment at constant pressure, at 3.6 kbars an astonishing time dependence of the intensity of all phonons investigated has been observed: In the first 60 h the intensities decreased to a minimum of 50% of the initial values and then in the next 40 h an intensity regain to nearly 100% was found. After a further pressure step at 3.7 kbars a similar time behavior was found, but the whole effect was somewhat attenuated. Moreover, a model for the initial stages of the NaCl-to-CsCl transition in RbI, mainly based on results of previous investigations, is put forward. The main idea of the model is centered around the fact that the NaCl structure can transform to the CsCl structure by creating a stacking fault in the NaCl(001) planes.

I. INTRODUCTION

Like many alkali halides, RbI transforms under hydrostatic pressure from the NaCl to the CsCl structure.[1] The transition is of first order with a large volume jump of about 14%.[2] Since the discovery of this transition by Slater[3] (1926) many attempts have been made to elucidate the mechanism of the NaCl-to-CsCl transformation in alkali halides. As early as 1931 Shoji[4] had described a lattice deformation, based on geometrical arguments, transforming the NaCl to the CsCl structure. Buerger[5] (1951) illustrated this mechanism which consists of a compression along the [111] direction and a dilatation perpendicular to it. More recently Fraser and Kennedy[6] (1974) and Watanabe *et al.*[7] (1977) presented further deformation mechanisms. However, most of these theories are based only on orientational relations observed during the transformation in some alkali halides and did not give a description of the microscopic origin of the proposed geometrical deformation.

For RbI, several stages of the pressure-induced NaCl-to-CsCl phase transition were described in a recent communication.[8] Somewhat below thermodynamic equilibrium, at 3 kbars, a rearrangement of imperfections starts showing up in the appearance of elastic diffuse scattering and also in small phonon frequency anomalies, as found for transverse-acoustic phonons in the [00ζ] direction.

At about 4 kbars, CsCl phase inclusions with rather well defined orientations relative to the NaCl matrix appear, in particular, NaCl(001) $\parallel$ CsCl(110). At about 4.6 kbars 75% of the NaCl phase have transformed to the polycrystalline CsCl phase; however, after pressure release nearly 100% of the original NaCl single crystal reappeared (shape memory). Finally, at 4.9 kbars the transition occurs explosively with an audible "click." Moreover, measurements of the mosaic structure showed above 3 kbars a narrowing of the mosaic distribution and a decrease of integrated intensity.[9] After pressure release the mosaic width was much broader than the original one. These effects were ascribed to the presence of partly coherent nuclei of the high-pressure CsCl phase.[9]

The phonon frequency anomalies investigated in the TA (00ζ) branch occur in the early stages of the transformation and may be due to the initial atomic regroupings leading finally to the CsCl structure. A more extended knowledge of the phonon behavior should contribute to the understanding of the atomic regroupings in transforming RbI. In the present work we report on measurements of phonon frequency and intensity changes for some phonons of the TA ($\zeta\zeta 0$) and LA (00ζ) branch in the early stages of the transformation (Sec. III). In Sec. IV a model for the initial stages of the NaCl-CsCl transition in RbI, based on the experimental results of the present work and of Refs. 8 and 9 is outlined.

II. EXPERIMENTAL

The measurements were carried out on a conventional triple axis spectrometer at the cold source of the E13 reactor at Saclay. Pyrolytic graphite crystals were used as monochromator and analyzer with a mosaic spread of 0.014 and 0.01 rad, respectively. The collimations in radians beginning with the in-pile collimator were 0.09, 0.01, 0.03, and 0.015. As sample a cylindrical single crystal of RbI (diameter 2 cm and length 5 cm) was mounted in an aluminum pressure cell, described elsewhere.[10]

Pressure of 0, 2.9, 3.4, 3.6, and 3.7 kbars was applied; the pressure history is shown in Fig. 1(a). Acoustic phonons in the main symmetry directions were measured several times at each pressure point. The position and the intensity of the phonon peaks were determined by a simultaneous Gaussian fit. The data-evaluation method was similar to that described in Ref. 11.

III. RESULTS

A. Frequency anomalies

The phonon frequency shifts versus pressure for the TA ($\zeta\zeta 0$) branch, as shown in Fig. 2, behave linearly, the data, however, may suggest a deviation towards higher frequencies between 3 and 4 kbars. This effect is similar but less pronounced than that found for the TA (00ζ) branch in Ref. 8. For longitudinal-acoustic phonons in the [00ζ] direction the frequency shifts versus pressure are linear, within the experimental errors (Fig. 3). No changes of the phonon widths were observed within experimental accuracy.

B. Phonon intensity behavior

A general decrease of phonon intensities of about 10% was noticed after the application of 3.4 kbars (period 4). The intensities further decreased on application of 3.6 and 3.7 kbars, respectively, indicating that immediately after pressurizing, parts of the NaCl matrix have already transformed. In an aging treatment at constant pressure of 3.6 kbars, an astonishing time dependence of the phonon intensities was observed [Fig. 1(b)]. (The intensities are corrected with respect to the frequency-dependent terms in the cross section and normalized with the intensities measured in period 3.) In the first 60 h at 3.6 kbars (period 5) the intensities of all phonons investigated decreased to a minimum of 50% of the initial values and then there is an increase up to nearly 100% at the end of the aging period. After a further pressure step at 3.7 kbars (period 6) a similar intensity behavior with time was observed, but now the variation was more attenuated but had nearly the same time period.

Relaxation effects in the scattering chamber with concomitant changes in the pressure might

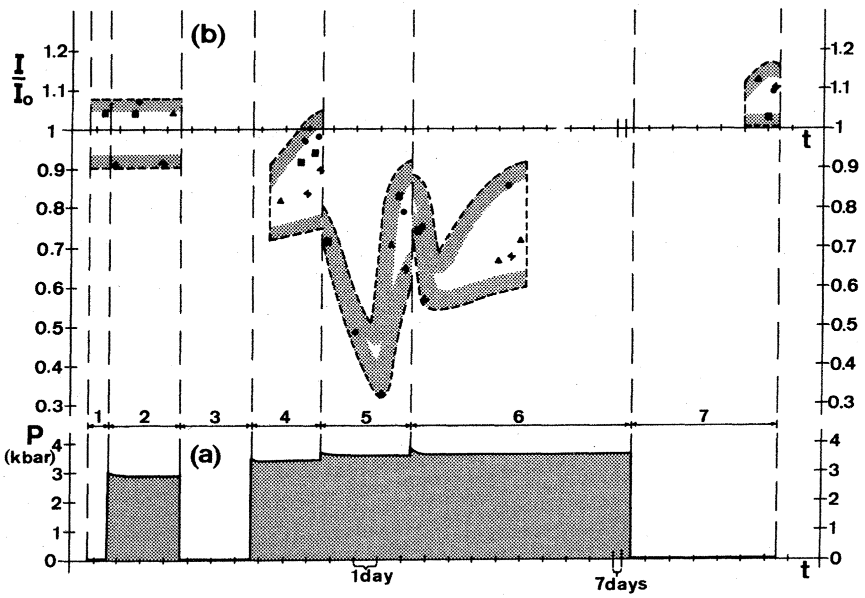

FIG. 1. (a) Applied pressure P versus time during this experiment. (b) Time dependence of the normalized phonon intensities. The intensities I_0 for normalization were measured in period 3. All phonons lie within the shaded regions, the positions of four of them are shown: ■—TA (4, 0.2, 0.2), ●—TA (4, 1, 1), ▲—LA (2.2, 0, 0), ✦—TA (2.1, 1.9, 1.9).

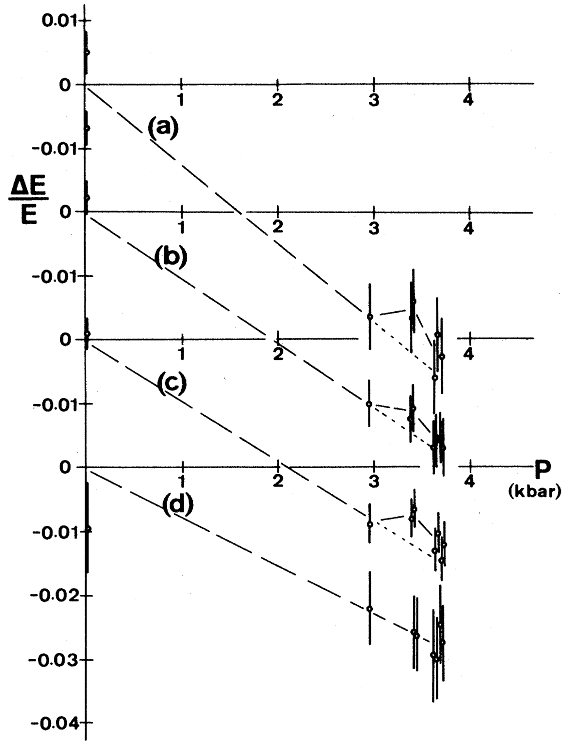

FIG. 2. Relative energy shift versus pressure for the phonons TA $(4, \zeta, \zeta)$. (a) $\zeta = 0.2$, (b) $\zeta = 0.3$, (c) $\zeta = 0.4$, and (d) $\zeta = 1$.

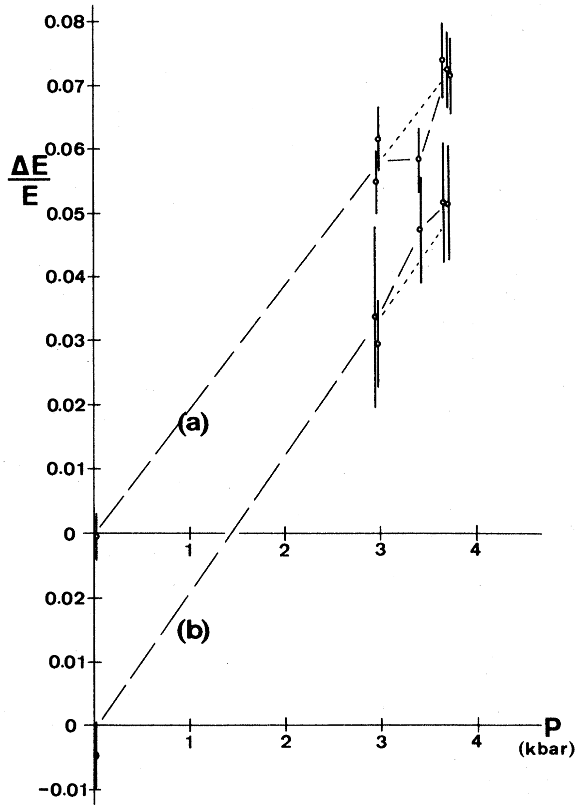

FIG. 3. Relative energy shift versus pressure for the phonons LA $(2+\zeta, 0, 0)$. (a) $\zeta = 0.2$ and (b) $\zeta = 0.3$.

cause some phenomena similar to that observed. The pressure was monitored during the aging experiment and the time dependence can be seen in Fig. 1(a). The relaxation effects show up in the small pressure decrease at the beginning of the periods 2, 4, 5, and 6. However, they cannot explain the aging phenomena because they are one-sided, and their time scale is much smaller than that of the aging phenomena. After release of the pressure (period 7) the phonon intensities showed the same value as at the beginning of the pressure of a "shape memory" effect as in Ref. 8.

The oscillating behavior of the phonon intensities at constant pressure of 3.6 and 3.7 kbars has not been observed up to now and its origin is at present not understood. Possibly, some insight may be given by the model of Sec. IV as discussed in Sec. V. (The question on the behavior of Bragg intensities during these changes arises naturally. For technical reasons the data we have at present are not sufficient to answer the question; a separate investigation on this subject is required and we hope to do it in the future.)

IV. A MODEL

The experimental results of Refs. 8 and 9 combined with those of the present work allow the formulation of a model for the microscopic mechanisms of the NaCl-CsCl phase transition in RbI. The proposed mechanism is based on the following experimental facts.

(a) The transformation is inhomogeneous, i.e., well defined CsCl inclusions appear, whereas the NaCl matrix is still present.[8]

(b) The occurrence of a strong orientation relation between the two phases, at some stages of the transformation, i.e., NaCl(100) ∥ CsCl(110) (Ref. 8).

(c) Phonon frequency anomalies occur for transverse-acoustic phonons mainly for the TA (00ζ) branch (Ref. 8) and, possibly, somewhat attenuated for the TA $(\zeta\zeta0)$ branch.

(d) The mosaic-structure behavior, i.e., the narrowing of the mosaic distribution above 3 kbars and its consequent broading after pressure release.[9]

In the NaCl and in the CsCl structure two crystallographic planes, i.e., NaCl(001) and CsCl(110) are topologically rather similar. Without changing the occupation of the lattice sites the NaCl(001) plane can be transformed to the CsCl(110) plane by simply adjusting the distances between the atoms [Fig. 4(a)]. In the real transformation, therefore, an NaCl(001) plane can transform to a CsCl(110) plane by rearranging the atomic distances in the plane. To convert the ionic arrangement of an NaCl(001) plane to that of a CsCl(110) plane an expansion of 20% and a reduction of 15% must occur, respectively, along two orthogonal [110] directions of the NaCl plane. The presence of the orientation relation NaCl(001) ‖ CsCl(110) in the transformation shows the importance of this correspondence for the transformation mechanism. Furthermore, a comparison of the stacking sequence of two subsequent NaCl(001) and CsCl(110) planes, respectively (Fig. 4), shows that a translation of the second NaCl(001) plane in Fig. 4(a) by a $(\frac{1}{2}, \frac{1}{2}, 0)$ NaCl vector leads to a stacking sequence similar to the CsCl structure. In a hypothetical homogeneous transformation each second NaCl(001) phase should be shifted by a $(\frac{1}{2}, \frac{1}{2}, 0)$ vector lying in the planes.

In the nucleation process of the high-pressure phase a local change of the stacking sequence may be favored by the (001) [110] glide system of the NaCl structure[12] and should more easily occur in regions of high dislocation densities, e.g., at mosaic block boundaries. The mosaic-distribution behavior, indeed, indicates the beginning of the transformation near the mosaic block boundaries of the NaCl matrix.[9] Moreover, the occurrence of local stacking faults of NaCl(001) planes described by a translation $(\frac{1}{2}, \frac{1}{2}, 0)$ vector, which may be created by a shear transformation in the nucleation process should influence the phonon frequencies, especially those of the TA (00ξ) branch, with a polarization in the [110] direction.

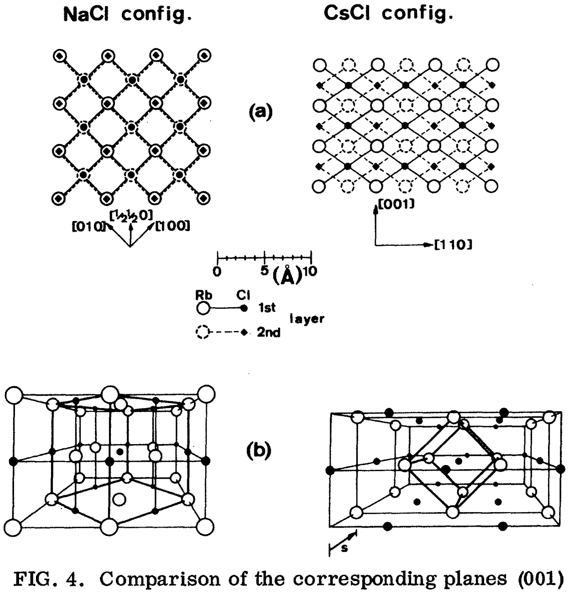

FIG. 4. Comparison of the corresponding planes (001) of the NaCl and (110) of the CsCl configuration with topologically equivalent occupation. (a) Arrangement within and stacking of two adjacent planes in the two configurations. The CsCl type of stacking can be achieved by shifting one plane by a vector of $(\frac{1}{2}, \frac{1}{2}, 0)$ in the NaCl configuration. (b) Three-dimensional plot of the two configurations. The unit cells are drawn with bold lines. The difference in the stacking is indicated by the vector $\vec{S}$.

In view of these arguments the following transformation sequence seems possible: The transformation starts locally, by atomic regrouping in a NaCl(001) plane leading to a stacking sequence of NaCl(001) planes similar to that of the CsCl(110) planes in the CsCl phase. During the formation of the stacking fault the NaCl(001) planes may remain unchanged in themselves. Once the stacking fault is created, then the accommodation to the CsCl arrangements occurs, i.e., the NaCl(001) planes reduce their distances by 15% to attain the distances between the CsCl(110) planes, combined simultaneously with an accommodation to the CsCl ionic arrangement in the planes itself.

A mechanism for the start of the shear transformation in the nucleation process may be deduced from mosaic-distribution measurements on RbI (and some other substances). These measurements show that under hydrostatic pressure the angular distribution of mosaic blocks in a single crystal becomes narrower, e.g., the crystallites turn closer to a common direction. This can be explained by assuming that the arrangement with somewhat misaligned mosaic blocks is less compact than an aligned one: Under rising hydrostatic pressure a $P\delta V$ term drives the misaligned blocks towards the mean direction. Thereby the mosaic blocks are rotated against their neighbors and shear necessary for the CsCl nucleation arises in their boundaries.

V. DISCUSSION

The qualitative mechanism put forward describes an inhomogeneous transformation, which starts in regions of high dislocation densities. It consists in a local shear of NaCl(001) planes in the [110] direction and is based on a correspondence between the NaCl(001) and CsCl(110) planes. The orientation relation observed and the occurrence of phonon "anomalies" mainly for transverse-acoustic branches for phonons with higher wavelengths support this picture. Transverse-acoustic phonons with smaller wavelengths are not affected by the beginning of the transformation, i.e., they "see" still important regions of the undisturbed lattice. Moreover the longitudinal-acoustic phonons show a much lower sensitivity to this shear transformation.

The present picture may give also an idea for the origin of the intensity oscillation, described in Sec. III. The phonon-intensity decrease at constant pressure may be due to the formation of the stacking faults, disturbing the coherency of the NaCl matrix; however, after parts of these disturbed regions have collapsed to CsCl nuclei with a volume jump of 14% a relaxation of the rest of the NaCl matrix increases the phonon intensities again.

At present, the shape memory effect in RbI is not understood. However, the proposed mechanism does not exclude its possibility and the correspondence of the NaCl(001) and CsCl(110) planes in the transformation may be one reason for its occurrence.

The proposed transformation mechanism for RbI has some similarity with that of Watanabe *et al.*[7] for the inverse CsCl-to-NaCl transition in CsCl. Their mechanism is also centered around the topological similarity of the NaCl(001) and CsCl(110) planes, but their mechanism is supposed to occur in a plate traversing the crystal and the transformation occurs in a change of zigzag (101) and (011) planes of the CsCl type to the flat (001) plane of the NaCl type. No experimental evidence for such a flattening of zigzag (101) and (011) planes has been found in our work for RbI. In the basic concepts, however, our model is similar to a general mechanism proposed by Olson and Cohen for martensitic nucleation in metals,[13] where the nucleation process takes place, also, in a sequence of steps, starting with the formation of stacking faults on close-packed planes.

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