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Sur les paramètres limites de la phase FeO.

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Dans le mémoire paru récemment dans cette Revue et intitulé 'Change of structure of ferrous oxide at low temperature' Willis & Rooksby (1953) ont étudié les variations du paramètre limite de la phase FeO en présence d'un excès de Fe ou de Fe_3O_4. Les valeurs obtenues à différentes températures comprises entre 570° C. et 1200° C. sont rassemblées dans la Fig. 1 de leur mémoire et comparées aux résultats obtenus antérieurement d'une part par Jette & Foote (1933*a*, *b*) et d'autre part par Bénard (1937, 1939). L'intérêt de cette confrontation se trouve malheureusement amoindri du fait que, en ce qui concerne la contribution de Bénard, Willis & Rooksby se réfèrent seulement à des publications concernant des travaux préliminaires qui furent interrompus par la guerre et passent sous silence un mémoire ultérieur très détaillé publié en 1949 (Bénard, 1949). En effet, si l'on compare les résultats décrits dans ce dernier aux résultats des auteurs précités, on constate qu'un accord très satisfaisant s'établit dans l'ensemble.

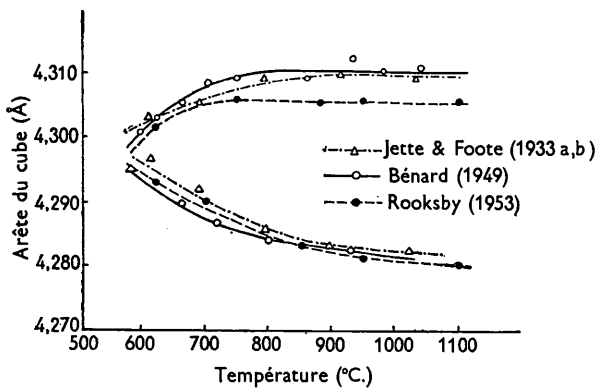

Fig. 1. Variation du paramètre limite de la phase FeO en présence d'un excès de Fe ou de Fe_3O_4, en fonction de la température.

Les valeurs originales des paramètres indiquées dans les mémoires de Jette & Foote et de Bénard ont été corrigées de manière à pouvoir être comparées aux valeurs de Rooksby qui sont données dans l'échelle absolue (Fig. 1). En ce qui concerne les paramètres de la phase FeO saturée d'oxygène, les trois courbes sont pratiquement superposées, l'écart moyen n'excédant pas 0,003 Å. En ce qui concerne les paramètres de la phase saturée de fer, l'accord entre les résultats de Jette & Foote et ceux de Bénard est excellent dans toute l'échelle des températures; un léger écart se manifeste toutefois dans les valeurs de Rooksby au délà de 700° C., cet écart étant de l'ordre de 0,005 Å à 1000° C. Si l'on tient compte des difficultés expérimentales auxquelles on se heurte lorsqu'il faut—comme dans le cas présent—éviter rigoureusement au cours du refroidissement toute variation du paramètre de FeO qui pourrait résulter de la précipitation de Fe ou de Fe_3O_4 proeutectoïdes, la convergence de ces résultats doit être considérée comme extrêmement satisfaisante.

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On the basic assumptions and the validity of Zachariasen's sign relations in X-ray crystal analysis.*

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Lavine (1952) has questioned the proof presented by Zachariasen (1952) in the latter's derivation of sign relations between structure factors in X-ray crystal analysis. Since the validity of Zachariasen's relation (11),

$$S_H = S(\overline{S_{K_i} S_{H+K_i}}),$$

has been demonstrated in a number of complex structure determinations, it has seemed wise to re-analyze the problem, while re-examining its basic assumptions.

Zachariasen's basic equality is expressible in the form

$$(U_H \pm U_K)^2 = 1 + U_{H+K} U_{H-K} \pm (U_{H+K} + U_{H-K}) - D_{\sin}^{\cos}, \quad (1)$$

where

$$D\cos = 8 \sum_{i=1}^{\frac{1}{2}N} \sum_{j=1}^{\frac{1}{2}N} n_i n_j \begin{vmatrix} \cos \tfrac{1}{2}(\mathbf{H}+\mathbf{K}).\mathbf{r}_i \cos \tfrac{1}{2}(\mathbf{H}-\mathbf{K}).\mathbf{r}_i \\ \cos \tfrac{1}{2}(\mathbf{H}+\mathbf{K}).\mathbf{r}_j \cos \tfrac{1}{2}(\mathbf{H}-\mathbf{K}).\mathbf{r}_j \end{vmatrix}^2 \quad (2)$$

holds for the + sign in (1). $D\sin$ has the form of (2), but with sines replacing cosines, and holds in (1) for the − sign.

In his derivation of the sign-limiting relation, Zachariasen replaces U_H by U_{H+K_i}, and averages the basic

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identity over all K_i. Let us instead use (2) directly, holding U_H constant and varying the index **K**. We will not expand the determinants $D_{\sin}^{\cos}$ at this point.

Assuming that

$$\overline{U_K} = 0\,, \tag{3}$$

and similarly that

$$\overline{U_{H+K}} = \overline{U_{H-K}} = 0\,,$$

one obtains immediately from (1):

$$\overline{D\cos} = \overline{D\sin} = 1-|U_H|^2-\overline{|U_K|^2}+\overline{U_{H+K}U_{H-K}}\,. \tag{4}$$

Zachariasen introduces the terms S_H and S_K for the signs of U_H and U_K respectively, which permits him to write equation (1) in the form

$$(|U_H|+|U_K|)^2 = 1+U_{H+K}U_{H-K}+S_HS_K(U_{H+K}-U_{H-K})-D_{\sin}^{\cos}\,. \tag{5}$$

Averaging over all K, this becomes

$$\overline{(|U_H|+|U_K|)^2} = 1+\overline{U_{H+K}U_{H-K}}+S_H.\overline{S_K(U_{H+K}-U_{H-K})}-\overline{D_{\sin}^{\cos}}\,. \tag{6}$$

If one immediately assumes that $\overline{D_{\sin}^{\cos}}$ in (6) is the equivalent of $\overline{D\cos}$ and $\overline{D\sin}$ in (4), one is led directly to Zachariasen's important sign relation. For, substituting (4) in (6), we find

$$2|U_H|\overline{|U_K|} = S_H.\overline{S_K(U_{H+K}+U_{H-K})}\,. \tag{7}$$

If we choose the sign of K properly, we can always write

$$|U_{H+K}| > |U_{H-K}|\,. \tag{8}$$

Then $U_{H+K}+U_{H-K}$ will have the sign of U_{H+K}, i.e. S_{H+K}. Since the left side of (7) is positive, we have

$$S_H.\overline{S_KS_{H+K}} \geqslant 0\,, \tag{9}$$

or

$$S_H = S(\overline{S_KS_{H+K}})\,, \tag{10}$$

which is Zachariasen's relation.

One other result is implied by (7). Since the left side of (7) is of second order in unitary structure factors, whose absolute values are always less than 1, and the right side involves only first-order terms, the right member of (7) is likely to be a *difference*: consequently, using (8), we have that

$$S_H.\overline{S_KS_{H+K}} \text{ is } \textit{likely} \text{ to be positive,} \tag{11a}$$

and

$$S_H.\overline{S_KS_{H-K}} \text{ is } \textit{likely} \text{ to be negative.} \tag{11b}$$

These conditions lead to the relations:

$$S_H \simeq S(\overline{S_KS_{H+K}}) \tag{12a}$$

and

$$S_H \simeq -S(\overline{S_KS_{H-K}})\,. \tag{12b}$$

The first of these, (12*a*), is of course the same as (10). Its extreme usefulness has been demonstrated by Zachariasen (1952), and in other analyses which are unpublished at this writing. In applying it, one begins by selecting structure factors satisfying the condition that $|U_H|+|U_K|+|U_{H+K}|$ is as large as possible. Where, alternatively, $|U_H|+|U_K|+|U_{H-K}|$ is large, (12*b*) may prove useful.

Re-examination of $\overline{D_{\sin}^{\cos}}$

The following objection can be made to the above, however. Whereas $\overline{D\cos}$ of (4) is the mean value of (2) over *all* values of K involved, a $D\cos$ term is encountered in (5) only when $S_H = S_K$, and a $D\sin$ term only when $S_H = -S_K$. Thus the mean value of D in (6) *may differ* from that in (4). We must, therefore, further examine the conditions under which (7) holds.

Let us denote by A the field of K values, p in number, for which $S_K = S_H$; and denote by B the field of K values, of which there are q, for which $S_K = -S_H$. Then we have

$$\overline{D^A} = \frac{1}{p}\sum_{j=1}^{p} D_j^A\,; \quad \overline{D^B} = \frac{1}{q}\sum_{j=1}^{q} D_j^B\,. \tag{13}$$

Also,

$$\overline{D\sin} = \frac{p}{p+q}\,\overline{D_{\sin}^A} + \frac{q}{p+q}\,\overline{D_{\sin}^B}\,, \tag{14}$$

with a similar equation holding for $\overline{D\cos}$.

The equality (6) then has the following actual value over the entire field $A+B$:

$$\overline{(|U_H|+|U_K|)^2} = 1+S_H.\overline{S_K(U_{H+K}+U_{H-K})}+\overline{U_{H+K}U_{H-K}} - \frac{p}{p+q}\,\overline{D_{\cos}^A} - \frac{q}{p+q}\,\overline{D_{\sin}^B}\,. \tag{15}$$

If we insert the value of $\overline{D\sin}$ from (14) in (4), and subtract (4) from (15), we obtain

$$2|U_H|\overline{|U_K|} = S_H.\overline{S_K(U_{H+K}+U_{H-K})}+\frac{p}{p+q}\left(\overline{D_{\sin}^A}-\overline{D_{\cos}^A}\right). \tag{16}$$

We must now find the mean value of

$$\Delta = D_{\sin}^A - D_{\cos}^A\,. \tag{17}$$

Expanding the sin and cos forms of (2), one finds that Δ is proportional to

$$\sum_i\sum_j\sum_k n_in_j\cos Hr_j\,(\cos Kr_j - \cos Kr_i) \tag{18}$$

in the field of A.

The mean value of Δ would evidently be zero if

$$\overline{\cos Kr_j}^K = \overline{\cos Kr_i}^K\,, \tag{19}$$

where $\overline{}^K$ indicates the mean value over all K in the field A. Equation (19) implies that *the mean phase contribution* $\overline{\cos Kr_i}^K$ *in the field of constant sign of* U_K *is the same for every kind of atom.* This is the condition under which relation (7) holds.

Thus the basic condition implicit in Zachariasen's analysis is that the structure to which it is applied is comprised of many atoms, in general positions. The condition is more or less implied in the title to Zachariasen's original paper.

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