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**Receiving aperture widths in single-crystal diffractometry.** By L. E. ALEXANDER and GORDON S. SMITH,† *Mellon Institute, Pittsburgh 13, Pennsylvania, U.S.A.*

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It has come to the authors' attention\* that the last term of equation (D.9) of their previous paper (Alexander & Smith, 1962) rests upon a faulty assumption, namely, that the minimum separation of the trailing edges of the diffracted rays and receiving aperture,  $T' - T$ , occurs when the crystal has turned to the angle  $+\frac{1}{2}\gamma_c$ . Actually this critical angle  $\beta_0$  can be precisely determined by minimizing  $T' - T$  as a function of  $\beta$  by the standard method of differential calculus, the principle recently applied by Burbank (1962), but in a somewhat different way, to the case of equal crystal-to-source and crystal-to-receiver distances ( $R_x = R_z$ ), a perfect spherical crystal, and a point source of X-rays.† In order to remedy the deficiency in their previous treatment, the present authors give herewith a brief revision of the pertinent passages of Appendix D (Alexander & Smith, 1962). As before, the case treated is the more general one of  $R_x \neq R_z$ ,  $R_x \gg r_c$ ,  $R_z \gg r_c$ , and a cylindrical mosaic crystal

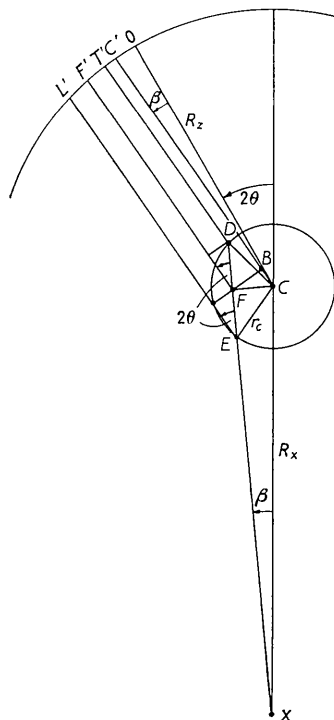


Fig. 1.

\* Burbank's paper was read by one of us (G. S. S.) as a refereeing assignment. The authors are much indebted to Dr Burbank for approving the submission of the present manuscript for publication.

† Ladell & Spielberg (1963) have also treated this same situation. Their results are in approximate accord with Burbank's.

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diffracting X-rays of imperfect monochromaticity from an extended source.

Referring to Fig. 1, and employing the nomenclature of the previous paper, we first express  $T$  and  $T'$  for the  $2\theta$  scan technique as functions of the crystal angle  $\beta$  for a non-mosaic cylindrical crystal and a point source of X-rays:

$$\begin{aligned} T' &= \beta + C'F' - T'F' \\ &= \beta(1 + (R_x/R_z) \cos 2\theta) - [(\gamma_c/2)^2 - \beta^2]^{\frac{1}{2}}(R_x/R_z) \sin 2\theta \\ T &= 2\beta - \frac{1}{2}\gamma_R. \end{aligned}$$

If we designate the crystal setting angle as  $\beta + \frac{1}{2}\gamma_x + \frac{1}{2}\gamma_m + \frac{1}{2}\gamma_\lambda$  in order to include in these expressions angular terms for the source width, mosaicity range, and spectral dispersion, we have:

$$\begin{aligned} T' - T &= \beta((R_x/R_z) \cos 2\theta - 1) \\ &\quad - [(\gamma_c/2)^2 - \beta^2]^{\frac{1}{2}}(R_x/R_z) \sin 2\theta + \frac{1}{2}\gamma_R - \frac{1}{2}\gamma_x - \gamma_m. \quad (1) \end{aligned}$$

We now determine  $(T' - T)_{\min}$  and  $\beta_0$  by differentiating (1) with respect to  $\beta$  and equating to zero, with the result

$$\begin{aligned} \beta_0 &= \frac{1 - (R_x/R_z) \cos 2\theta}{[(R_x/R_z) \sin 2\theta]^2 + ((R_x/R_z) \cos 2\theta - 1)^2]^{\frac{1}{2}}} \cdot \gamma_c/2 \\ &= F \cdot \gamma_c/2. \quad (2) \end{aligned}$$

The minimal receiving aperture width corresponds to  $(T' - T)_{\min} = 0$ :

$$\begin{aligned} (\gamma_R)_{\min} &= |2\gamma_m + \gamma_x + \gamma_c[F(1 - (R_x/R_z) \cos 2\theta) \\ &\quad + (1 - F^2)^{\frac{1}{2}}(R_x/R_z) \sin 2\theta]|. \quad (3) \end{aligned}$$

The quantity  $F$  in (3) is defined in (2).

If we now define the leading aperture and beam edges,  $L$  and  $L'$ , and minimize their separation  $L - L'$  by a similar treatment, we obtain

$$\beta'_0 = -F \cdot \gamma_c/2 = -\beta_0. \quad (4)$$

Thus the locations of the aperture limits and diffracted beam edges are symmetrical about  $2\theta_0$  and  $\beta = 0$ . We may conclude that the present equation (3) should replace (D.9) of the previous publication. For the common experimental case  $R_x = R_z$  we find  $F = \sin \theta$ , and (3) reduces to

$$(\gamma_R)_{\min} = |2\gamma_m + \gamma_x + 2\gamma_c \sin \theta|. \quad (5)$$

The last term of (5) is Burbank's result.

For the  $\omega$  scan  $(\gamma_R)_{\min}$  must equal  $L'_{\max} - T'_{\min}$ , but owing to the symmetry about  $2\theta_0$  this is equivalent to  $2L'_{\max}$  or  $-2T'_{\min}$ . Thus

$$\begin{aligned} L' &= \beta(1 + (R_x/R_z) \cos 2\theta) \\ &\quad + [(\gamma_c/2) - \beta^2]^{\frac{1}{2}}(R_x/R_z) \sin 2\theta + \frac{1}{2}\gamma_x + \gamma_\lambda. \quad (6) \end{aligned}$$

Differentiation with respect to  $\beta$  and equation to zero leads to

$$\beta_0 = \frac{1 + (R_x/R_z) \cos 2\theta}{[(R_x/R_z) \sin 2\theta]^2 + (1 + (R_x/R_z) \cos 2\theta)^2} \cdot \gamma_c/2$$

$$= G \cdot \gamma_c/2, \quad (7)$$

from which

$$(\gamma_R)_{\min} = |2\gamma_\lambda + \gamma_x + \gamma_c [G(1 + (R_x/R_z) \cos 2\theta) + (1 - G^2)^{1/2} (R_x/R_z) \sin 2\theta]|. \quad (8)$$

Equation (8) may then replace (D.10) of the previous paper. For  $2\theta \rightarrow 0^\circ$  this expression reduces to (D.11). For  $R_x = R_z$  we note that  $G = \cos \theta$ , and (8) becomes

$$(\gamma_R)_{\min} = |2\gamma_\lambda + \gamma_x + 2\gamma_c \cos \theta|, \quad (9)$$

the last term of which is Burbank's result.

The effect of the revision of equations (D.9) and (D.10) is actually very small. Thus in Fig. 34 of the previous paper the end-points of the curves ( $2\theta = 0^\circ$  and  $180^\circ$ )

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**Refinement of an iron chromium boride with the  $Mn_4B$  structure.** By BRUCE E. BROWN and D. J. BEERNTSEN, *Materials Research, Allis-Chalmers Mfg. Company, Milwaukee 1, Wisconsin, U.S.A.*

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### Introduction

Several transition metal borides having the  $Mn_4B$  structure have been prepared in this laboratory as part of a study of the boride phases appearing in boron-containing chromium steels. Similar phases were studied by Andersson & Kiessling (1950), who reported an orthorhombic  $Cr_2B$  phase with space group  $Abmm$  or  $Abm2$ . Bertaut & Blum (1953) found the  $CuAl_2$  type structure for  $Cr_2B$  but also found the  $Mn_4B$  structure at  $Cr_2B$ . Aronsson & Aselius (1958) prepared  $Cr_2B$  with the  $Mn_4B$  structure, analogous to the material prepared in connection with the present project, and first reported that significant amounts of chromium could be replaced by iron. Beerntsen & Brown (to be published) found by quantitative extraction and extract analysis that over half of the chromium could be replaced by iron. Other variations of the  $Mn_4B$  structure attempted were  $(Cr,Mn)_2B$ ,  $(Cr,Co)_2B$ ,  $(Cr,Ni)_2B$ , and  $(Cr,V)_2B$ . Only with manganese and cobalt were significant solubilities observed in  $Cr_2B$ . Complete solubility might be expected only between  $Cr_2B$  and  $Mn_4B$  ( $Mn_2B$  has the  $CuAl_2$  structure) since none of the borides of vanadium, cobalt and nickel have the  $Mn_4B$  structure. Powder X-ray photographs of the manganese sample,  $CrMnB$ , can be interpreted on the basis of a single phase with the  $Mn_4B$  structure. It was estimated that about one quarter of the chromium could be replaced by Co in  $Cr_2B$ . The chromium took all the boron from the nickel preparation to yield  $CrB$  and free nickel. In the vanadium sample, the predominant product was  $V_3B_2$  in a smaller cell than when pure, apparently because of having dissolved significant amounts of chromium.

### Crystal preparation

The crystals for X-ray work were prepared by vacuum melting (melting point about  $1450^\circ C$ ) equimolar amounts

are unchanged; only at intermediate points they now rise more quickly with increasing  $2\theta$ . For  $\gamma_m = 0^\circ$ ,  $\gamma_x = 0.70^\circ$ , and  $\gamma_c = 0.1^\circ$  the maximum change is only 5%, while for small mosaic crystals the change is negligible. Attention is also drawn to the various practical factors which may necessitate aperture widths somewhat in excess of the minimal values specified by (3) and (9) (Alexander & Smith, 1962; Alexander & Smith, 1963).

### References

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of chromium, iron, and boron in a zirconia crucible. Ten minutes after melting occurred, the temperature was lowered to about  $100^\circ C$  below the melting point for 15 minutes and was then lowered to room temperature by furnace cooling. The composition of the well-developed crystals at the bottom of the 30 g ingot was 51.0% iron, 38.6% chromium and 8.1% boron giving a formula of  $Fe_{1.1}Cr_{0.9}B_{0.9}$  assuming  $Fe + Cr = 2.0$ . The orthorhombic cell dimensions from precession photographs were

$$a = 14.57, \quad b = 7.32, \quad c = 4.22 \text{ \AA}.$$

### Refinement

The  $Mn_4B$  structure (Kiessling, 1950) is in space group  $Fddd$  with 32 metal atoms on two sets of special positions, 16(e) and 16(f). The boron atoms are on a second set of 16(e) positions. All boron sites are occupied in  $FeCrB$  as in  $Cr_2B$  in contrast to  $Mn_4B$  where eight boron atoms must be distributed among sixteen sites. Ordering of iron and chromium was tested by means of a least-squares refinement.

X-ray intensity data were gathered by a peak intensity method from photographs made by the Weissenberg technique. Three levels about the  $a$  axis and six levels about the  $c$  axis were measured, giving a total of 335 separate reflections. A crystal was made into a sphere with a Bond sphere grinder (Bond, 1951), and absorption corrections were made from tables for spherical crystals (Evans & Ekstein, 1952). The intensities were also corrected for Lorentz-polarization,  $\alpha_1$ ,  $\alpha_2$  separation, and upper level Weissenberg extension contraction effects (Phillips, 1956).

In space group  $Fddd$  the  $y$  and  $z$  parameters are fixed for position (e) and the  $x$  and  $z$  parameters are fixed for position (f). Only three positional parameters are variable, one per atom of the asymmetric unit. Ordering can occur such that: (1) iron is on (e), chromium