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**Crystallographic data for KCN(III) at 100°C, 30 kbar.** By P. W. RICHTER and CARL W. F. T. PISTORIUS, *Chemical Physics Group of the National Physical and National Chemical Research Laboratories, South African Council for Scientific and Industrial Research, P. O. Box 395, Pretoria, South Africa*

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The high-pressure high-temperature phase KCN(III) is cubic, probably space group  $Pm\bar{3}m$ , with  $a_0 = 3.801 \pm 0.010$  Å at 100°C, ~30 kbar.

The  $P$ - $T$  phase diagram of KCN to 40 kbar has been reported (Bridgman, 1937; Pistorius, Clark & Rapoport, 1968; Suga, Matsuo & Seki, 1965). At 25°C KCN(I), which is cubic, space group  $Fm\bar{3}m$  (Elliott & Hastings, 1961) with the NaCl-type structure, reversibly transforms to dense KCN(IV) at 19.72 kbar (Bridgman, 1937; Kennedy & LaMori, 1962). KCN(IV) is rhombohedral, space group  $R\bar{3}m$  (Pistorius, 1971), with a structure similar to that of low-temperature CsCN(II). Upon heating at elevated pressure, KCN(IV) reversibly transforms to KCN(III), which is only slightly less dense than KCN(IV). It has been suggested (Pistorius *et al.*, 1968) that KCN(III) will be cubic, space group  $Pm\bar{3}m$ , with the CsCl-type structure and the same disorder as in cubic CsCN(I).

The high-pressure X-ray diffraction cell used was similar to that described by Perez-Albuerne, Forsgren & Drickamer (1964). Detailed experimental techniques have been described elsewhere (Pistorius, 1972). Temperatures above ambient were obtained by wrapping a heating coil around the pressure cell and pistons, and measured by a chromel-alumel thermocouple 0.7 cm from the sample position. Thermal gradients were low, and the recorded temperatures are expected to be correct within 10°C. Sample pressures were calculated from the observed unit-cell volumes by using Bridgman's (1948) volume compressibility data. The KCN was BDH Analar grade, containing 0.5% KCl and 1–2%  $K_2CO_3$ .

Pressure was raised until a diffraction pattern showed the presence of only KCN(IV) (~100°C, ~45 kbar), and then lowered in steps past the IV/III transition line. This was done to avoid possible confusion upon compression due to the large volume change at the KCN I/III transition. The powder pattern of KCN(III) at ~100°C is shown in Table 1. The peaks could be indexed on the basis of a cubic cell

Table 1. Powder pattern of KCN(III) at 100°C, ~30 kbar (filtered Mo  $K\alpha$  radiation)

Recorded on a flat-film camera 8.5 cm from the sample position.

$d_{obs}$ (Å)	$d_{calc}$ (Å)	$hkl$	$I$
3.76	3.801	001	$vw$
2.69	2.687	011	$s$
2.20	2.195	111	$m$
1.89	1.900	200	$m$
1.71	1.702	210	$w$
1.203	1.201	310	$w$

with  $a_0 = 3.801 \pm 0.010$  Å. The unit-cell volume obtained assuming  $Z=1$ , allowing for the volume change (~0.49  $cm^3 \cdot mole^{-1}$  at 30 kbar) (Richter & Pistorius, 1971) of the IV/III transition, and making an estimated correction for thermal expansion, is consistent with a pressure of ~30 kbar, *i.e.* just below the KCN III/IV transition pressure at 100°C.

The observed selection rules (no restriction) are, amongst others, consistent with the space group  $Pm\bar{3}m$  of CsCN(I) (Natta & Passerini, 1931), and we suggest that the structures of these phases are the same. The  $CN^-$  ions in CsCN(I) are randomly oriented along the possible eight directions of the four body diagonals, yielding a configurational entropy of  $R \ln 8$  (Sugisaki, Matsuo, Suga & Seki, 1968) as is the case for TICN(I) (Matsuo, Sugisaki, Suga & Seki, 1969). If the initial volume change of the KCN III/IV transition is ~0.56  $cm^3 \cdot mole^{-1}$  (Richter & Pistorius, 1971), the entropy of this transition is ~ $R \ln 4$ , yielding a configurational entropy of  $R \ln 8$  also for KCN(III), and thus confirming the isostructural nature of these phases.

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