Redetermination of the Crystal Structure of Calcium Cyanamide

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The crystal structure of calcium cyanamide has been studied by Dehlinger and Hanawalt, and later by Bredig[1]. Bredig reached the conclusion from his Debye-Scherrer X-ray analysis that the crystal structure of calcium cyanamide is based upon a rhombohedral lattice with $a_{rh}=5.40$ Å and $\alpha=39°55'$, which correspond to the following values for a hexagonal lattice; $a=3.67$ Å, $c=14.85$ Å. This crystal structure is similar to that of sodium azide.

The specimen used by Bredig, however, was obtained by treating calcium carbide with nitrogen. By this preparation the purity of the product can usually be reached about 70 % at the highest, always containing an appreciable amount of such impurities as calcium oxide (or hydroxide) and carbon. Accordingly, the question naturally arises as to whether pure calcium cyanamide would have the same crystal structure. For this reason the X-ray diffraction patterns of calcium cyanamide of high purity were examined.

The specimen used in this experiment was prepared from dicyandiamide and calcium carbonate according to the method enunciated by Inoue and Kanaji[2]. Dicyandiamide used was obtained by a repeated recrystallization of a commercial sample, and calcium carbonate was obtained from ammonium carbonate and calcium acetate in the presence of ammonia. A mixture of 1.5 g. of calcium carbonate and 30 g. of dicyandiamide was heated up to 770°C for 15 min. The product, white powder, was analyzed by Volhard's method[3], which revealed the product to be calcium cyanamide of 98.5% purity. X-ray diffraction patterns of this specimen were taken using an X-ray diffractometer. The experimental conditions were as follows; filtered copper radiation (Cu K_α, 1.5418 Å); 40 kV; 20 mA; scanning speed, 1/2° 2θ per min.; time con-

1) Bredig, *J. Am. Chem. Soc.*, **64**, 1730 (1942).
2) Y. Inoue and Y. Kanaji, *J. Chem. Soc., Japan, Ind. Chem. Sec.* (*Kogyo. Kagaku Zassi,*), **56**, 524 (1953).
3) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis" (third edition), p. 456, MacMillan & Co. Ltd., N.Y. (1952).

stant, 4 sec.; receiving slit, 0.4 mm.; angular aperture, 1°. The mean values of the results are summarized in the Table.

TABLE

No.	2θ	d_{obs}	d_{calc}	hkl	I_{obs}	I_{calc}
1	18.05	4.91	4.90	003	0.37	0.32
2	30.43	2.94	2.94	102	1.00	1.00
3	36.55	2.458	2.45	006	0.03	0.03
4	37.20	2.417	2.417	014	0.16	0.20
5	41.62	2.168	2.166	105	0.23	0.30
6	49.28	1.849	1.849	110	0.28	0.31
7	51.92	1.762	1.757	017	0.08	0.14
8	52.91	1.730	1.731	113	0.09	0.06
9	57.77	1.596	1.593	201	0.03	0.01
10	59.06	1.564	1.565	022	0.08	0.13
11	63.19	1.471	1.469	204	0.03	0.04

Using the chart of Hull and Davey, it was possible to assign indices (hKl) to all of the observed spectra referring to a hexagonal lattice $a=3.70$ Å and $c=14.70$ Å. The calculated values for spacings from these parameters are also listed in the Table as $d_{calc.}$.

The density of the specimen was determined by a pycnometer using benzene, which gave a value 2.36 g. per cc at 25°. From the density and the lattice constants the number of chemical units contained in the unit cell was calculated as three, the calculated density being 2.19 g. per cc.

As the indices given in Column 5 are only those of such kind as $h-k+1=3n$, the translational lattice should be rhombohedral, so that the unit cell can be given as $a_{rh}=5.35$ Å and $\alpha=40°28'$. The probable space group is one of C_{3i}^{2}—R$\bar{3}$, D_{3}^{7}—R32 and D_{3d}^{5}—R3m. These space groups give the following positions for the calcium, carbon and nitrogen atoms, referring to the rhombohedral lattice,

1Ca: 000,
1C: 1/2 1/2 1/2,
2N: xxx, $\bar{x}\bar{x}\bar{x}$.

Thus we have confirmed that the structure reported by Bredig is essentially correct. The positional parameter x for the nitrogen atoms was further refined by the trial-and-error method, the final value being 0.415. The calculated relative intensities are given in Column 7, which show a satisfactory agreement with the observed ones. It follows that the interatomic distances are C—N=1.25 Å and Ca·····N=2.45 Å.

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