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Determination of Stacking Faults in the Spinel-Type Lattice

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Full dislocations in a lattice of spinel type are dissociated into half and quaternary dislocations. In view of this, the common theory for f.c.c. crystals does not apply to stacking faults in spinel. Diffraction effects in the presence of half and quaternary dislocations are considered and expressions for the estimation of the probability of their appearance obtained. The results of calculations allow one to explain the broadening of lines on the magnesium spinel diffractogram and on that of γ-Al_2O_3.

On diffractograms of magnesium spinel obtained by the crystallization of glass ceramic as well as on those of the annealed hydroxide $Al_2O_3.4H_2O$ slightly broadened 400 and 440 lines are observed. The rest of the lines are abnormally broadened (Fig. 1). This effect seems to be associated with stacking faults but it cannot be explained on the basis of the generally recognized theory of stacking faults in f.c.c. crystals (Warren, 1959), because for f.c.c. crystals it is precisely the 400 line that should be broadened most of all.

The explanation lies in the fact that dissociation of full dislocations in the spinel lattice proceeds otherwise than in ordinary f.c.c. structures. According to Hornstra (1960*a*, *b*) dissociation of dislocations in the spinel lattice due to the presence of vacancies in the sublattice of cations results in the formation of half and quaternary dislocations (Fig. 2). As shown in Fig. 3 there are six half dislocations with $\bar{\mathbf{\Delta}}_K^{(1)}$ Burgers vectors, each having a probability of γ, one of which is represented in Fig. 3 by a full line.

There are 18 quaternary dislocations with $\bar{\boldsymbol{\delta}}_i$ Burgers vectors. From the point of view of probability of their appearance these dislocations should be combined in six sets of three since each set occurs simultaneously as a result of full dislocation dissociation. One set includes for instance $\bar{\boldsymbol{\delta}}_1$, $\bar{\boldsymbol{\delta}}_2$ and $\bar{\boldsymbol{\delta}}_3$ dislocations (Fig. 3). The probability of error due to a set of dislocations will be taken as α. We are interested not in dislocations themselves but in displacements of atoms in the faulty zone relative to the perfect lattice. It is evident that $\bar{\mathbf{\Delta}}_i^{(2)}$ displacement vectors for a set of dislocations shown by the full line in Fig. 3 are

$$\bar{\mathbf{\Delta}}_1^{(2)}=\bar{\boldsymbol{\delta}}_1=\tfrac{1}{6}\mathbf{A}_1+\tfrac{1}{3}\mathbf{A}_2;$$
$$\bar{\mathbf{\Delta}}_2^{(2)}=\bar{\boldsymbol{\delta}}_1+\bar{\boldsymbol{\delta}}_2=\tfrac{1}{2}\mathbf{A}_2;$$
$$\bar{\mathbf{\Delta}}_3^{(2)}=\bar{\boldsymbol{\delta}}_1+\bar{\boldsymbol{\delta}}_2+\bar{\boldsymbol{\delta}}_3=\tfrac{1}{6}\mathbf{A}_1+\tfrac{5}{6}\mathbf{A}_2\,.$$

[We ignore the synchronous shift according to Hornstra (1960*a*, *b*) since it must give diffuse scattering of the Suzuki atmosphere type.]

Let us consider the products of structural amplitudes and their probabilities. We shall choose the origins of packet coordinates in different layers at the same point along the $\mathbf{A}_1$ and $\mathbf{A}_2$ axes. Structural amplitudes of packets in the A, B and C layers are

$$F_A=F_0;\quad F_B=F_0\exp\left(i2\pi\frac{H-K}{3}\right);$$
$$F_C=F_0\exp\left(-i2\pi\frac{H-K}{3}\right).$$

When the packet and all overlying packets are displaced owing to the movement of dislocations F is changed to the factor $\exp(-i2\pi\bar{\mathbf{S}}\,.\,\bar{\mathbf{\Delta}})$ where $\bar{\mathbf{\Delta}}=\bar{\mathbf{\Delta}}_K^{(1)}$ or $\bar{\mathbf{\Delta}}=\bar{\mathbf{\Delta}}_K^{(2)}$ depending on the type of dislocation. We shall denote the structural amplitude by F_n^i where the lower index refers to the layer in which the packet in question was situated before any displacement, and the upper one to the value and direction of the displacement after the dislocation has passed. Possible changes of the upper indices of F^i packets (and consequently, structural amplitudes) while passing from a packet in the 0 layer to a packet in the m layer are shown in Fig. 4. It can be seen that the probability of retaining the upper indices is proportional to $1-6m\alpha-6m\gamma$, the probabilities that the upper index is changed to $\bar{\mathbf{\Delta}}_K^{(1)}$ or to a combination of $\bar{\mathbf{\Delta}}_1^{(2)}$, $\bar{\mathbf{\Delta}}_2^{(2)}$ and $\bar{\mathbf{\Delta}}_3^{(2)}$ being proportional

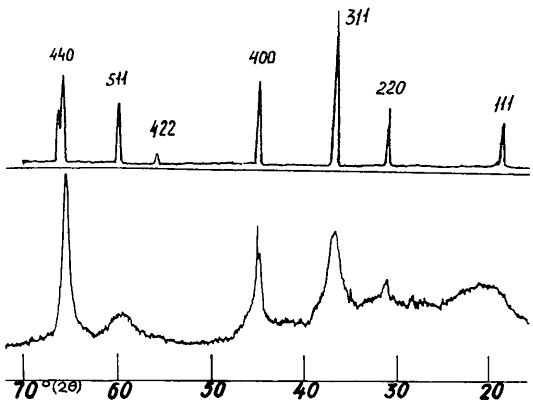

Fig. 1. The diffractogram of magnesium spinel obtained by sital crystallization.

to $m\gamma$ and $m\alpha$ respectively. The upper indices between packets cannot differ by more than $\bar{\Delta}_K$; otherwise more than one stacking fault must pass between the 0 and m packets, the probability of which, with the usual assumption of α and γ small ($\alpha^2 \simeq \gamma^2 \simeq \alpha\gamma \simeq 0$), can be ignored.

In the case of $n=p$; $i=j$; $F_nF_p^*=F_0^2$; the probability of this combination equals the product of the probabilities that in m and 0 layers there are packets with the same lower indices and that they also have the same upper indices; the former probability is

$$P_m^0=\tfrac{1}{3}\left[1+(-1)^m 2\cos\frac{\pi}{3}m\right],$$

the latter is $1-6m\alpha-6m\gamma$. Thus the contribution of these combinations to the mean product of structural amplitudes $\langle F_nF_K^*\rangle$ is $P_m^0F_0^2(1-6m\alpha-6m\gamma)$.

When $n=p$; $i\neq j$, for each packet in the 0 layer there are 12 packets in the m layer displaced relative to the 0 layer by $\bar{\Delta}_K^{(1)}$ or $\bar{\Delta}_K^{(2)}$. Consequently, the contribution of these combinations to $\langle F_nF_K^*\rangle$ is

$$P_m^0F_0^2\left[\frac{\alpha m}{3}\sum_{K=1}^{18}\exp(-i2\pi\mathbf{S}.\bar{\Delta}_K^{(2)})+\gamma m\sum_{K=1}^{6}\exp(-i2\pi\mathbf{S}.\bar{\Delta}_K^{(1)})\right].$$

The factor $\frac{1}{3}$ was taken here because the shift areas under dislocations from $\bar{\Delta}_1^{(2)}$, $\bar{\Delta}_2^{(2)}$ and $\bar{\Delta}_3^{(2)}$ combinations were assumed to be equal.

If $n\neq p$, *e.g.* $n=A$, $p=B$, and $i=j$, the contribution to $\langle F_nF_K^*\rangle$ equals

$$P_m^+F_0^2\exp\left(-i2\pi\frac{H-K}{3}\right)(1-6m\alpha-6m\gamma);$$

and when $i\neq j$ the contribution is

$$P_m^+F_0^2\exp\left(-i2\pi\frac{H-K}{3}\right)$$
$$\times\left[\frac{\alpha m}{3}\sum_{K=1}^{18}\exp(-i2\pi\mathbf{S}.\bar{\Delta}_K^{(2)})+\gamma m\sum_{K=1}^{6}\exp(-i2\pi\mathbf{S}.\bar{\Delta}_K^{(1)})\right].$$

If $n\neq p$, *e.g.* $n=A$, $p=C$, and $t=j$, the contribution $\langle F_nF_K^*\rangle$ is

$$P_m^-F_0^2\exp\left(i2\pi\frac{H-K}{3}\right)(1-6m\alpha-6m\gamma);$$

and when $i\neq j$ this contribution is

$$P_m^-F_0^2\exp\left(i2\pi\frac{H-K}{3}\right)\left[\frac{\alpha m}{3}\sum_{K=1}^{18}\exp(-i2\pi\mathbf{S}.\bar{\Delta}_K^{(2)})+\gamma m\sum_{K=1}^{6}\exp(-i2\pi\mathbf{S}.\bar{\Delta}_K^{(1)})\right].$$

P_m^+ and P_m^- are accordingly the probabilities of a packet in the m layer before any displacement in the ABC alternation being subsequent or precedent in relation to the packet in the 0 layer. As shown by Kagan & Baurova (1968),

$$P_m^+=\tfrac{1}{3}\left[1-(-1)^m\left(\cos\frac{\pi}{3}m+\sqrt{3}\sin\frac{\pi}{3}m\right)\right];$$

$$P_m^-=\tfrac{1}{3}\left[1-(-1)^m\left(\cos\frac{\pi}{3}m-\sqrt{3}\sin\frac{\pi}{3}m\right)\right].$$

Summing $\langle F_nF_K^*\rangle$ values for all p, n, i and j combinations we obtain for $m>0$

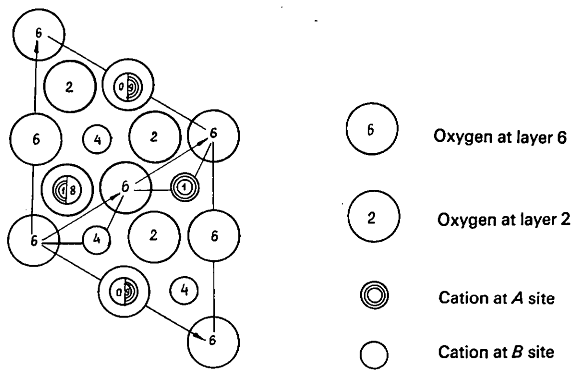

Fig. 2. Diagram of the spinel crystal structure and the arrangement of partial dislocations. The numbers refer to the layers.

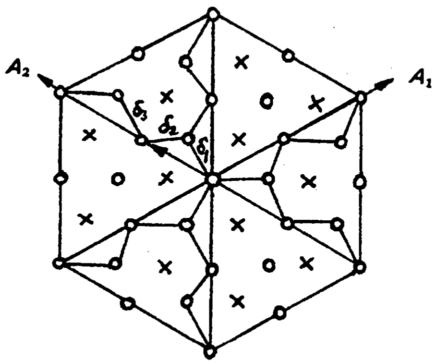

Fig. 3. Diagram illustrating the dissociation of full dislocations into partial ones.

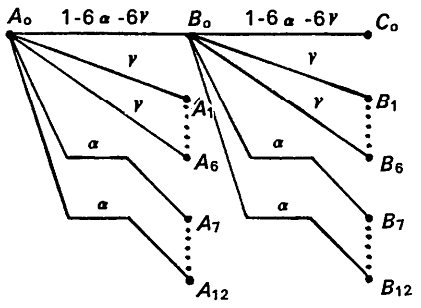

Fig. 4. Diagram for the calculation of probability of faults.

$$\langle F_nF_K^*\rangle = F_0^2\left[P_m^0 + P_m^+ \exp\left(-i2\pi\frac{H-K}{3}\right) + P_m^- \exp\left(i2\pi\frac{H-K}{3}\right)\right]$$
$$\times\left[1-6m\gamma-6m\alpha+m\gamma\sum_{K=1}^{6}\exp(-i2\pi\bar{\mathbf{S}}.\bar{\Delta}_K^{(1)}) + \frac{m\alpha}{3}\sum_{K=1}^{18}\exp(-i2\pi\bar{\mathbf{S}}.\bar{\Delta}_K^{(2)})\right]$$
$$= F_0^2[A(m)+iB(m)];$$

$$m\gamma\sum_{K=1}^{6}\exp(-i2\pi\bar{\mathbf{S}}.\bar{\Delta}_K^{(1)}) = m\gamma q_1;$$

$$\frac{\alpha m}{3}\sum_{K=1}^{18}\exp(-i2\pi\bar{\mathbf{S}}.\bar{\Delta}_K^{(2)}) = \frac{\alpha m}{3}\left[q_1+q_2\exp\left(-i2\pi\frac{H-K}{6}\right)\right],$$

where

$$q_1 = 2[\cos\pi H + \cos\pi K + \cos(\pi H)\cos(\pi K)];$$
$$q_2 = 4(1+\cos\pi H+\cos\pi K);$$

$$A(m) = \left[P_m^0+(P_m^+ + P_m^-)\cos 2\pi\frac{H-K}{3}\right]\times\left[1-6m\alpha-6m\gamma+\frac{m\alpha}{3}q_1 + \frac{m\alpha}{3}q_2\cos\left(2\pi\frac{H-K}{6}\right)+m\gamma q_1\right]$$
$$+[P_m^- - P_m^+]\sin\left(2\pi\frac{H-K}{3}\right)\frac{m\alpha}{3}q_2\sin 2\pi\frac{H-K}{6};$$

$$B(m) = (P_m^- - P_m^+)\sin\left(2\pi\frac{H-K}{3}\right)\times\left[1-6m\alpha-6m\gamma+\frac{m\alpha}{3}q_1+\frac{m\alpha}{3}q_2\cos\left(2\pi\frac{H-K}{6}\right)+m\gamma q_1\right]-\left[P_m^0+(P_m^+ - P_m^-)\cos 2\pi\frac{H-K}{3}\right]$$
$$\times\frac{m\alpha}{3}q_2\sin 2\pi\frac{H-K}{6}.$$

Hence, using

$$I=\sum\langle F_nF_K^*\rangle\exp\left(i2\pi\frac{H}{3}m\right)$$

(Wilson, 1949), we shall obtain the intensity of scattering at $H-K=3M$:

$$I(H,K,h) = F_0^2\sum_{m=-\infty}^{\infty}\left[1-6m\gamma\left(1-\frac{q_1}{6}\right) - 6m\alpha\left(1-\frac{q_1}{18}-\frac{q_2}{18}\cos\pi M\right)\right]\cos 2\pi\frac{h}{3}m.$$

(This expression is used if

$$H-K=3M,\ \cos 2\pi\frac{H-K}{6}=\cos\pi M,\ \sin 2\pi\frac{H-K}{6}=0,$$

and when

$$H-K=3M\pm1,\quad \cos 2\pi\frac{H-K}{6}=\tfrac{1}{2}\cos\pi M,\quad \sin 2\pi\frac{H-K}{6}=\pm\frac{\sqrt{3}}{2}\cos\pi M.)$$

Using the formula for intensity (Guinier, 1961):

$$I=F_0^2\sum_{m=-\infty}^{\infty}A(m)\cos 2\pi hm - F_0^2\sum_{m=-\infty}^{\infty}B(m)\sin 2\pi h|m|,$$

we shall obtain the intensity of scattering at $H-K=3M\pm1$:

$$I(H,K,h)=F_0^2\sum_{m=-\infty}^{\infty}\left[1-6m\gamma\left(1-\frac{q_1}{6}\right)-6m\alpha\left(1-\frac{q_1}{18}-\frac{q_2}{36}\cos\pi M\right)\right]\times\cos 2\pi m\left(\frac{h\mp1}{3}\mp\frac{\alpha\sqrt{3}}{4\pi}\frac{q_2}{3}\cos\pi M\right)$$

[assuming that, as α is small, $\sin\alpha\simeq\alpha$; $(1-a\alpha)\alpha\simeq\alpha$].

Hence Fourier coefficients and displacements of lines for different H, K and M combinations can be calculated (Table 1).

Hence, it is seen that half and quaternary dislocations result in the broadening of nodes with $H-K=3M$ except that, M even, quaternary dislocations result in different broadening of different nodes and that half dislocations do not broaden nodes with even H and K.

Summing by $K_{hkl}=[\sum(a'\alpha+b'\gamma)|L|]/(u+b)h_0$ (Warren, 1959) we obtain mean Fourier coefficients for the

Table 1. *Fourier coefficients and line displacements for various combinations of H, K and M*

$H-K$	M	H and K	Fourier coefficient	Δ
$3M$	Even	Even	1	0
	Uneven	Uneven	$1-8m\alpha-8m\gamma$	0
	Uneven	Mixed	$1-8m\alpha-8m\gamma$	0
$3M+1$	Even	Mixed	$1-6m\alpha-8m\gamma$	$-\frac{1}{\sqrt{3}\pi}\alpha$
	Uneven	Even	$1-6m\alpha$	$+\frac{\sqrt{3}}{\pi}\alpha$
		Uneven	$1-6m\alpha-8m\gamma$	$-\frac{1}{\sqrt{3}\pi}\alpha$
$3M-1$	Even	Mixed	$1-6m\alpha-8m\gamma$	$+\frac{1}{\sqrt{3}\pi}\alpha$
	Uneven	Even	$1-6m\alpha$	$-\frac{\sqrt{3}}{\pi}\alpha$
		Uneven	$1-6m\alpha-8m\gamma$	$+\frac{1}{\sqrt{3}\pi}\alpha$

Table 2. *Mean Fourier and line-displacement coefficients for the diffraction lines of spinel*

hkl	K_{hkl}	$\frac{\sum \pm \Delta L_0}{(u+b)h_0^2}$
111	$2{\cdot}60\alpha+3{\cdot}46\gamma$	$+0{\cdot}046\alpha$
220	$4{\cdot}26\alpha+5{\cdot}66\gamma$	$+0{\cdot}046\alpha$
311	$6{\cdot}33\alpha+6{\cdot}63\gamma$	$-0{\cdot}033\alpha$
400	$6{\cdot}00\alpha$	$-0{\cdot}138\alpha$
422	$4{\cdot}90\alpha+6{\cdot}53\gamma$	0
333	$3{\cdot}46\alpha+3{\cdot}46\gamma$	0
511	$6{\cdot}06\alpha+5{\cdot}00\gamma$	$-0{\cdot}053\alpha$
440	$4{\cdot}24\alpha$	$+0{\cdot}069\alpha$

lines of spinel and by $(\sum \pm \Delta L_0)/(u+b)h_0^2$ obtain the mean coefficient of displacement of the lines (Table 2).

The data given in Table 2 fully correspond to the broadening of the lines shown in Fig. 1 and are evidence of the fact that the lattice of magnesium spinel mainly contains half partial dislocations.

The proof of the existence of quaternary dislocations is the result obtained from γ-Al_2O_3 spinel. This spinel is obtained by annealing the hydrooxide $Al_2O_3.4H_2O$ at temperatures of 650, 800 and 900°C for periods of 4 h. When a diffractogram has a form similar to that shown in Fig. 1 but with broadened 400 and 440 lines, displacement of these lines is also observed. By a method proposed by Kovalsky & Pivovarov (1960) stacking faults were estimated from the displacements of lines and appeared to be at the temperatures 650, 800 and 900°C 0·010, 0·021 and 0·027 respectively (calculated for six quaternary dislocations). The transition temperature to a hexagonal phase is 1100–1260°C. Consequently, in approaching this temperature the number of errors associated with estimated quaternary dislocations increase. Besides, it should be noted that according to Hornstra (1960*a*, *b*) in the presence of half dislocations the cubic structure is maintained while quaternary dislocations lead to hexagonal interlayers.

In conclusion it should be noted that the probability of stacking faults occurring in spinel was earlier incorrectly estimated according to the theory for usual f.c.c. structures (Fagherazzi & Lanzavecchia, 1969; Gorter, 1957). Strinkhaut & Rao (1972) showed that the common theory of the influence of stacking faults on X-ray diffractograms cannot be applied to spinel, however, no solution was given as to what the diffraction effects in the case of half and quaternary dislocations would be. The first attempt at such a theory was made by Kagan, Portnoi & Fadeeva (1974) who took two quarternary dislocations into account, but their attempt does not give the correct quantitative results either.

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