OPTICAL OBSERVATIONS OF THE f.c.c. → s.c. TRANSFORMATION IN SINGLE CRYSTALS OF RbI AT HIGH PRESSURES

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Abstract—The transformation of rubidium iodide from its low pressure sodium chloride structure to its high pressure cesium chloride structure takes place at a pressure of about 3500 b. This transformation has been studied optically in single crystals, using a high pressure vessel with sapphire windows, a modified Vickers metallographic microscope and time lapse photographic techniques. The transformation behavior of the crystal depends sensitively on the condition of its *surface*. Freshly cleaved crystals or crystals which have been etched in RbI solution transform in two stages. Firstly, the transformation proceeds from a *few* surface sites and spreads over the entire *surface* of the crystal, then the *interior* of the crystal transforms. We hypothesize that the first stage of surface transformation reflects a condition of relative compression of the surface layers of the NaCl structured phase of RbI compared with the interior with the consequence that the surface layers transform at a lower value of applied pressure than does the interior. In cleavage crystals which have been stored under oil for a long time prior to observation, the surface transformation is absent and the pressure at which observable transformation occurs is much higher, in agreement with optical observations by other investigators.

The equilibrium pressure between the two phases has been found to lie in the range 3430–3650 b at room temperature, somewhat lower than the range 3500–3900 b previously established by Bridgman's measurements.

INTRODUCTION

THE alkali halides are known to crystallize in either the f.c.c. NaCl structure or the simple cubic CsCl structure. Polymorphism between the structures occurs in many of the cases. For instance, CsCl transforms at high temperatures to the f.c.c. phase and transformations at high pressures discovered by SLATER,[1] BRIDGMAN[2] and PIERMARINI and WEIR[3] in potassium and rubidium halides have been established by high pressure X-ray methods to be to the simple cubic CsCl structure.[3-9]

The alkali halides constitute one of the simplest and best understood systems of solids i.e. they have a simple structure, their cohesive energy is accounted for in a relatively simple way, and their

behavior is not complicated by the presence of conduction electrons as is the case in even the simplest polymorphic metals, lithium and sodium. It might be expected that any study of their transformation properties will provide information useful to the theory of polymorphic phase transformations. Rubidium iodide was chosen as the object of this study because at room temperature the transformation occurs at an easily accessible pressure of less than 4000 b.

Several accounts in the literature[10,11] describe the effect of the transformation process on transmission of light through the crystal. In JACOB's[10] optical observation of RbCl, the transformation took place at pressures much higher than values established by Bridgman as the equilibrium pressure for the transformation. Our experiments were carried out using single crystals with the goal of making systematic microscopic optical observations on the transforming material, and of obtaining an

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improved value of the pressure at equilibrium between the two phases.

METHOD

The single crystal samples in the high pressure ambient were observed optically by means of single crystal sapphire windows in the pressure vessel shown in Fig. 1, similar to that described by
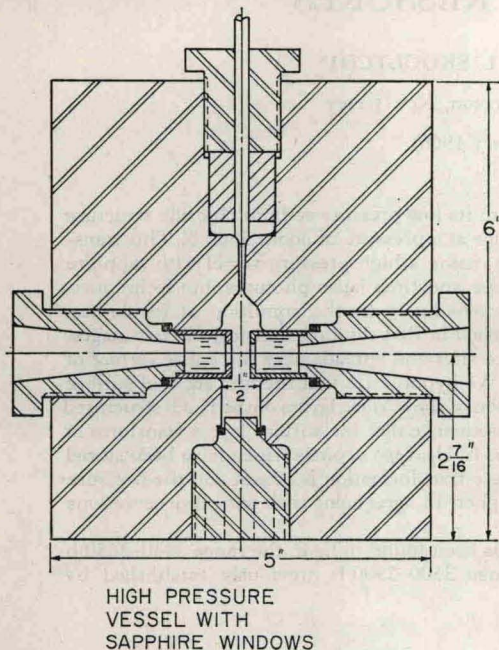

HIGH PRESSURE
VESSEL WITH
SAPPHIRE WINDOWS

FIG. 1. High pressure optical cell with oriented single crystal synthetic sapphire windows. (Crystal "C" axis along cylinder axis.)

FISHMAN and DRICKAMER[12] but using armored O-ring seals[13] on the plugs and connecting with the pressure generator by 0·125 in. o.d. × 0·26 in. i.d. type 316 ss tubing. The vessel has been used over a pressure range to 10 kb. Pressure was measured using a Manganin cell calibrated against the freezing pressure of mercury at 0°C, taken to be 7640 kg/cm² following Bridgman. The vessel was mounted on the stage of a Vickers metallographic microscope. The focal length of the Vickers' objective lens was lengthened using a double concave lens resting on top of the normal objective lens. The final magnification of the sample was 10–40 dia. depending on the eyepiece used. The single crystal sample rested unconstrained on a plexiglass frame in the pressure

vessel. Arrangements were made to take still, time lapse or moving pictures of the transforming crystal. The time lapse photography which permitted observations to be carried out continuously over periods as long as 48 hr was particularly useful at pressures only slightly above the equilibrium pressure, where the transformation proceeded quite slowly.

RESULTS

In crystals with contaminated surfaces (caused for example by long storage under oil), the observations qualitatively resembled those of JACOBS[10] that is, at pressures well above the equilibrium pressure (i.e. at approximately 5000 b, the equilibrium pressure being about 3500 b) the crystals were observed suddenly to become opaque to white light. In some cases an audible click accompanied this phenomenon. As the pressure was then released, the crystal became approximately transparent again at pressures below 1500–2000 b. Crystals examined microscopically at atmospheric pressure, after having been transformed, revealed a definitely polycrystalline character.

Quite different behavior was observed in freshly cleaved or etched single crystals. In these the transformation was observed to start from relatively few centers at the surface of the crystals which grew to cover the entire *surface* of the crystal with a rough appearing layer before opaque regions in the interior began to spread through the volume of the crystal. These effects are shown on Figs. 2 through 6. The photographs were taken with transmitted white light using a microscope magnification of approximately 30 dia. The samples are cleavage blocks. The pressure was maintained at a constant value for this series of photographs. These photographs illustrate first the growth of the surface transformation in Figs. 2–5; then that of the bulk in 5 and 6. The crystal becomes completely opaque during final stages of the transformation, but clears slightly on long exposure to pressures above the equilibrium. Use is made of this latter phenomenon in establishing a value for the equilibrium pressure to be discussed later. By comparison with dimensions of samples and by differential focusing, the thickness of the transformed surface layer is estimated to be 150 μ.

FIG. 2. Photograph of RbI crystal at a very early stage of its transformation to the high pressure phase. The near face of the crystal is in clear focus. Note the steps in the cleaved surface, the transformed "island" of surface on the back face of the crystal at the bottom of the photograph, and the island on the near surface at the upper right.
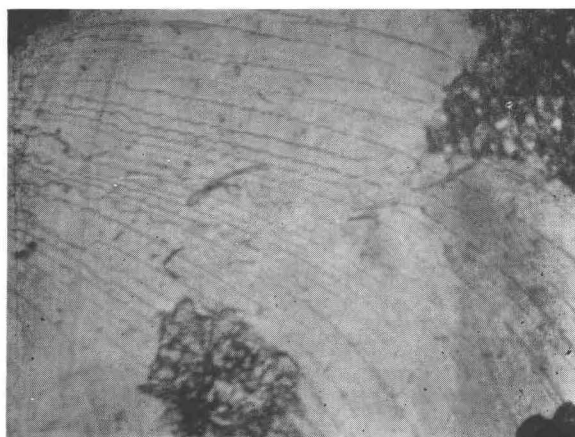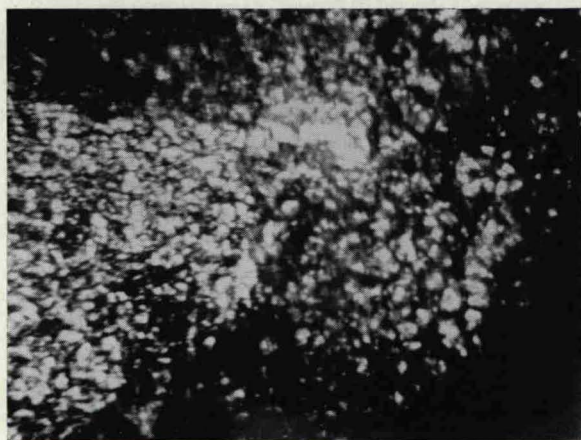

FIG. 3

(See overleaf for figure caption)

FIG. 4

FIG. 5

FIGS. 3–5. Progress of the transformation on the *surface* of the crystal.

FIG. 6 Loss of transparency due to scattering from the transformed material in the *interior* of the crystal. Exposure time for Fig. 6 is considerably larger than for Figs. 3–5.

This phenomenon of two steps in the transformation process relating to surface and bulk of the sample has not previously been observed. A simple explanation would be merely that the free surface has a higher *rate* of transformation than the interior of the crystal, but we like to consider as well the following possibility, namely that the surface layers of the crystal have sufficiently different crystal binding compared to the interior, that they will transform at a lower value of the applied pressure than does the interior. For example, a local spacing of the surface layers 0·1% less than the bulk average reflects a local volume change the same as that produced by 1100 b applied pressure. Thus there would be some pressure range below the "true" equilibrium pressure in which the structure of the surface layers of the crystal was unstable with respect to that of the bulk. The nature of the propagation of the surface instability into the crystal interior would determine, in a complicated way, the observed *thickness* of disturbed material. Further experiments are under way to investigate this proposal.

The optical observations, together with time lapse photography (using a 16 mm Bolex) permitted an accurate evaluation of the pressure of the transformation. In addition, the crystals became transparent once more if maintained in the high pressure phase for a 24 hr period. As the pressure was released the opacity returned during the transformation back to the low pressure phase so that the equilibrium pressure could be established to lie between the pressure of the low-high transformation and that of the high-low. Values obtained are: pressure for low-high transformation 3650 b; pressure for high-low transformation 3430 b. The difference of the pressure values is less than 7% which represents a quite narrow region of indifference for a solid-solid transformation carried out at room temperature. The range of values of the equilibrium pressure previously established by Bridgman is 3500–3900 b.[14]

DISCUSSION

We feel that the study of polymorphic transformations by direct observation of single crystals during the transformation process will reveal new and interesting effects. For example, it is possible to see directly in Figs. 2–6 the explanation of R. B. JACOBS[4] and JAMIESON[5] observations that transformation was more likely to occur in a large crystallite than in a small one. That is, the figures show that the transformed region prefers to extend by growth of a few nuclei rather than by formation of a multitude of nucleation centers as the transformation proceeds; the possibility that the surface layers of a crystal might be stable in a different structure than the interior of the crystal leads to interesting speculations concerning the possibility of propagation of the surface instability into the bulk. That is, the question arises whether in these circumstances the surface layers will transform and if they do, whether the adjacent layers will become unstable etc. whence the entire crystal would assume one structure in ambient conditions in which a surface-less crystal would have a different structure.

The observations were not capable of providing any evidence for the transformation mechanism proposed by BUERGER,[15] namely that the change from NaCl to CsCl structure be accomplished by relative compression along one of the trigonal axes of the crystal. The mechanism of the transformation and its relation to elastic stability of the structure is discussed in a paper in preparation.

REFERENCES

1. SLATER J. C., *Phys. Rev.* **23,** 488 (1924); *Proc. Am. Acad.* **61,** 135 (1926).
2. BRIDGMAN P. W., *Phys. Rev.* **48,** 893 (1935); *Proc. Am. Acad.* **74,** 21 (1940).
3. PIERMARINI G. J. and WEIR C. E., *J. Chem. Phys.* **37,** 1887 (1962).
4. JACOBS R. B., *Phys. Rev.* **54,** 468 (1938).
5. JAMIESON J. C., *J. Geology* **65,** 334 (1957).
6. VERESCHAGIN L. F. and KABALKINA S. L., *Dokl. Akad. Nauk. S.S.SR* **113,** 797 (1957).
7. KASPER J., Private communication quoted in *Modern Very High Pressure Techniques* (editor R. H. Wentorf), p. 73. Butterworths (1962).
8. WEIR C. E. and PIERMARINI G. J., *J. Res. Natn. Bur. Stand.* **68A,** 105 (1964).

9. JAMIESON J. C. and LAWSON A. W., *J. Appl. Phys.* **33**, 776 (1962).
10. JACOBS I. S., *Phys. Rev.* **93**, 993 (1954).
11. MAISCH W. G. and DRICKAMER H. G., *J. Phys. Chem. Solids* **5**, 328 (1958).
12. FISHMAN E. and DRICKAMER H. G., *Analyt. Chem.* **28**, 804 (1956.)

13. DANIELS W. B. and HRUSCHKA A. A., *Rev. Scient. Instrum.* **28**, 1058 (1957).
14. BRIDGMAN P. W., *Z. Kristallogr. Kristallgram.* **67**, 363 (1928).
15. BUERGER M. J., *Phase Transformations in Solids*, (editors Smoluchowski, Mayer and Weyl). Wiley, New York (1951).