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Planar Defects in Mo_2BC. An Electron Microscope Study

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Structural relationships between Mo_2BC, σ-MoB, β-MoB, and β-MoC_{1-x} are described and possibilities for planar intergrowth defects (Wadsley defects) and nonstoichiometry are considered. The term *chemical stacking fault* is proposed. Electron microscopy of Mo_2BC specimens revealed crystals that were rich in planar defects with widths consistent with the defects postulated.

Introduction

In recent years it has become increasingly apparent that deviations from ideal stoichiometry in chemical compounds are accommodated not by point-defects but by extended (organized) defects. The structure of the defect is often that of a related structure type and such defects are known as Wadsley (intergrowth) defects.

It is important to establish how general this principle is; accordingly we have undertaken an electron microscope study of Mo_2BC. This compound was chosen, as the structure (1, 2), shown in Fig. 1, suggested that it should be a good candidate for exhibiting Wadsley defects that could readily be observed by electron microscopy.

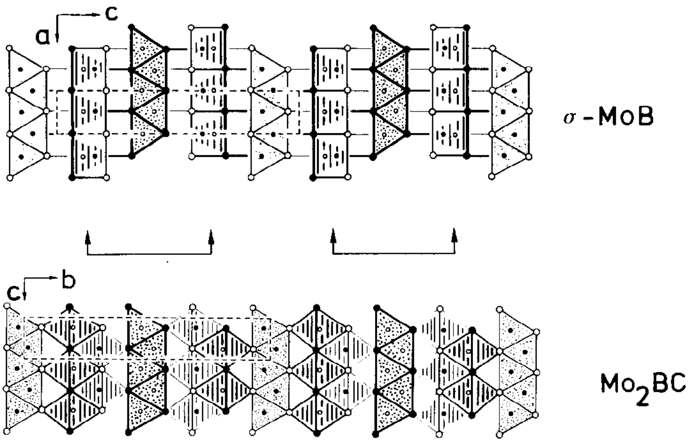

FIG. 1. The structures of σ-MoB and Mo_2BC. Large circles, molybdenum; small circles, carbon or boron. All atoms at 0 or $\frac{1}{2}$ (filled circles).

Structural Relationships between Mo_2BC, σ-MoB, β-MoB, and β-MoC_{1-x}

The Mo_2BC structure can be described in two complementary ways. In the first description, slabs of CMo_6 octahedra arranged as the NaCl structure type are separated by

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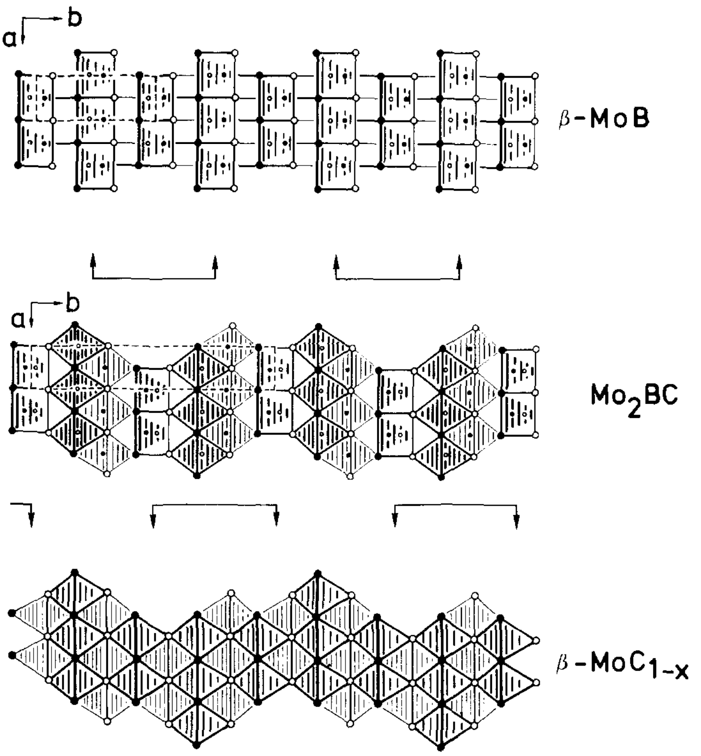

FIG. 2. The structures of β-MoB, Mo_2BC, and β-MoC_{1-x}. Large circles, molybdenum; small circles, carbon or boron. All atoms at $\frac{1}{4}$ or $\frac{3}{4}$ (filled circles). The positions of the carbon atoms are not shown in β-MoC_{1-x}.

slabs of face-sharing BMo_6 trigonal prisms. Drawings illustrating this aspect of the structure are given in Figs. 1 and 2. An alternative is to describe the packing of Mo atoms as layers of square (4^4) nets parallel to (010). We recognize four positions for a node in a net relative to that of a reference net as described by Pearson (*3*). These are labeled A, B, C, D (Fig. 3) in a way analogous to the familiar symbolism for describing the 3^6 nets of close packing. In this description the Mo packing is described by the sequence ···ABABCDCD···.

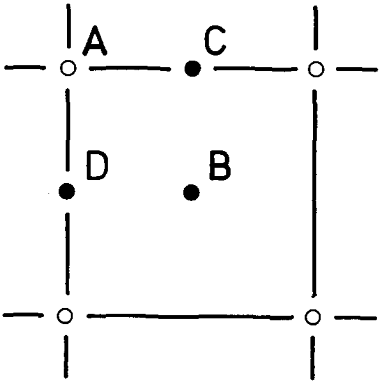

FIG. 3. Scheme for labeling positions of 4^4 nets.

σ-MoB (the low-temperature form) is isostructural with WB (4) and GaZr (5). In this structure (Fig. 1), BMo_6 trigonal prisms share faces forming slabs of the same sort as in the structure of Mo_2BC, the slabs being separated by a layer of empty square pyramids. The Mo packing is now the repeating sequence ···ABDCBACD···. This differs from that of Mo_2BC in the third to sixth layers by interchanging A and D and also interchanging B and C, this in turn corresponds to shifting all the Mo atoms in Mo_2BC within the slab $\frac{1}{4} < y < \frac{3}{4}$ (marked with arrows in Fig. 1) by **c**/2. In this way octahedra in the planes $y = \frac{1}{4}$ and $y = \frac{3}{4}$ are transformed into trigonal

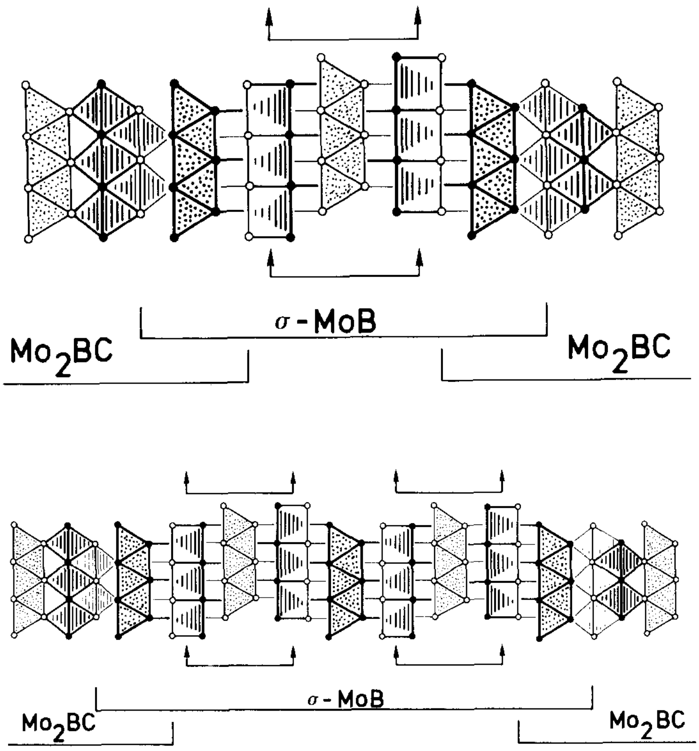

FIG. 4. Two possible defects in the structure of Mo_2BC with slabs of σ-MoB.

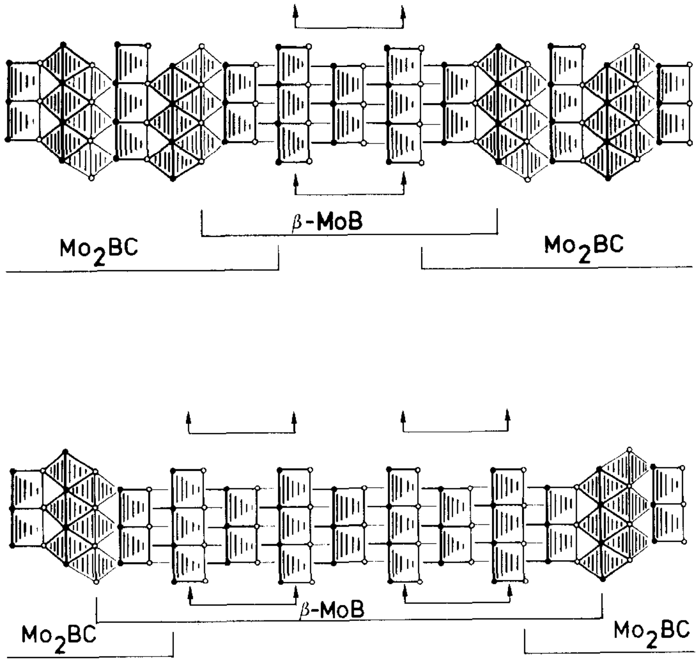

FIG. 5. Two possible defects in the structure of Mo_2BC with slabs of β-MoB.

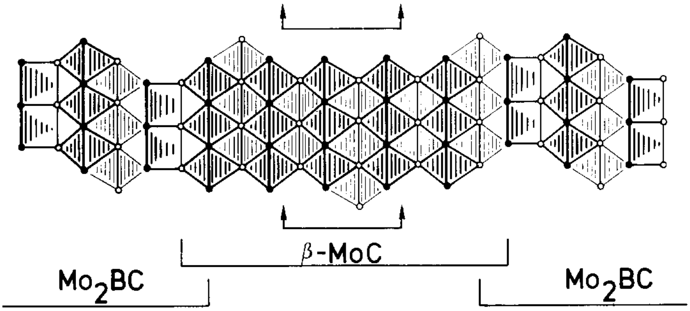

FIG. 6. A possible defect in the structure of Mo_2BC with a slab of β-MoC.

prisms. Note that the interstitial positions in the prisms are very close to the interstitial positions of the corresponding octahedra from which they derive.

The high-temperature form of the boride, β-MoB (*6*) is a member of the large family of compounds with the B33 (TlI or CrB) structure type (*7*). A projection on (001) of the structure is shown in Fig. 2. One has slabs of BMo_6 trigonal prisms as in σ-MoB but every second slab is differently oriented in the two compounds. The Mo packing sequence is

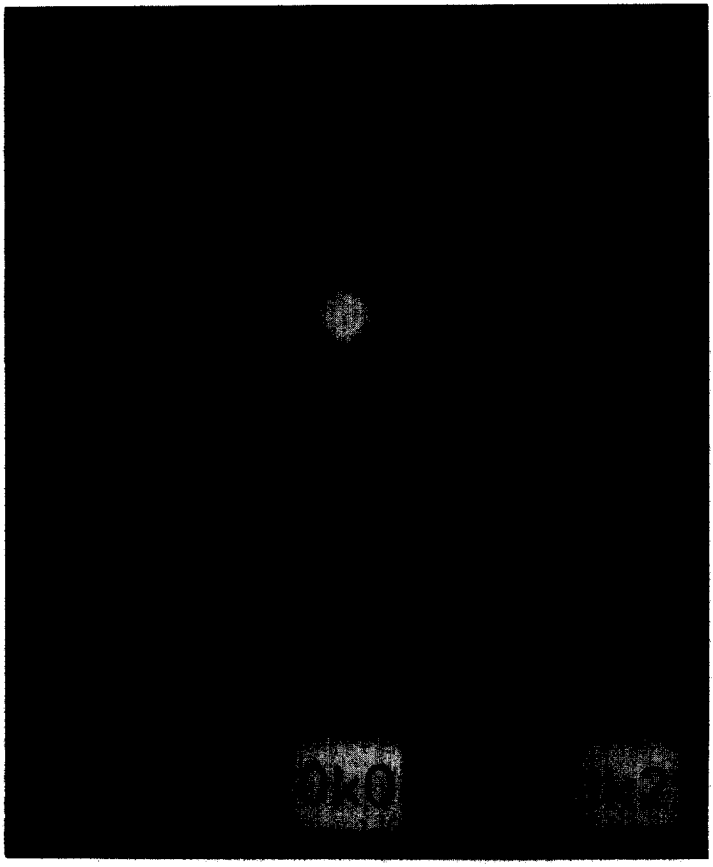

FIG. 7. A typical electron diffraction pattern for Mo_2BC.

now ···ABCD···. This differs from Mo_2BC again in the third to fifth layers but now one must interchange A and C and interchange B and D; the corresponding shifts of Mo atoms in Mo_2BC are all now **a**/2.

Finally there is a cubic MoC (β-MoC_{1-x}) with the familiar structure type of NaCl (*8*) (Fig. 2). The Mo stacking is now just ··· AB ···; the translations of the layers to produce the other structure types can readily be worked out. The interrelationships between the structures of β-MoC_{1-x} and of β-MoB and Mo_2BC are shown in Fig. 2.

Possibilities for Planar Defects and Nonstoichiometry in Mo_2BC

The structures of the molybdenum borides and carbides just described suggest the possibilities for intergrowth of these structure types. In particular the apparent preference of boron for trigonal prism sites and of carbon for octahedral sites suggests that, on the one hand carbon-rich Mo_2BC might contain intergrowth elements of β-MoC, and on the other hand, boron-rich Mo_2BC might contain elements of β-MoB and/or σ-MoB.

In Fig. 4 we show how planar defects consisting of elements of σ-MoB can be accommodated in Mo_2BC. In the upper part of the figure a slab ($\frac{1}{4} < y < \frac{3}{4}$) of Mo atoms is displaced by **c**/2 to produce an element of MoB with the width of the **b**-axis repeat of Mo_2BC. The lower part of the figure shows the effect of two such translations in adjacent unit cells producing a defect of twice the width. In producing these defects the relative positions of the matrix Mo_2BC layers on either side of

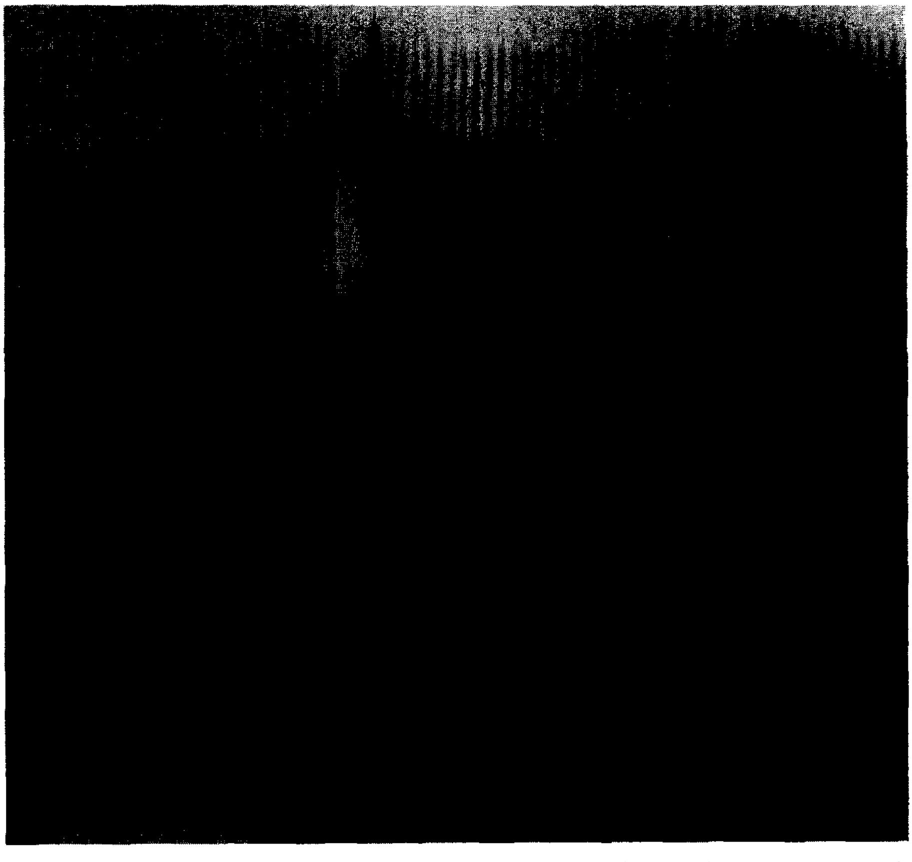

FIG. 8. Image of Mo_2BC formed using the ±(002) reflections. The normal fringe spacing is interrupted by three faults.

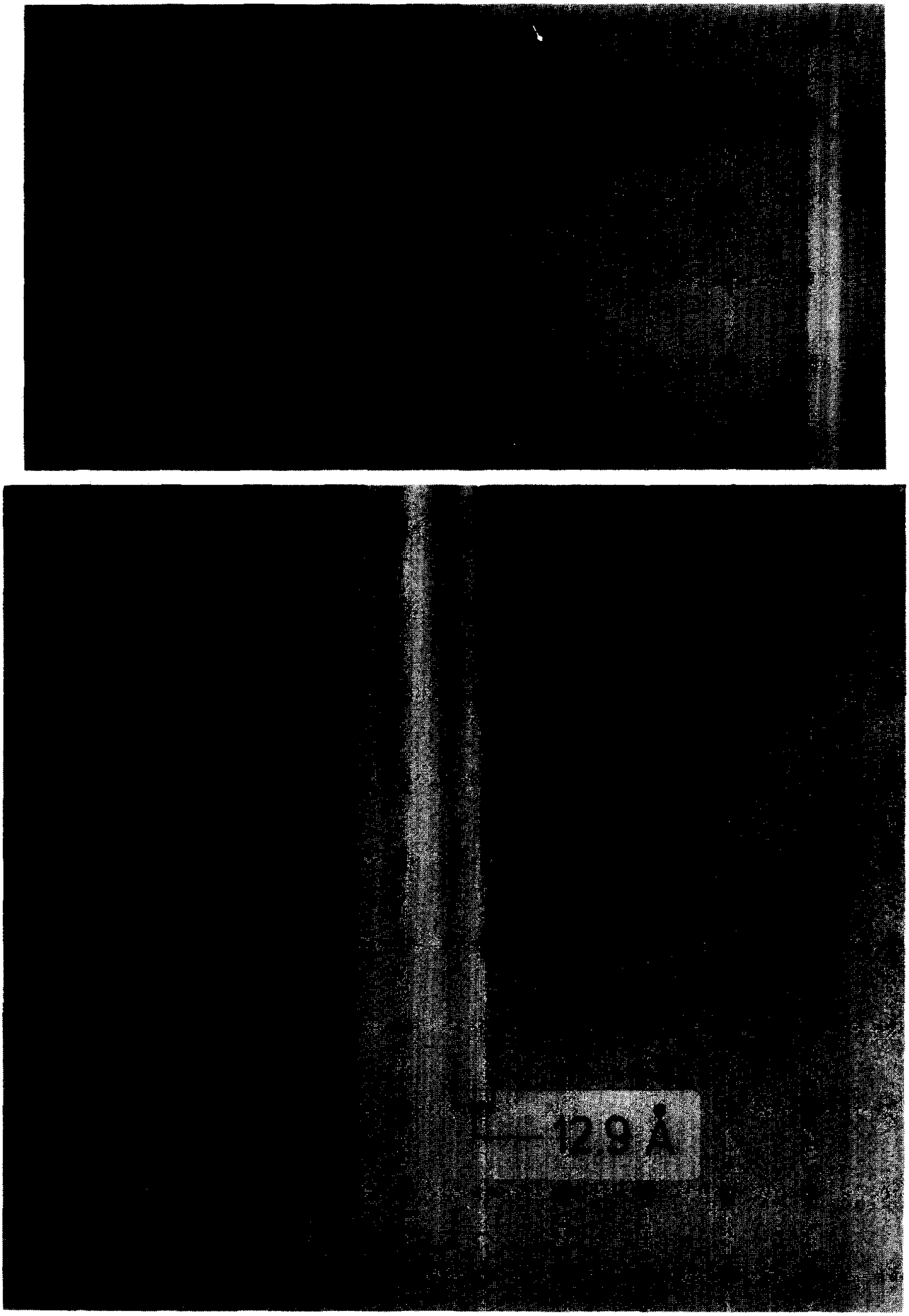

FIG. 9. Image of part of a crystal of Mo_2BC. The 002 fringe spacing is 8.7 Å. The faults in the left part of (a) are magnified in (b).

the defect are unchanged. On the other hand, a single slip by the same vector in the plane $y = \frac{1}{4}$ (displacing two parts of a Mo_2BC crystal relative to each other) would produce an element of σ-MoB with a width of only one-half of the **b**-axis repeat of Mo_2BC.

Figure 5 shows how elements of β-MoB can similarly be intergrown in Mo_2BC. In this case the layers of intergrown boride are produced by displacement of layers (again $\frac{1}{4} < y < \frac{3}{4}$) of Mo_2BC by **a**/2.

Figure 6 shows how displacement by **a**/2 of layers, now $\frac{1}{2} < y < 1$, of Mo_2BC will produce an element of β-MoC in the host crystal. In this instance the element of MoC has a width one-and-a-half times the **b**-axis repeat distance for Mo_2BC.

We have by no means exhausted all possibilities. The defects we have described are the simplest planar defects that could occur in Mo_2BC and for that reason perhaps most likely. The salient feature of all the proposed defects is the change in interstitial sites from octahedra to trigonal prisms (or vice versa) by a change in the stacking pattern of metal atoms, i.e., by the introduction of stacking faults either singly or in pairs. The introduction of different interstitial sites (allowing change of stoichiometry) at stacking faults is analogous to corresponding process occurring in chemical twinning (*9*) (in which, e.g., octahedral sites in h.c.p. are converted to a plane of trigonal prism sites by twinning) so that we propose to call the defects *chemical stacking faults*. Seen in this light all the ideal structures we have described (and indeed others) may be considered as derived from the simplest (MoC: stacking sequence $\cdots AB \cdots$) by periodic production of stacking "faults."

Experimental

(*a*) *Sample Preparation*

Mo_2BC was prepared by arc-melting appropriate amounts of molybdenum, boron, and carbon (graphite) in argon atmosphere. An X-ray powder pattern revealed that beside Mo_2BC a considerable amount of the high-temperature form of MoB existed in the sample. The powder pattern was readily indexed and the unit cell parameters refined with the orthorhombic unit cell $a = 3.088$ (1), $b = 17.348$ (1), and $c = 3.046$ (1) Å for Mo_2BC, and the orthorhombic cell, $a = 3.147$ (1), $b = 8.485$ (3), and $c = 3.080$ (1) Å for β-

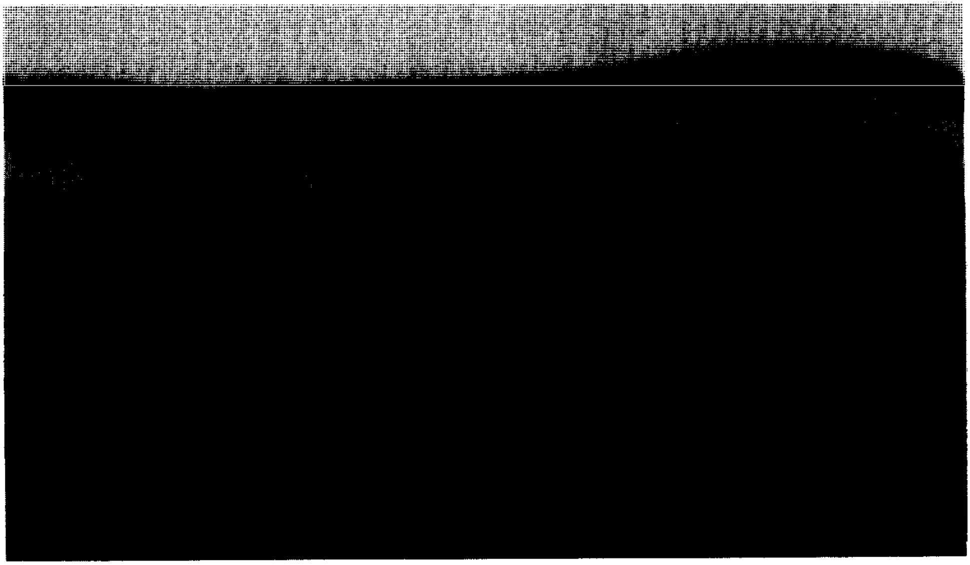

FIG. 10. Images showing faults terminating within a crystal. The fringe spacing is 8.7 Å.

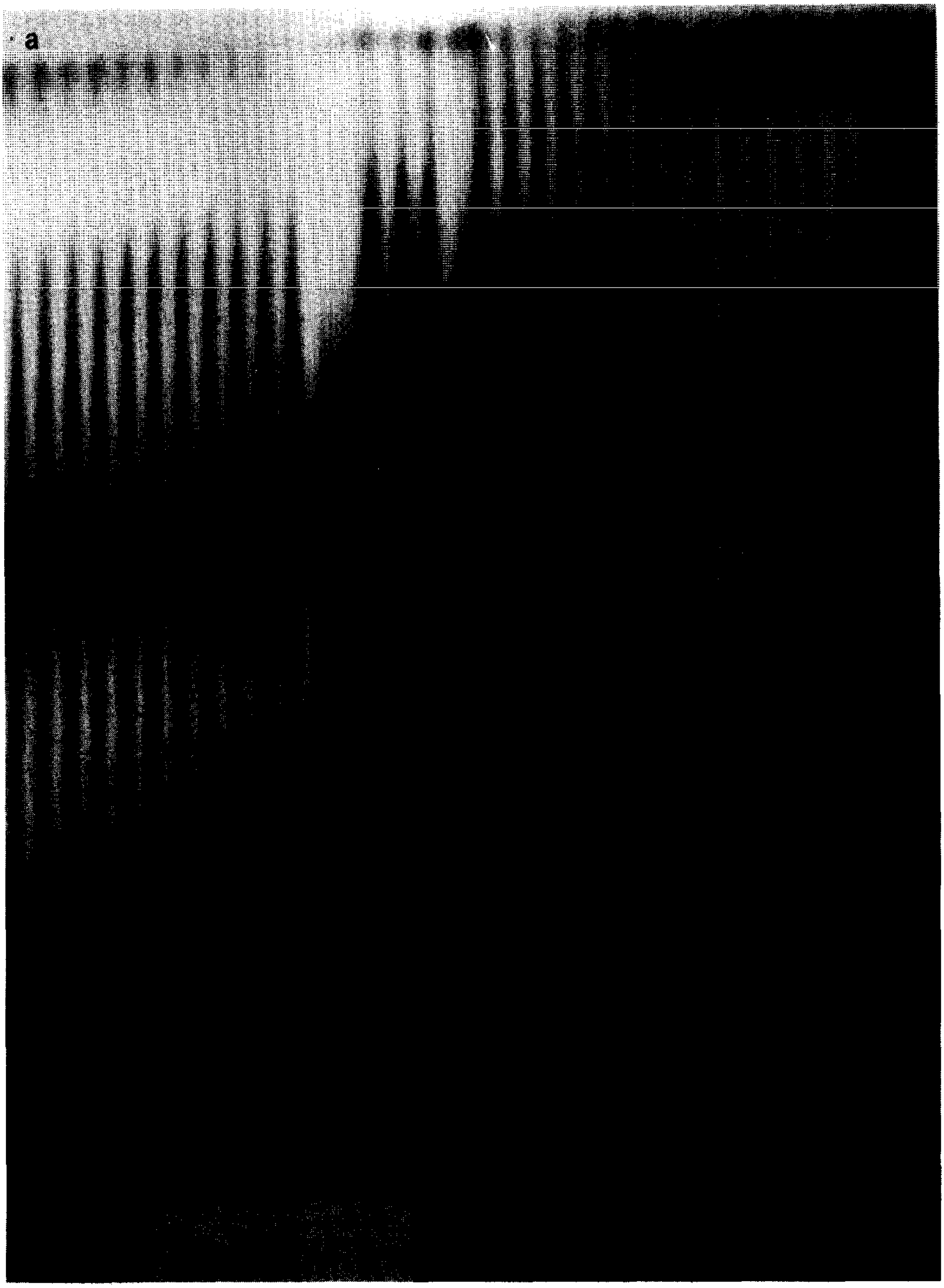

FIG. 11. (a) Image with normal fringe spacing of 8.7 Å interrupted by terminating faults which are 26.0 and 17.4 Å wide. (b) Polyhedron model of the 26.0 Å fault on the left in (a), projected along the c-axis. Carbon-centered octahedra are black (within the Mo_2BC part) and gray within the β-MoC part). Boron-centered trigonal prisma are white.

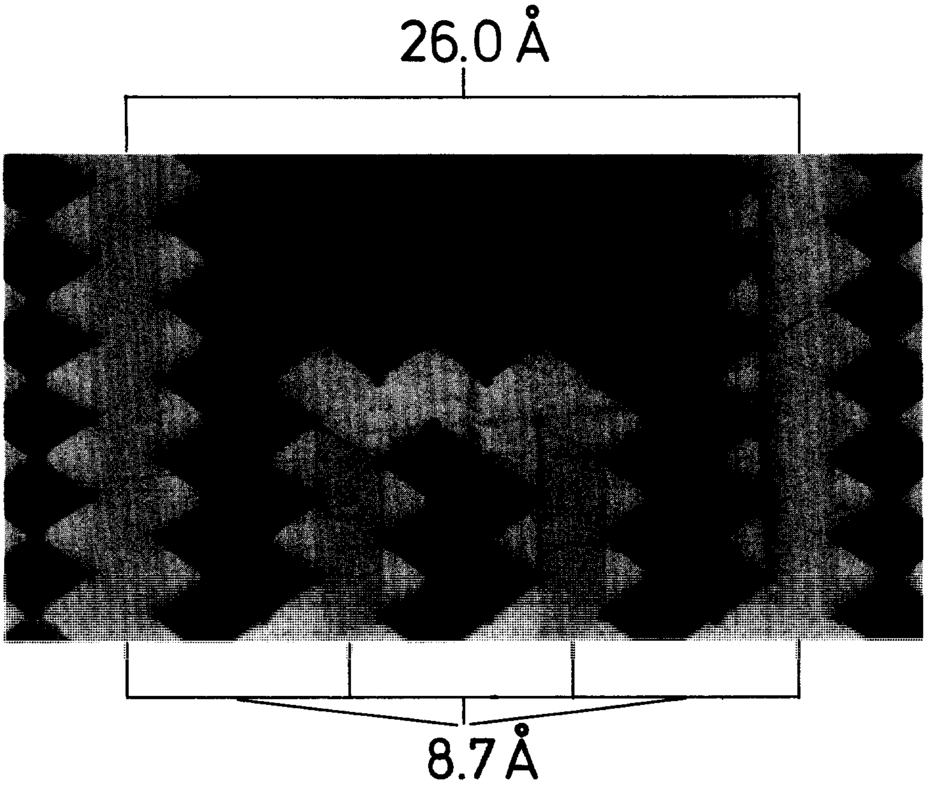

FIG. 11 (*cont.*).

MoB; these are in agreement with earlier published data (*1, 10*).

(*b*) *Electron Microscopy*

A small amount of the sample was ground in an agate mortar, dispersed in carbon tetrachloride and collected on carbon-coated grids. The electron microscope used was a Philips EM 301G equipped with a tilting stage. Small single crystals, reasonably transparent to 100-kV electrons, were found which could be aligned with their longest axis normal to the electron beam. With the ±(002) reflections it was possible to observe structure images using ojective apertures of 30–80 μm.

It was easy to distinguish the two phases of the sample from each other in the electron microscope by means of their different diffraction patterns (an example of that for Mo_2BC is shown in Fig. 7) and by the fact that the high-temperature form of MoB was not stable in the electron beam.

Many crystals of Mo_2BC aligned with the b-axis normal to the beam, showed a fringe pattern with constant spacing between the fringes. The spacing was determined to be 8.7 Å ($=b/2$). However, in a number of crystals different types of fault were found. The following few examples from a great number represent the types of defect most commonly observed.

In Fig. 8 an image of a crystal formed using the ±(002) reflections is shown. The normal fringe spacing of 8.7 Å is interrupted by faults of width 35 and 17.4 Å (two in the right part). The width of the defects corresponds respectively to twice and once the length of the b-axis in Mo_2BC. The most plausible interpretation of these defects is in terms of a transformation giving rise to units of σ-MoB or β-MoB in the crystal as illustrated in Figs. 4 and 5.

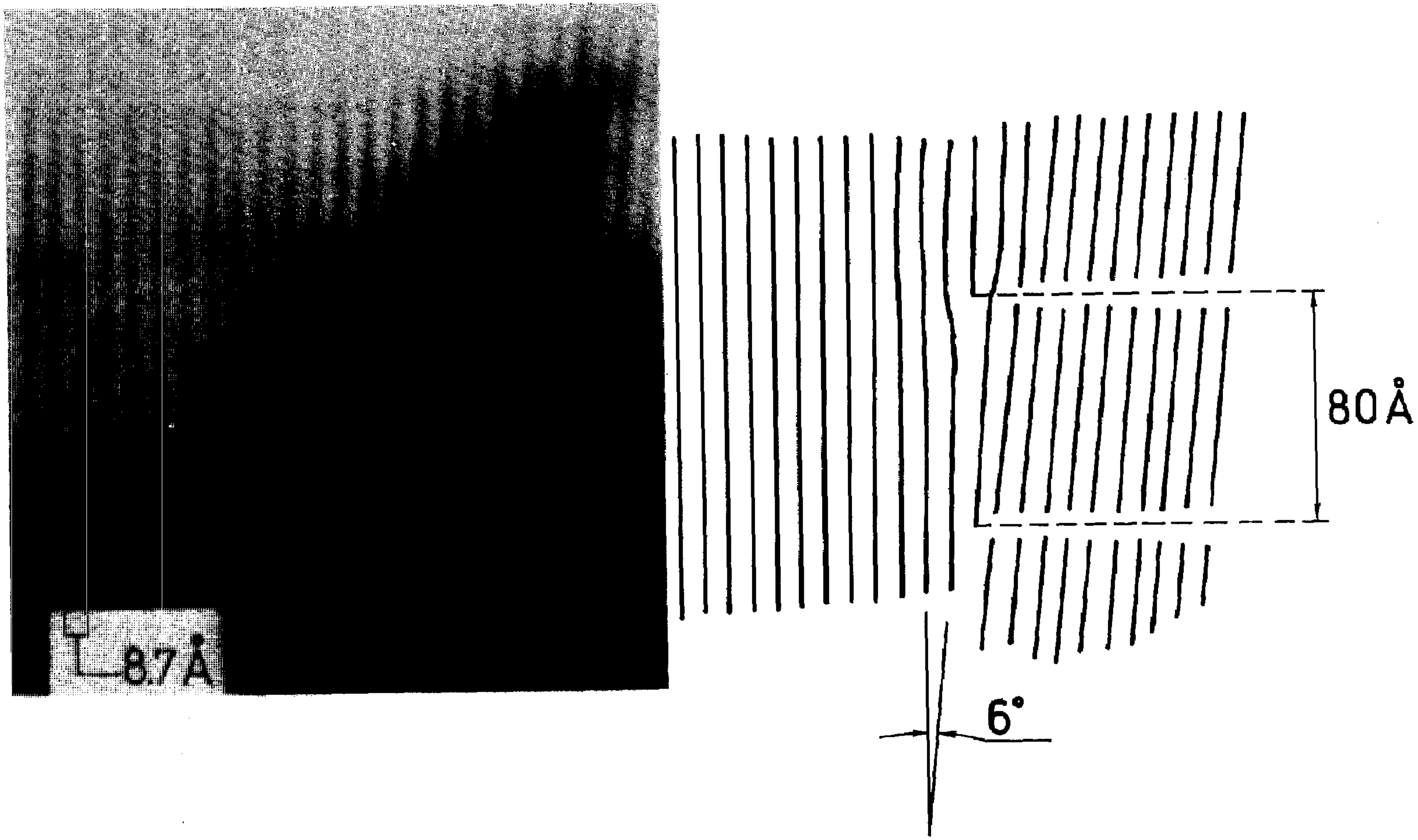

FIG. 12. Image of a tilt boundary, in Mo_2BC showing dislocation.

Figure 9a shows an image in which the normal fringe spacing of 8.7 Å is interrupted by defects of another kind. Besides the defects of 17.4 Å shown previously, there is a fault of approximately $\frac{3}{4}$ of that width (=12.9 Å). In the fault shown in the left part of Fig. 9a (magnified in Fig. 9b) the fringe spacing sequence in angstroms from the left is ..., 8.7, 8.7, 17.4, 17.4, 12.9, 8.7, 8.7, ... The defect in the right part shows the ordering ..., 8.7, 8.7, 17.4, 12.9, 8.7, 8.7, ... Å. The fault with spacing 12.9 Å is quite possibly a β-MoC defect caused by a slip along the **a**-axis in the plane of $y = \frac{1}{2}$ and with a width $3b/4$.

Although in most cases the faults traverse the entire field of the crystal which is transparent to electrons, there have been occasional examples of faults terminating within a crystal; an example is shown in Fig. 10. We have been able to propose a reasonable model for the simpler faults contained in Fig. 11a. The normal fringe spacing of 8.7 Å is interrupted here by two faults near the edge of the crystal. One is 26.0 Å and the other is 17.4 Å. Both the faults terminate in the crystal. A possible model for the 26 Å fault is illustrated by a polyhedron model presented in Fig. 11b. This shows how a slab of the β-MoC type is grown into the Mo_2BC structure. At the interface between the β-MoC and Mo_2BC structural units, there are almost regular polyhedra (left empty in the model) with molybdenum at the corners, these are tetrahedra, square pyramids, and trigonal bipyramids. A possibility is that impurities which prefer these coordinations to molybdenum can aggregate at such defects.

Line defects such as dislocations were also commonly observed in the crystals of Mo_2BC; an example is shown in Fig. 12 in which it can clearly be seen that the plane of the fringes on the left is tilted with respect to the corresponding plane of those on the right (a symmetrical tilt boundary). In order to clearly illustrate the angle difference a drawing of the dislocation is given in the right part of the figure. The angle was measured to be approximately 6° and knowing the fringe spacing it was possible to calculate the expected distance between positions where new fringes would be inserted. This is $(b/4) \cot 3° = 83$ Å. The measured distance in Fig. 12 is approximately 80 Å.

Conclusions

The experimental observations have clearly shown that several types of planar defect occur in Mo_2BC. The exact nature of each defect is not known, but could probably be established using a higher-resolution instrument than we have presently available, although then the experimental image contrast should be compared with that calculated (*11*). The agreement of the observed fault spacing with that expected for the various intergrowth (Wadsley) defects that we have proposed does lend support, however, to our proposal that these are the type that do occur.

Acknowledgment

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