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EXPERIMENTAL CONFIRMATION OF THE PREDICTED HIGH-PRESSURE TRANSFORMATION IN RUBIDIUM CYANIDE

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The previously predicted high-pressure transformation of RbCN from the NaCl structure to the CsCl structure was found at 5.6 ± 0.5 kbar, 24.5°C with a volume change of at least 2.6 cm^3/mole. The transition becomes much sharper at higher temperatures and occurs 6.111 ± 0.039 kbar at 105.5°C. The small entropy of transition, viz., 1.6 J/deg-mole, suggests that the high-pressure phase is disordered.

THE POLYMORPHISM at high pressures of the alkali halides has been thoroughly studied.[1] No polymorphic transitions are known to occur in the lithium halides, while the sodium halides transform from the NaCl structure to the CsCl structure at pressures near ~ 0.3 Mbar.[2,3] The potassium halides undergo this transition at ~ 20 kbar,[4] and the rubidium halides at ~ 5 kbar.[4] It appears that the transition pressure is primarily determined by the nature of the cation, and that the anion has comparatively little effect on the transition pressure.[5]

The cyanide ions in the alkali cyanides at elevated temperatures rotate freely,[6,7] and the crystal structures of the high-temperature phases of the alkali cyanides can therefore be predicted on the basis of the above picture. KCN I with the NaCl structure transforms to KCN III with probably the CsCl structure at 20.6 kbar.[8] NaCN I with the NaCl structure can be expected to transform to a phase with the CsCl structure near ~ 0.3 Mbar, while RbCN I, also with the NaCl structure, has been predicted to transform to a high-pressure phase with the CsCl structure at ~ 5 kbar.[5] The present study was undertaken to test this prediction.

Rubidium cyanide was prepared by ion exchange.[9] The material was heavily contaminated with rubidium acetate but free of rubidium halides. It was subsequently freed of acetate by extraction with ethanol, but still contained several per cent rubidium carbonate. Rb_2CO_3 is, however, known not to have any high-pressure transitions to ~ 40 kbar.[10] Both the raw and purified materials were studied by means of volume-displacement techniques in a piston-cylinder apparatus, using piston rotation to reduce friction. The apparatus and method have been described elsewhere.[11]

A typical compression–decompression curve is shown in Fig. 1. Identical results were obtained for the raw and purified materials. The RbCN I/II transition has a volume change of 2.6 cm^3/mole. This is a lower limit, as is invariably the case for measurements on bulk samples. Piston-rotation yields transition pressures of 5.6 $\pm$ 0.5 kbar at 24.5°C and 6.111 $\pm$ 0.039 kbar at 105.5°C. The transition is considerably faster and sharper above ~ 60°C. The transition line is shown in Fig. 2. There is no clear deviation from linearity in the range studied, and the slope is 165°C/kbar. Using the above
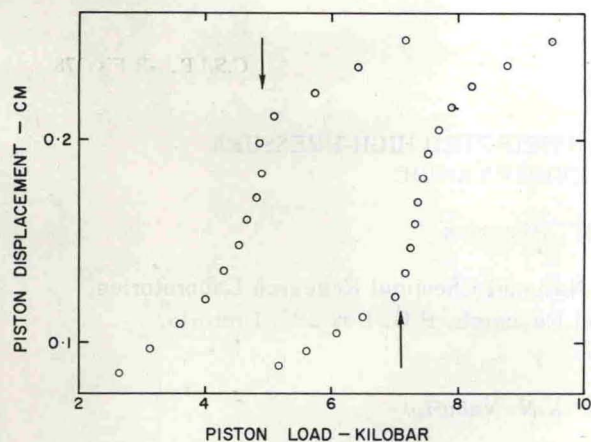
FIG. 1. Curves of piston displacement vs. piston load for RbCN at $\sim 80°C$, showing the new high-pressure transformation. The results are not corrected for the compression of the talc fillers and the deformation of the pressure vessel.

value for the volume change, the entropy of transition is found to be 1.6 J/deg-mole. This low entropy of transition suggests that the difference in entropy between RbCN I and II is due only to a vibrational entropy contribution, with no difference in disorder. RbCN II is therefore the counterpart of KCN III,[5] and can be expected to possess the CsCl structure. At lower temperatures and high pressures a transition to an ordered, or partly ordered, phase similar to KCN IV and CsCN II[12] can be expected.
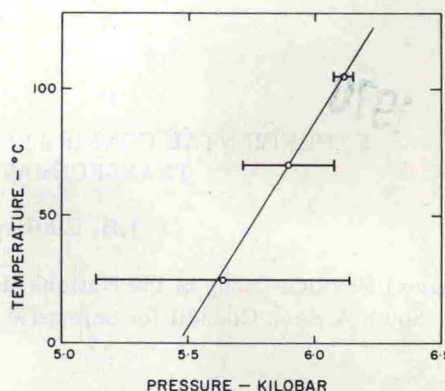

FIG. 2. RbCN I/II transition line.

The above interpretation was supported by differential thermal analysis of the samples at ~ 15 kbar, 20–400°C. No order–disorder transition could be observed in this range. It is, of course, possible that the presence of Rb_2CO_3 supressed or broadened the transition to the extent that it could not be observed. However, KCN containing 6 per cent K_2CO_3 still shows a sharp and clear order–disorder transition.[8]

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Die bereits vorausgesagte Hochdrucktransformation des RbCN von der NaCl-Struktur zur CsCl-Struktur wurde bei 5.6 ± 0.5 Kbar und 24.5°C gefunden mit einer Volumänderung von wenigstens 2.6 cm^3/Mol. Der Übergang wird bei höherer Temperatur wesentlich schärfer und findet statt bei 6.111 ± 0.039 Kbar und 105.5°C. Aufgrund der kleinen Übergangsentropie von 1.6 J/°C—Mol scheint die Hochdruckphase ungeordnet zu sein.