Ca_2N: A Nitride with a Layer Structure

By E. T. KEVE and A. C. SKAPSKI
(*Chemical Crystallography Laboratory, Imperial College, London, S.W.7*)

AHMAD and TOMLINSON[1] have recently prepared a new nitride of the stoicheiometry Ca_2N and recorded its X-ray powder pattern. Corresponding subnitrides of strontium and barium are also known.[2] We have determined the structure of dicalcium nitride by three-dimensional X-ray methods, and find it to have some unusual features.

Ca_2N forms greenish black lustrous crystals which quickly decompose in air, and have to be sealed under argon. Their symmetry is rhombohedral, and the unit-cell dimensions, determined by indexing Ahmad's powder data, are a = 6·603 Å, α = 31° 59′, U = 71·7 Å^3, D_m = 2·17 g. cm.$^{-3}$, D_c = 2·18 g. cm.$^{-3}$ for $Z = 1$. The corresponding hexagonal cell has a = 3·638, and c = 18·78 Å. The space group has proved to be $R\bar{3}m$.

The structure was solved by standard methods on the basis of a morphologically and computationally convenient monoclinic unit cell (a = 6·299, b = 3·638, c = 7·535 Å, β = 123° 51′, Z = 2 and space group $C2/m$). Least-squares refinement has now reached R = 0·16 for 121 reflections, collected with Cu-K_α radiation and visually estimated. Further refinement using data from a better-quality crystal will be carried out.

Figures 1a and b show that Ca_2N has a layer structure. The nitrogen atoms lie on inversion triads, and their co-ordination is octahedral with some angular distortion (Ca–N–Ca angles of 96·9° and 83·1°) and six equal N–Ca distances of 2·43 Å. By comparison the N–Ca distance found in the usual nitride, Ca_3N_2, is 2·47 Å.[3] Within each layer every calcium atom is in contact with three nitrogens at 2·43 Å. Its nearest calcium neighbours are three at 3·23 Å and six at 3·64 Å. The shortest Ca–Ca distance between the layers is 4·35 Å. The Ca–Ca distances found in the metal are 3·947 Å in the α-form and 3·877 Å in the γ-form.[4]

The nearest structural equivalent is Cs_2O,[5] which has an anti-$CdCl_2$ type structure. The main difference is that in Ca_2N the shortest metal–metal distance between layers is substantially greater than the corresponding one within the layer (see Figure 1a), whereas they are of the same order in Cs_2O. Further comparison can be made with a lower oxide of cæsium, Cs_3O,[6] which is reported to have a greenish metallic appearance. It has columns of O–Cs octahedra with interatomic distances similar to those in Cs_2O, but the Cs–Cs distances between the columns are about 0·5 Å greater than those in the metal.

It is probably best to think of the structure as being essentially ionic. Thus Ca_2N gives off

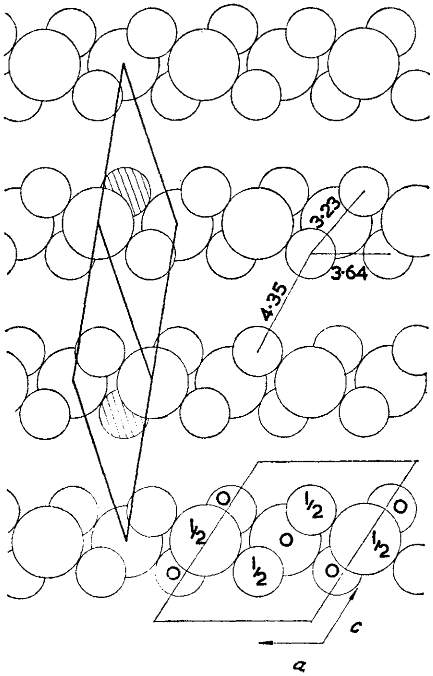

FIGURE 1a

A view of the layer structure of Ca$_2$N *showing the rhombohedral cell and its calcium content (hatched). The projection corresponds to* [010] *of the monoclinic cell indicated. The estimated standard deviations of the bond lengths are* $\sim$0·01 Å.

ammonia and hydrogen in contact with water,[1] and the difference in the electronegativities of the two elements also favours this view. The greenish black graphitic appearance is due to the excess electrons.

Tsai *et al.*[6] have found that powdered Cs$_3$O shows metallic conductivity. This implies that single crystals must have metallic conductivity in all directions, and therefore suggests that the "free" electrons are situated in the gaps between the columns of O–Cs octahedra. We favour an analogous view of Ca$_2$N, with the excess electrons being situated in the large gaps between layers, which, being essentially ionic, form a barrier to conduction. Such a view also gives the calcium ions a more balanced electrostatic environment.

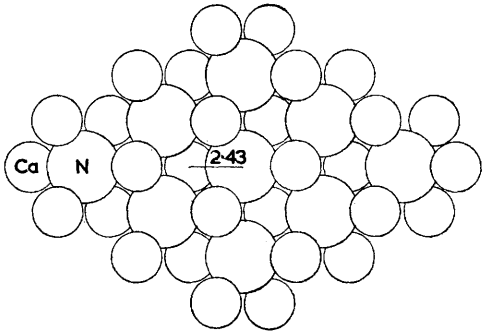

FIGURE 1b

A single layer in the Ca$_2$N *structure.*

A preliminary investigation of the electrical properties of powder compacts of Ca$_2$N[7] indicates that the conductivity is in the semiconductor range (about 0·2 ohm^{-1} cm.$^{-1}$ at room temperature) and that the temperature coefficient is positive. These observations are consistent with the structure. A single crystal should have excellent conductivity parallel to the layers, but a much lower conductivity normal to them. A rise in temperature should reduce the effectiveness of the ionic layers as barriers, so conduction perpendicular to the layers, which in a powder specimen would be the determining factor governing overall conductivity, should increase.

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