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Recognizing Fragments of the Metal Structure in Metal Compounds

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The structures of β-$CsBeF_3$ and $KClO_3$, showing a cation arrangement of the CrB-type, can be described on the basis of their parent metal structure. The three compounds contain fragments, similar in topology and *M–M* distances (within a few percent), to the bcc metallic structure, which is common to their respective parent elements Cs, K, and Cr. Slightly distorted fragments are formed by the inclusion of "foreign" atomic groups. The arrangement of Ti atoms in TiO_2 (rutile) can also be related to the parent hcp Ti metal, the (100) planes being identical in both the metal and the oxide.

Recently it has been shown that in many cases the cations in oxides and fluorides adopt the structure of either simple alloys or elements; therefore, they have been described as anion-stuffed cation arrays (*1*). Examples are presented by the structures of β-$CsBeF_3$ and $KClO_3$, whose cationic arrays are those of the CrB-type alloy, and TiO_2, where the Ti arrangement is that of β-Hg (*1*).

In spite of the utility of this model in correlating compounds as different as β-$CsBeF_3$, $KClO_3$, and CrB, we think that objections could be raised in the sense that the structure type itself remains unrelated to any other parent structure.

In a previous paper (*2*) we have applied the cationic model to describe $Ca_3(BO_3)_2$ as an anticorundum structure, with BO_3 groups occupying flattened Ca_6 octahedra of a distorted hexagonal arrangement of Ca atoms, similar to that of the oxygens in Al_2O_3. The fact that the element calcium crystallizes in the hcp phase (*3*), which appears distorted in calcium orthoborate, suggested to us the possibility that many other structures could be correlated with their parent metal structure.

We report briefly here how the three structures of the CrB-type mentioned above can be derived from a bcc structure, which is common to all three elements Cs, K, and Cr. As an example, we describe, in this new approach, the structure of the CrB alloy, shown in Fig. 1 as reported previously (*4*). The discussion is then extended to the rutile structure which can be directly related to that of the parent Ti metal.

Figures 1a and 1b show the classical description in terms of CrB_6 trigonal prisms sharing trigonal faces along the *a* axis and rectangular faces (almost square) along the *c* axis, thus forming layers of prisms, perpendicular to the *b* axis and shifted to each other by *a*/2. However, the Cr–Cr distances between atoms belonging to adjacent layers

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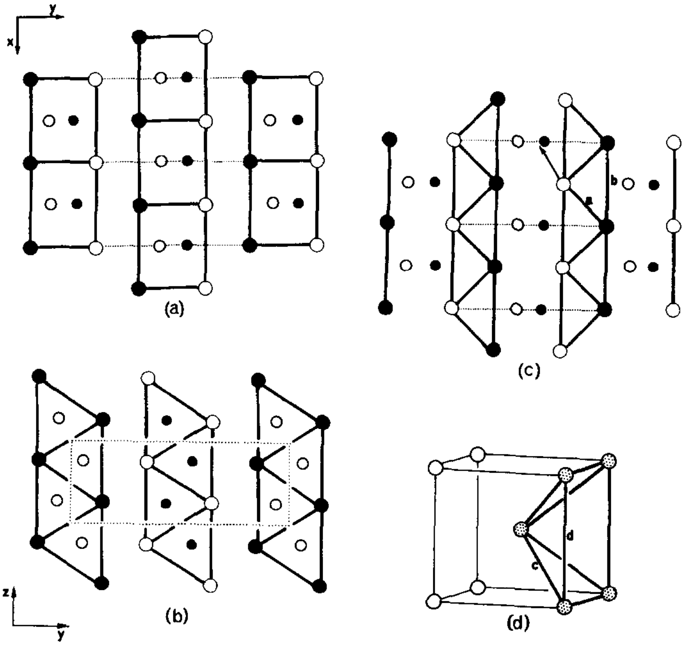

FIG. 1. (a) The structure of CrB projected on the *ab* plane. The unit cell is marked with dotted lines. Large and small circles represent Cr and B atoms, respectively. Black and open circles at $z = 1/4$ and 3/4, respectively. (b) The CrB structure projected on the *bc* plane to show the triangular faces of the BCr_6 trigonal prisms. (c) The CrB structure as in (a) showing the alternative edge segments defining the fragments of the parent bcc metal structure. The interatomic distances are $a = 2.58$ and $b = 2.70$ Å. The distance between Cr atoms in direction perpendicular to the drawing plane is 2.93 Å (*c* axis of the CrB unit cell). (d) The same fragment as in (c) referred to a bcc unit cell. The interatomic distances are $c = 2.50$ and $d = 2.89$ Å.

are shorter than those defining the trigonal prisms. These distances are drawn in Fig. 1c and suggest an alternative description of the structure in terms of fragments of the bcc Cr structure. Figure 1d shows a Cr unit cell in which the fragments appearing in the CrB alloy are depicted. This similarity is based not only on topological features but also on interatomic distances. Thus, each Cr atom caps the nearly square faces of prisms in adjacent layers, as does the body-center atom in a bcc unit cell. Thus, the capped faces correspond to the unit cell faces (see Fig. 1d), which, in CrB, are slightly distorted. The dimensions are 2.70 and 2.93 Å (mean value of 2.81 Å), very close to the value of 2.88 Å of the unit cell edge of bcc Cr. The four distances, from the capping atom to the four atoms defining the capped face, are 2.58 Å which compare quite favorably with the equivalent distance of 2.50 Å in chromium.

In the case of $KClO_3$ (*5*), the rectangular faces are somewhat more irregular than in CrB. Their dimensions are 5.58 and 4.65 Å along the *b* and *a* axes, respectively, but the mean value (5.12 Å) is also very similar to the unit cell edge of bcc K (5.32 Å). The corresponding four distances (*c* in Fig. 1) range between 4.57 and 4.60 Å, in agreement with 4.60 Å in elemental potassium.

Finally, in β-$CsBeF_3$ (*6*), the situation is more complicated. The rectangular faces have dimensions 6.00 × 4.83 Å; only the former could be assigned to the unit cell edge of bcc Cs (6.14 Å). The same situation

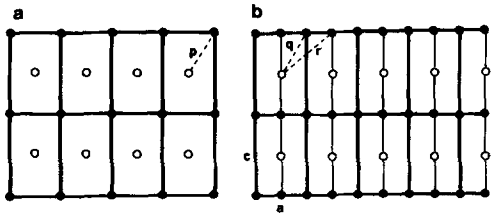

FIG. 2. (a) The cation array in TiO_2 structure projected on the bc plane. The Ti–Ti distance is $p = 3.56$ Å. (b) The structure of hcp Ti metal projected on the bc plane. The Ti–Ti distances are $q = 2.96$ and $r = 4.13$ Å (mean value 3.55 Å).

arises with the four c distances, whose values of 2×4.65 and 2×4.79 Å, are very far from the shortest Cs–Cs distance of 5.32 Å in bcc Cs. However, besides the bcc phase of Cs, there exists another fcc phase with $a = 5.98$ Å and a shortest Cs–Cs distance of 4.24 Å; the distances observed in $CsBeF_3$ are very close to the mean values of the two Cs phases. Thus, the mean shortest Cs–Cs distance is 4.78 Å (compare with the mean a distance of 4.72 Å), and the value of 6.00 Å corresponds to the b axis of $CsBeF_3$ unit cell; it just lies between the values of 6.14 and 5.98 Å of the Cs unit cells. The other dimension of the rectangular faces (4.83 Å), corresponding to the a axis of the fluoride unit cell, is also very close to the mean value (5.12 Å) between the cubic a axis and the shortest Cs–Cs distance in the fcc Cs (4.24 Å). This last observation probably needs an additional explanation: It seems as if Cs had adopted an intermediate configuration between the bcc and the tetragonal body-centered cell which can be defined on the basis of the fcc unit cell. The reasons for this are unknown to us at present but they should reflect the most thermodynamically stable state for the system.

We conclude that all the three compounds can be regarded as the parent bcc metal structure which is opened up and slightly distorted by the inclusion of "foreign" groups. The reconstruction of the parent metal structure should be ideally accomplished by the displacement of whole layers, as indicated by the arrow in Fig. 1c.

As a further example, we may note that the Ti arrangement in rutile is achieved by the relative displacement of the (100) and (300) layers of hcp Ti in such a manner that the eight Ti–Ti distances, 3.54 Å (p in Fig. 2a) are equal to the mean value of the Ti–Ti distances marked by q and r in Fig. 2b, which are 2.96 and 4.13 Å, respectively.

These principles have also been successfully applied to other structures of FeB-type, apatite, and those of the humite series. This will be the object of a further report to be published soon.

References

1. M. O'KEEFFE AND B. G. HYDE, "Structure and Bonding," Vol. 61, pp. 77–144, Springer-Verlag, Berlin (1985).
2. A. VEGAS, *Acta Crystallogr. Sect. C* **41**, 1689 (1985).
3. LANDOLDT BÖRNSTEIN, New Series, Vol. III/6, 5, "Structure Data of Elements and Intermetallic Phases," Springer-Verlag, Berlin (1971).
4. A. J. FRUEH, JR., *Acta Crystallogr.* **4**, 66 (1951).
5. J. W. BATS, *Acta Crystallogr. Sect. B* **34**, 1679 (1978).
6. H. STEINFINK AND G. C. BRUNTON, *Acta Crystallogr. Sect. B* **24**, 807 (1968).