

TABLE V. Critical transformation conditions for germanium in the vicinity of 300 K.^a

Author	p_x^{TL} GPa	\bar{p}^{TL} GPa	P^T GPa	η_{TL} %
<i>Shock loading</i>				
McQueen, 1964	12.5±0.7
Graham <i>et al.</i> , 1966	13.6–14.2	11.4–12.2	...	12–13
Pavlovskii, 1968	14.3	12.0
Gust and Royce, 1972	12.5±1.5 ^b	c	...	11.6 ^b
<i>Static loading</i>				
Minomura and Drickamer, 1962	12.0–12.5	...
Jamieson, 1963a	12.5

^a p_x^{TL} is the observed stress associated with the transition; \bar{p}^{TL} is the mean pressure computed from p_x^{TL} and a shear strength correction based on the HEL; P^T is the transition pressure measured in a hydrostatic environment; and η_{TL} is the volume compression to initiate the transition.

^bThe value shown is that observed for [111] orientation samples. Measurements on [110] and [100] showed the same result within the stated errors.

^cNo strength correction was attempted on these data due to the large stated errors in both p_x^{TL} and the HEL values.

In 1964, McQueen reported wave profile measurements obtained by Wackerle on shock-loaded silicon. No transition was identified since the wave profiles showed slowly rising plastic waves with inflections which were not consistent under different loading conditions. Pavlovskii (1968) reported similar measurements and was able to determine a value of 4.0 GPa for the HEL and 11.2 GPa for the suspected phase transition. As indicated previously, however, there are questions about his experiment since his elastic wave velocities differ considerably from those predicted from elastic constants.

Gust and Royce (1971) performed a thorough investigation of Si with explosive loading applied in [111], [110], and [100] directions. In addition to the HEL values, which varied from 9.2 to 5.4 GPa, they observed, in most cases, two successive apparent phase transitions at 10 and 14 GPa. (In the [100] orientation, only the higher-pressure transition was observed.) Volume compression to initiate the second transition, 10.3%, corresponds reasonably well with Jamieson's measurements. Gust and Royce did not observe higher-pressure transitions, even though their work extended to much higher pressure.

Electrical measurements of emf generated during shock compression of Si do not appear to give any new insights into the nature of the transition (Coleburn *et al.*, 1972; Mineev *et al.*, 1971).

Thus neither static nor shock loading investigations give a clear picture of the pressure-induced transitions in silicon. Since the transition or transitions are sensitive to shear, the relation between static and shock observations is confused. Certainly, one or both of the shock transitions may well be to metastable phases.

H. Alkali halides—KBr, NaCl, and KCl

Transition pressure measurements in several alkali halides have been of considerable interest under both static and shock loading. NaCl plays a crucial role as an internal standard for high-pressure x-ray diffraction

studies based on the work of Decker (1971) and shock loading investigations of Fritz *et al.* (1971); hence, several reports of low-pressure phase transitions have been of concern. The thermodynamics of solid solutions of KCl–RbCl, KCl–KBr, KCl–KF, and KCl–NaCl systems at elevated temperatures under static high pressure have been extensively studied by Darnel and McCollum (1970, 1971). Transition pressure measurements under shock loading are of particular interest since the alkali halides exhibit very low HEL values and shear strength corrections should be minor if not negligible. Furthermore, the transitions in crystals such as KCl, KBr, and RbCl are at sufficiently low pressure that the quartz gauge can be used to provide accurate time-resolved wave profile or impact surface measurements. Work in the Soviet Union on alkali halides under shock loading is summarized by Al'tshuler (1965).

Christian (1957) inferred from shock measurements at high pressures that transitions had occurred in KF, KCl, KBr, KI, RbCl, RbBr, and RbI, but his measurements provided neither irrefutable evidence of transition nor values of transition pressures. He also found that NaCl crystals with [111] orientation experienced lower pressures than those with [100] orientation, at approximately 27 GPa, using the same driver system. He suggested that this might be evidence for transition to the CsCl structure, since such a transition should occur more easily in the [111] than in the [100] orientation.

The transition pressure in KBr under shock loading was first measured by Al'tshuler *et al.* (1963). The transition pressure in crystalline KBr observed at 1.85 ± 0.08 GPa (Larson, 1965) with the quartz gauge under shock loading is in excellent agreement with the transition pressure of 1.80 GPa determined for static loading (Darrel and McCollum, 1970). Shock loading measurements on porous polycrystalline samples showed no dependence of p_x^{TL} on sample thickness, but the transition pressure of 2.38 GPa obtained from wave profile measurements with the electromagnetic gauge seems unaccountably high (Dremin *et al.*, 1965). A more recent

measurement by the same group, Adadurov *et al.* (1970), on pressed powder shows the transition at 2.05 GPa.

Static high-pressure x-ray diffraction measurements on NaCl have shown evidence for a phase transformation near 1.7 GPa (Evdokimova and Vereshchagin, 1963a, 1963b; Pistorius, 1964), and a transition at 2.9 GPa under shock loading has also been reported (Larson, 1965; Larson *et al.*, 1966). Johnson (1966) reexamined the static x-ray diffraction experiments, found no transition, and concluded that earlier reports of a transition were due to a lithium impurity. Furthermore, Samara and Chrisman (1971) and Corll and Samara (1966) found no evidence for a phase transition in dielectric and elastic constant measurements to 2.6 GPa. White *et al.* (1968) reexamined the shock transition and traced the reported transition in powdered samples to a problem in the loading system. The presence of secondary yielding was a possible explanation for the small anomaly in single-crystal shock experiments (Royce, 1969). Weidner and Royce (1970), however, in their last examination of the problem, concluded that there is a residual disturbance in pressure-time profiles of shocked single-crystal NaCl between 2 and 3 GPa which resists explanation as either experimental error or secondary yield. It seems unlikely that a phase transition exists in this region, but the case cannot yet be considered closed.

High-pressure phase transitions have been observed in NaCl under shock loading (Hauver, 1966a; Hauver and Melani, 1970; Fritz *et al.*, 1971) and under static loading (Bassett *et al.*, 1968). The flash gap data from which the transition conditions are derived under shock loading (Fig. 16) indicate a difference in behavior between [111] and [100] crystals. The shock transition pressure for the [111] orientation is about 23 GPa at a volume compression of 31.7% and calculated temperature of 1120 K. The static pressure transition is observed at a volume compression of 35.7%, which corresponds to a pressure of 30 GPa according to the isotherm derived by Fritz *et al.* The Hauver and Melani data are in essential agreement with those of Fritz *et al.*, though they contain a suggestion of a higher-pressure transition. The substantial difference between static and shock pressures indicates that two different transitions may be involved, or that error may exist in the static pressure calibration. Brazhnik *et al.* (1969) have examined shock-loaded NaCl samples subjected to a range of conditions and found evidence for material that had transformed to a high-pressure phase and "recrystallized" to the low-pressure phase.

Al'tshuler *et al.* (1963) first reported a phase transition in potassium chloride under shock loading in the vicinity of 2 GPa. Hayes (1974) has reported a very complete study of the 2.0 GPa transition in potassium chloride (NaCl to CsCl structure) under impact loading. Unlike previous shock loading investigations, Hayes utilized direct measurements of the stress and particle velocity at the impact surface provided by quartz gauges in projectile impact experiments. This technique provides a time-resolved record of the stress and particle velocity at the impact face, from which a direct measure of relaxation from initial to final states and an accurate measure of the transition conditions can be ob-

TABLE VI. Critical transformation conditions for KCl in the vicinity of 300 K.^a

Author	p_x^{TL} GPa	\bar{p}^{TL} GPa	P^T GPa	η_{TL} %
<i>Shock loading</i>				
Hayes, 1974	2.12	2.08	...	8.6
Al'tshuler <i>et al.</i> , 1967	1.9	8.0
Dremin <i>et al.</i> , 1965 ^b	1.89	9.8
<i>Static loading</i>				
Darnel and McCollum, 1970	1.96	...
Samara and Chrisman, 1971	2.13	...

^a p_x^{TL} is the observed stress associated with the transition; \bar{p}^{TL} is the mean pressure computed from p_x^{TL} and a shear strength correction based on the HEL; P^T is the transition pressure measured in a hydrostatic environment; and η_{TL} is the observed volume compression to initiate the transition.

^bThe porosity of this pressed polycrystalline sample was 5%.

tained. Hayes observed a very fast transformation, complete in less than 10^{-8} s, to a metastable state in both [111] and [100] crystals, followed by slower transformations at rates that depended upon crystallographic orientation.

Hayes' measurements are compared to other shock and static loading measurements in Table VI. Excellent agreement exists between Hayes' and static measurements. Transition pressure values of Al'tshuler *et al.* (1967) and Dremin *et al.* (1965), obtained from wave profile measurements with the electromagnetic gauge, are somewhat lower than Hayes' values. An extension of Hayes' work for [110] orientations and for initial temperatures of 318 K is reported by Gupta and Duvall

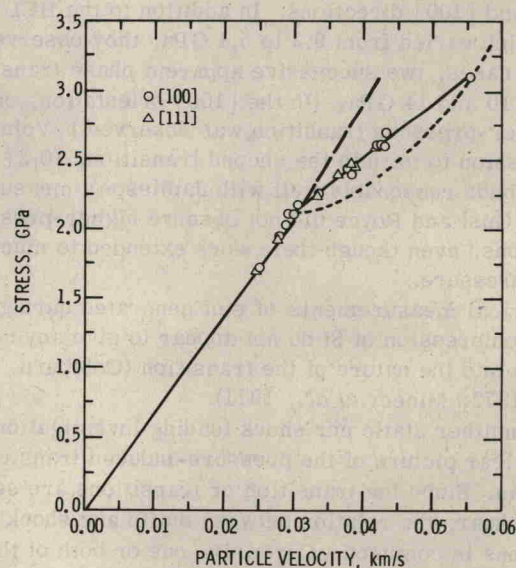


FIG. 27. The stress versus particle velocity relation observed in impact surface measurements on KCl by Hayes (1974) indicates a transition at a stress of 2.12 GPa. In the mixed phase region above the transition the compressibility is much smaller than indicated by the equilibrium thermodynamic calculations (dashed line). The calculated line that fits in the mixed phase region was characterized by a nonequilibrium high-pressure phase with an excess entropy of 3.9×10^2 m²/s² K.