Investigation of the mosaic structure of RbI-single crystals in the NaCl-phase near the transition point to the high pressure CsCl-phase

O. Blaschko, G. Ernst, J.R. Schneider

To cite this version:
O. Blaschko, G. Ernst, J.R. Schneider. Investigation of the mosaic structure of RbI-single crystals in the NaCl-phase near the transition point to the high pressure CsCl-phase. Journal de Physique, 1977, 38 (4), pp.407-410. <10.1051/jphys:01977003804040700>. <jpa-00208599>

HAL Id: jpa-00208599
https://hal.archives-ouvertes.fr/jpa-00208599
Submitted on 1 Jan 1977

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
INVESTIGATION OF THE MOSAIC STRUCTURE OF RbI-SINGLE CRYSTALS IN THE NaCl-PHASE NEAR THE TRANSITION POINT TO THE HIGH PRESSURE CsCl-PHASE (*) (**)

O. BLASCHKO
1. Physikalisches Institut der Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria and Forschungszentrum Seibersdorf, Physikinstitut, A-2444 Seibersdorf, Austria

G. ERNST
Forschungszentrum Seibersdorf, Physikinstitut, A-2444 Seibersdorf, Austria

J. R. SCHNEIDER (***)
Hahn-Meitner Institut, Glienickerstrasse 100, D-1000 Berlin 39, Germany

(Reçu le 15 novembre 1976, accepté le 21 décembre 1976)

Résumé. — Les changements sous pression de la structure mosaïque de cristaux de RbI, avec un équilibre thermodynamique entre la phase à basse pression du type NaCl et la phase à haute pression du type CsCl à 3,56 kbars, ont été étudiés par diffusion de rayons γ à 412 keV jusqu'à des pressions de 5,1 kbars. On a montré que la transition dans les quatre cristaux étudiés se produit à des pressions entre 4,7 bars et 5,1 kbars, dépendant du traitement thermique préliminaire.

La transition est accompagnée par la disparition des réflexions de Bragg de la phase à basse pression et par un signal acoustique (click). Jusqu'à une pression de 4 kbars on n'a pas pu observer des changements significatifs, mais à quelques centaines de bars en dessous de la pression de transition la structure mosaïque commence à diminuer en largeur (30 %) et en intensité intégrée (30 %). En accord avec une de nos études récentes [2] nous supposons que cette diminution de la largeur de la structure mosaïque — c'est-à-dire l'alignement des blocs mosaïques — et la diminution de l'intensité intégrée due à formation de germes de la nouvelle phase préparent la transition.

Abstract. — Pressure-induced changes of the mosaic structure in RbI crystals, with a thermodynamic equilibrium between the low-pressure NaCl-phase and the high-pressure CsCl-phase at 3.56 kbars, have been investigated by means of 412 keV-γ-rays at pressures up to 5.1 kbars. It has been shown that the actual transition in the four crystals under investigation took place between 4.7 kbars and 5.1 kbars, depending on the previous thermal treatment.

The transition was accompanied by the disappearance of the Bragg-reflection of the low pressure phase and an audible click. No significant changes occurred at pressures up to 4 kbars but a few hundred bars below the transition pressure the mosaic structure started to decline in width (30 %) and in the integrated intensity (30 %). In agreement with our previous work [2] this narrowing of the mosaic width — i.e. the alignment of the mosaic blocks — and the decrease of the integrated intensity due to the formation of germs of the high pressure phase are supposed to prepare the transition.

1. Introduction. — RbI shows a pressure induced phase transition from the low pressure NaCl-phase to the high pressure CsCl-phase. This transition, which has recently been investigated by volumetric methods by Lacam and Peyronneau [1], shows a transformation hysteresis depending on the previous thermal and mechanical treatments of the sample and implying an actual transformation pressure different from the thermodynamic equilibrium point at 3.56 kbars [1].

Investigation of changes in the mosaic structure below and near the actual transition point may give some insights into the mechanisms involved in the transformation. In earlier work [2] we have investigated with 412 keV-γ-rays the mosaic structure changes...
in RbI-crystals under hydrostatic pressures up to 4.2 kbars, for various preliminary thermal treatments. In the pressure region up to 4.2 kbars it was found that the mosaic structure changed considerably in samples thermally treated at temperatures near the melting point of RbI (642 °C); whereas in samples without thermal treatment the mosaic structure remained unchanged.

By modifying the design of the pressure cell used it was possible to extend the available pressure region up to 5.2 kbars, which allowed us to study the mosaic structure up to the actual transition pressure, lying between 4.7-5.1 kbars in our crystals, especially the changes occurring in a rather small neighbourhood of the transition point.

2. Apparatus. — The measurements were carried out on the γ-ray-diffractometer of the Institut Laue-Langevin in Grenoble, using the 412 keV-γ-radiation of radioactive 198Au (Schneider 1974) [3]. The angular divergence in the scattering plane of the incoming beam was 60 seconds and the relative line width was $\frac{\Delta \lambda}{\lambda} = 10^{-6}$. Cylindrical samples of RbI-single-crystals with a diameter of 1 cm were used.

The crystals were mounted in a high pressure cylindrical aluminum cell, as described in [4], but designed to sustain pressures up to 5.2 kbars. Perfluorated cyclic ether (C₈F₁₆O) was used as a pressure-transmitting liquid.

3. Experimental. — Four single crystals of RbI were used for the present investigations:

CRYSTAL A. — No thermal treatment. Crystal A had no significant changes during pressure cycles up to 4.2 kbars. The pressure was then increased from 0 kbar until 5.1 kbars, where a sudden click was heard, followed by a pressure drop of 200-300 bars and the disappearance of the (002) reflection. A rocking curve around the old position of the (002)-reflection showed a flat background; but when the pressure was removed a broad peaked intensity distribution centered around the old Bragg-position appeared, with an intensity of about 50% higher than the background and a width of about 3 degrees.

CRYSTAL B. — Rocking curves were measured up to 3.6 kbars and no significant changes occurred. A pressure increase up to 4.8 kbars was made and the peak intensity was measured with the ratemeter and did not change significantly. At 5.1 kbars, as for crystal A, an audible click was heard, followed by a pressure drop of 200-300 bars and the disappearance of the (002) reflection.

A rocking curve around the old position of the (002)-reflection showed a flat background; but when the pressure was removed a broad peaked intensity distribution centered around the old Bragg-position appeared, with an intensity of about 50% higher than the background and a width of about 3 degrees.

CRYSTAL C. — No significant changes were observed from 0 to 4.2 kbars. But an increase to 4.75 kbars induced a decrease of the width (33%) and of the integrated intensity (47%) of the rocking curve. From 4.75 kbars the pressure then dropped slowly to 4.5 kbars, where the width and the integrated intensity returned to higher values. A further pressure decrease to 4.4 kbars showed a further increase of width and integrated intensity. (The width and the integrated intensity regained 99% and 93% respectively of their original values.) Figure 1 shows the measured pressure dependence of the width and integrated intensity.

The pressure was then brought to 4.8 kbars, where the audible click was again accompanied by the disappearance of the (002)-peak. — At 0 kbar no peaked intensity distribution was observed near the old (002)-reflection position.

![Fig. 1. Relation between integrated intensity (Int), variance ($\sigma$, in seconds of arc), and applied pressure (P, in kbar) for RbI crystal C.](image-url)
CRYSTAL D. — First pressure cycle. — From 0 to 3.6 kbars no significant changes were observed. From 3.6 to 4.4 kbars the width and the integrated intensity decreased by 5% and 16% respectively. After return to 0 kbar the rocking curve was considerably broader (17%) and the integrated intensity was higher (4%) than at 4.4 kbars.

Second pressure cycle. — An increase of the pressure to 4.4 kbars showed again a narrowing of the mosaic distribution (3.5%) and an integrated intensity decrease (9.5%). A return to 0 kbar showed again a considerably increase in the width of the peak (26%). The integrated intensity decreased by 7%.

Third pressure cycle. — A pressure increase to 4.4 kbars showed a narrowing of the mosaic distribution by 8%, whereas the integrated intensity remained unchanged. A further increase to 4.65 kbars induced a 21% decrease of the integrated intensity and the width becomes still smaller (10%).

After 15 minutes at 4.65 kbars the (002) reflection had disappeared and no audible click could be detected.

Figure 2a-g shows the mosaic structure at different pressures. Figure 3 shows the pressure dependence of the width and integrated intensity respectively. At 0 kbar no peaked intensity distribution could be observed near the old (002)-reflection position.

4. Discussion. — For all four crystals the transformation to the high pressure phase was detected in a pressure range from 4.6 to 5.1 kbars. For crystals A, B, C the transformation was indicated by an audible click and the disappearance of the whole reflection. With an increasing temperature during the thermal treatment the click-pressure decreased by 200-300 bars. For crystal D, which had been thermally heated at 620 °C, the transformation pressure was even at 4.65 kbars, but the transformation occurred slowly in about 15 minutes without any audible signal.

After the transformation no significant peaked intensity was found near the old Bragg-position of the low-pressure phase, whereas, when the pressure was released, some intensity (about 100% above the background) was found for crystals A and B, which shows that for these crystals a certain remanence of the old lattice orientation was present.

For all crystals a successive non-linear reduction in width was observed for pressures greater than 3.5 kbars — which is the thermodynamic equilibrium pressure — and becomes very important at pressures very near the click-point above 4.4 kbars.

When lowering the pressure from the high pressure region to 0 kbar a considerably increase in the width is observed. (This breaking up of the mosaic structure has already been reported by us in [2] for crystals treated thermally at about 640 °C after a pressure release from 4.2 kbars.)

Figure 4a, b shows the quantitative changes of the mosaic structure width and integrated intensity under successive pressure cycles.
In figure 2 typical mosaic structure changes are depicted. The comparison between the curves e) and f) for instance shows clearly the effect of narrowing. The curve e) is broader and the peak intensity is lower than in curve f) where due to the alignment of the mosaic blocks the peak intensity has increased and the distribution has become smaller.

So it seems that for our single crystals the transition phenomenon is announced or prepared by a narrowing of the mosaic distribution width and a decline of the integrated intensity — both effects become rather important in the neighbourhood of the transition point.

The narrowing of the mosaic distribution has to be the result of rearrangement of the mosaic blocks and consequently of changes along the small angle grain boundaries in the single crystal. It could be that a transformation which occurs suddenly and quickly, as indicated by the existence of audible clicks, can take place only after these changes at the small angle boundaries have been completed.

This hypothesis is partly supported by the fact that thermal treatment decreases the click pressure, or in other words, that in thermally treated crystals the grain boundaries rearrangement can be achieved with less energy i.e. lower applied hydrostatic pressure and so the click-pressure must decrease.

On the other hand we see a broadening of the mosaic distribution when the pressure is lowered. This broadening is sometimes (as for crystal D) greater than the initial narrowing; so it must be concluded that this broadening is not only a simple reversal of the narrowing, but that other mechanisms induce this breaking up of the mosaic structure.

In our previous paper we have proposed the hypothesis that this breaking up may be caused by germs of the high pressure phase which, when lowering the pressure, retransform to the low pressure phase but do no more fit coherently with the low pressure matrix. In the case of crystal C we have seen a considerable broadening when the pressure dropped from 4.75 to 4.4 kbars and a regain in the integrated intensity. The regain in intensity may be due to a retransformation to the low pressure phase of germs of the high pressure phase when the pressure is released. This retransformation must result in partly coherent domains, so that an increase in the Bragg-intensity is possible, but with enough misfits generating stresses which induce the breaking up of the mosaic structure.

For crystal D no audible click was observed. This may be due to the fact that crystal D has been hold for longer times in the critical pressure region, so that a successive transformation of smaller blocks may become more probable, generating sound waves of lower intensity which could not be detected outside the pressure vessel.

In the previous work [2] some aspects in the mosaic structure changes have already been reported. Samples used in that work were heated at a higher temperature (642 °C, very near the melting point) than in the present investigation and it has been found that the transition and the associated mosaic structure changes occurred at even smaller pressures (~ 4.2 kbars). This fact may also support the hypothesis that the actual transition is prepared by the sudden mosaic structure narrowing below the transition point: i.e. in crystals with lower small angle grain boundary energies due to a thermal treatment at higher temperatures the transition takes place at a lower pressure.

Acknowledgments. — We would like to thank Dr. A Freund for his help during this experiment.

We are indebted to Prof. P. Weinzierl for his continuous support. Drs. O. J. Eder and G. Quittner are acknowledged for valuable discussions.

Finally we want to thank Les Services culturels de l'ambassade de France en Autriche for a research grant, which has allowed us to carry out this work.

References