

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 BUEGER,⁽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.

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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. SSSR* **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).