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Neutron Diffraction Investigation of KCN*

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Neutron diffraction measurements on KCN agree with the results calculated for a model containing freely rotating cyanide groups. They do not agree with the calculations made for a static model having CN^- groups randomly oriented along 111 directions.

Potassium cyanide has the sodium chloride structure at room temperature. Two models have been proposed to account for this. Bozorth (1922) carried out an investigation of KCN in 1922 in which he obtained reasonable intensity agreement by orienting the CN groups along the body diagonals of the cubic unit cell. Cooper (1922), in a note to *Nature*, disagreed with this analysis and suggested that the rapid falling off in intensities could be accounted for better by assuming that the CN^- groups were rotating freely in the crystal. Quantum mechanical calculations by Pauling (1930) supported the free rotation model in cyanides and other crystals. This subject was further discussed by Frenkel (1935) who concluded that CN^- groups did not rotate in alkali cyanides.

Later, X-ray studies were made by Verweel & Bijvoet (1938) and by Bijvoet & Lely (1940) on both the cubic structure and the low temperature orthorhombic modification. These authors assumed a rotating cyanide model for the room temperature phase and found a C–N bond length of 1·06 Å. They obtained a slightly shorter bond length of 1·05 Å in the orthorhombic phase. An attempt was made by Siegel (1949) to distinguish between the free rotation structure and one in which the cyanides were randomly directed along body diagonals. The low scattering power of carbon and nitrogen for X-rays prevented him from reaching any conclusion.

A neutron diffraction investigation of KCN has been carried out at this laboratory, using a neutron wave length of 1·064 Å. The large scattering cross sections of carbon and nitrogen led us to considerably different intensity calculations for the two models and allowed a choice to be made.

nF^2 values for reflections of the cubic phase of KCN, assuming free rotation, were calculated using the equation

$$|F|^2 \sim [4b_K \pm (4b_C + 4b_N)\ (\sin x/x)]^2,$$

where

$x = 4\pi r \sin \theta / \lambda$

r = radius of rotating group

$b_K = 0{\cdot}351 \times 10^{-12}$ cm.

$b_C = 0{\cdot}661 \times 10^{-12}$ cm.

$b_N = 0{\cdot}94 \times 10^{-12}$ cm.

A comparison of the observed and calculated nF^2 values, using as a radius of the sphere of rotation $r = 0{\cdot}580$ Å, is shown in Table 1. This value of r gave the best intensity agreement.

Table 1. *Observed and calculated* nF^2 *values*

		nF^2 $r=0{\cdot}58$	
hkl	nF_o^2	Rotating model	Static model
111	103	103	103
200	206	206	226
220	257	261	322
311	39	36·5	75
222	96	91	154
400	30	30	56

nF^2 values were calculated for the static model and for a C–N bond length in the range 1·06–1·26 Å. Agreement with the observed nF^2 values could not be obtained. A comparison of the calculations and observed data is shown in Table 1, also.

Over a range in the C–N bond distance, 1·06–1·26 Å, only the dynamic model gave agreement between observed and calculated intensities. Assuming the observed intensities to be measured to ±7·5%, the best agreement was obtained for the C–N distance 1·16 ± 0·01 Å.

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