Studies of the Cation Atom Distribution in ZnCr\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4} Spinels using the Channeling Effect in Electron-Induced X-ray Emission

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Abstract
The channeling effect in electron-induced X-ray emission has proved useful as a method to get immediate information about the cation atom distribution between octahedral and tetrahedral positions in the recently synthesized spinels: ZnCr\textsubscript{0.4}Fe\textsubscript{1.6}O\textsubscript{4}, ZnCrFeO\textsubscript{4} and ZnCr\textsubscript{1.6}Fe\textsubscript{0.4}O\textsubscript{4}. It is concluded that the Zn atoms are in tetrahedral positions and the Cr atoms in octahedral positions. The Fe atoms also have a strong octahedral site preference, but the analysis indicates that ~50% of them are in tetrahedral positions.

I. Introduction
The distribution of the cation atoms between octahedral and tetrahedral positions in spinels is a classic problem in crystallography. Often cations which are neighbors in the periodic system are involved. Most of these problems can now be solved by neutron diffraction, anomalous scattering of X-rays or a combination of different methods. For the present work a rapid and inexpensive technique, the channeling or Borrmann effect in electron-induced X-ray emission, has been used to study the cation distribution in ZnCr\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4} spinels. The main aim of the investigation is to find out to what extent this method is useful for the determination of the positions of atoms in crystals.

This channeling effect is observed through a variation of the rate of characteristic X-ray emission with crystallographic direction of the incident electron beam. In crystals containing more than one type of atom, so orientated that the different types of atoms are distinguished in the projected structure, the electron intensity maxima may be localized at one or other type of atom, depending on the crystallographic direction of the incident beam. Hence the ratio between the characteristic X-ray emission intensities will change with incident beam direction (Tafto, 1979).

It was pointed out by Cowley (1964) and Gjønnes & Høier (1971) that this effect could be used to get information about the crystallographic position of atoms in crystals. Until now studies have been restricted to known structures, however, for the purpose of gaining insight into the phenomenon itself. On the other hand, a similar effect with X-rays as the incident wave (Batterman, 1964) was used to determine the site of a small amount of foreign atoms in a large perfect crystal more than ten years ago (Batterman, 1969).

We have used the orientation dependence of the electron-induced X-ray emission to study the cation distribution in spinels with compositions ZnCr\textsubscript{0.4}Fe\textsubscript{1.6}O\textsubscript{4}, ZnCrFeO\textsubscript{4} and ZnCr\textsubscript{1.6}Fe\textsubscript{0.4}O\textsubscript{4}.

II. Summary of the theory
A detailed treatment of the channeling effect in electron-induced X-ray emission has been given by Cherns, Howie & Jacobs (1973). For a parallel electron beam with crystallographic direction $\mathbf{k}$, incident on a crystal the rate of characteristic X-ray emission may be written

$$\int \int B(\mathbf{r}) I(\mathbf{k}, \mathbf{r}, z) \, dr \, dz,$$

where $B(\mathbf{r})$ is the probability that a fast electron at the coordinate $\mathbf{r}$ in the projected unit cell will produce the characteristic X-ray under consideration. $I(\mathbf{k}, \mathbf{r}, z)$ is the electron intensity distribution over the projected...
unit cell a distance \( z \) from the entrance surface measured along the incident beam direction and \( t \) is the value of \( z \) at the exit surface.

Assuming \( B(r) \) to be localized at the mean atomic position, i.e. \( B(r) = B_0 \delta (r) \), the rate of emission of characteristic photons from element \( A \) is

\[
N(k_i) \sim \int_0^t I(k_i, r, z) \rho_i \, dz, \tag{2}
\]

where \( \rho_i \) is the site occupancy at the coordinate \( r_i \) in the projected structure for element \( A \). Hence, for a known structure the problem of calculating the variation of the X-ray emission with incident direction \( (k_i) \) is reduced to that of calculating the intensity distribution of the fast electrons in the crystal.

For this purpose it is convenient to divide the electron intensity into two parts:

\[
l(r, z) = I_c(r, z) + I_d(r, z), \tag{3}
\]

where \( I_c(r, z) \) is the intensity due to the electrons which have not undergone diffuse scattering at a distance \( z \) from the entrance surface and \( I_d(r, z) \) is the intensity contribution from the electrons which have been diffusely scattered. If the probability of scattering out of the Bragg reflections, i.e. the absorption parameters, is known, \( I_c(r, z) \) can be calculated quite accurately either by the Cowley–Moodie multislice method (see, for example, Cowley, 1975) or by the Bloch-wave method. The remaining electrons, \( I_d(r, z) \), are assumed to behave like a plane wave on the average in producing X-rays (Hall, 1966):

\[
l_d(r, z) = I(z) = 1 - \int I_c(r, z) \, dr, \tag{4}
\]

where the total intensity has been normalized to unity.

In the Bloch-wave description the amplitude at depth \( z \) in the crystal for the electrons not having undergone diffuse scattering may be written as a linear combination of Bloch waves

\[
\Psi_c(r, z) = \sum_j C_j \exp \left( -\mu_j z \right)
\]

where \( C_j \) are reciprocal-lattice vectors and \( \mu_j \) Bloch-wave coefficients. \( C_j \) is the excitation strength of the \( j \)th Bloch wave at the entrance surface and \( \mu_j \) the anpassung. A simplified expression for the intensity modulation over the projected unit cell is obtained by neglecting the interference term between the Bloch waves, caused by the different \( \mu_j \), and the absorption. Then we get from (5)

\[
l(r) = \Psi(r) \Psi^*(r) = \sum_j |C_j|^2 \sum_g C_g \exp (2\pi i g \cdot r)^2. \tag{6}
\]

This would have been the thickness average of the intensity at coordinate \( r \) in the projected unit cell for a crystal without diffuse scattering (i.e. \( \mu_j = 0 \)).

For a qualitative understanding of this effect the two-beam approximation, which can be solved analytically, is useful (Hirsch, Howie & Whelan, 1962). In the two-beam approximation two Bloch waves are excited. In a simple planar case where all atomic planes are equidistant and identical one of the Bloch waves is concentrated at the atomic planes and the other midway between them when the incident beam direction is such that the first-order reflection is close to the Ewald sphere. For negative excitation error for the first-order reflection (i.e. the incident beam inside the corresponding Kikuchi band), the Bloch wave concentrated at the atomic planes is strongly excited whereas for positive excitation error the Bloch wave with intensity maxima in the middle of the channel is strongly excited. A two-beam calculation [based on (6)] of the variation of the intensity at the atomic planes and in the middle of the channel as a function of the deviation from the Bragg reflecting position is shown in Fig. 1. These curves are the same when there are atoms in the middle of the channel as long as the sign of the structure factor as referred to the original origin does not change.

### III. Experiment

The (100) planar case of \( \text{ZnCr}_x\text{Fe}_{2-x}\text{O}_4 \) spinels was studied. Along the [100] direction the main atomic planes contain the octahedral atoms, i.e. all oxygen atoms and 2/3 of the cations. The tetrahedral atoms (1/3 of the cations) are midway between the planes containing the octahedral atoms (Fig. 2).

The experiments were done with a Tracor Northern energy-dispersive X-ray spectrometer attached to a Philips 400T electron microscope which was fitted

Fig. 1. Two-beam calculations of the variation of current density at the atomic position (full line) and midway between the atoms (dotted line) with deviation from the Bragg reflecting position for the first-order reflection in a simple planar case. \( K \) is the wave vector of the incident electron, \( U_0 \) the Fourier potential and \( s \) the excitation error.
with a LaB$_6$ filament with 100 keV incident electrons. The specimens were grown by chemical transport with Cl$_2$ as the transport agent and were crushed in an agate mortar to fragments of several micrometers. A suspension of these crystals in acetone was placed on a copper grid covered with a holey carbon film. To reduce the X-ray contribution from the specimen chamber, a double-tilt specimen holder coated with beryllium was used. Thin areas at the edges of the grains, often wedge-shaped, were analyzed. The thickness was estimated to be typically in the range 500–1000 Å and the illuminated area about a few thousand ångströms in diameter. For each composition (i.e., ZnCr$_{0.4}$Fe$_{1.6}$O$_4$, ZnCrFeO$_4$, and ZnCr$_{1.8}$Fe$_{0.2}$O$_4$) different grains were analyzed. For each area analyzed two X-ray spectra were taken, one with the incident beam inside (negative excitation error) and one with the incident beam outside the first-order Kikuchi band (i.e., the 400 band). The divergence of the incident beam was about 1/4 of the [400] reciprocal-lattice vector. As expected no significant difference could be observed in the diffraction patterns from the three compositions. Diffraction patterns from ZnCrFeO$_4$ for the two different diffraction conditions are shown in Fig. 3. Figs. 4, 5 and 6 show pairs of typical X-ray emission spectra for the three different compositions for negative excitation errors (Figs. 4a, 5a and 6a) and positive excitation errors (Figs. 4b, 5b, 6b). From the X-ray spectra a considerable inhomogeneity with respect to Cr and Fe content was observed. This was the case for all the three nominal compositions studied. But with respect to the change in the ratio between the intensities of the $K\alpha$ lines for the two directions of incidence the results were similar for all pairs of spectra. For abbreviation let us denote this ratio as

$$R = \frac{I(X)}{I(Y)} = \frac{I(I(X))_{(s^-)}}{I(Y)_{(s^+)}},$$

where $I(X)$ and $I(Y)$ are the intensities of the $K\alpha$ lines of two elements and $(s^-)$ and $(s^+)$ refer to positive and negative excitation error, respectively. In Table 1, $R$(Cr/Zn) and $R$(Cr/Fe) are shown for different analyses of the three nominal compositions. These ratios were obtained by adding the number of counts from nine channels around the peak maxima for each $K\alpha$ line. The channel width was 20 eV. We notice that $R$(Cr/Zn) is between 2 and 3 in all cases and $R$(Cr/Fe) between 1-00 and 1-15. Similar experiments for natural MgAl$_2$O$_4$ spinel gave $R$(Al/Mg) also between 2 and 3 and for TiFe$_2$O$_4$ $R$(Fe/Ti) between 0-65 and 0-75.

In the spectra (Figs. 3, 4 and 5) we also notice a strong $K\alpha$ line from Cu due to the copper grid. This was present also when the electron beam was placed outside the specimen, either on the carbon film or in a hole in the film. No significant peak from Cr, Fe and Zn could be observed in these cases, indicating that all the X-rays from these elements come from the illuminated area of the specimen.
Table 1. Ratio change of the X-ray intensities for pairs of spectra with incident beam inside and outside the 400 Kikuchi band for the three compositions

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Measurement</th>
<th>R(Cr/Zn)</th>
<th>R(Cr/Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCr_{0.4}Fe_{1.6}O_{4}</td>
<td>1</td>
<td>2.00</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.31</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.51</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.32</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.04</td>
<td>1.14</td>
</tr>
<tr>
<td>ZnCrFeO_{4}</td>
<td>1</td>
<td>2.60</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.33</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.15</td>
<td>1.08</td>
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<tr>
<td></td>
<td>4</td>
<td>2.95</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.55</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.56</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>2.89</td>
<td>1.09</td>
</tr>
<tr>
<td>ZnCr_{1.6}Fe_{0.4}O_{4}</td>
<td>1</td>
<td>2.01</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.20</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.11</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.84</td>
<td>1.04</td>
</tr>
</tbody>
</table>

IV. Discussion

The two-beam calculation of the electron intensity distribution based on (6) as shown in Fig. 1 is qualitative for three reasons:

1. More than two beams are needed for a quantitative treatment.
2. The interference term between the Bloch waves has been neglected.
3. Diffuse scattering out of the initial Bloch-wave states has not been taken into account.

The two-beam approximation has proved to be good in similar situations. Comparison between two-beam and many-beam calculations gave similar results close to the Bragg reflecting position for the 200 reflection in Ni and the 220 reflection in Ge (Hall, 1966). This is also found to be the case for the 200 reflection in ZnS (Taftø, 1979) and the 111 reflection in MgO (Lehmpfuhl & Taftø, 1980). The neglect of the interference term between the Bloch waves gives results not much different from the complete calculation when the crystal thickness is about half an extinction length or thicker. The extinction lengths for the 400 reflection in the spinels studied here are about 700 Å, and even shorter, when the Bragg condition is not fulfilled. At the present stage there is little reason for doing many-beam calculations and including the interference terms between the Bloch waves because the most serious assumption is that there is no diffuse scattering out of the initial Bloch-wave states. The absorption parameters are not known, and with the rather complicated shape of the illuminated crystal area (neither constant thickness nor perfect wedge) it is difficult to get a good estimate for the thickness. However, the diffuse scattering out of the initial Bloch-wave states will not change the qualitative features of the intensity variation on the different lattice sites with incident beam direction (Fig. 1), but will only reduce the effect. Thus, for a \(XY_2O_4\) spinel, one can easily distinguish between the three alternatives: normal, random and inverse cation distribution. For a random distribution, the ratio between

![Fig. 5. Spectra from ZnCrFeO$_4$. (a) Inside the band; (b) outside the band.](image)

![Fig. 6. Spectra from ZnCr$_{1.6}$Fe$_{0.4}$O$_4$. (a) Inside the band; (b) outside the band.](image)
the intensity of the K lines of Y and X on changing the
direction of incidence from negative to positive excitation error for the 400 reflection is 1, i.e. \( R(Y/X) = 1 \).
If the spinel is normal (all Y atoms on the octahedral
sites) we find from Fig. 1 that \( R(Y/X) > 1 \) and for an
inverse spinel \( R(Y/X) < 1 \).
From the two-beam calculation (Fig. 1) the in-
tensity on the Y atoms in a normal spinel may be three
times as large as the intensity on the X atoms for
negative excitation error whereas the same ratio may
be \( 1/3 \) for positive excitation error. The ratio, \( R \), may
therefore be as great as 9. The divergence of the
incident beam will reduce this ratio somewhat, but
more important is the diffuse scattering.
It may well be that half of the X-rays have been
produced by the electrons which have been scattered
out of the initial Bloch-wave states. This is the case for
an 800 Å thick crystal if the normal (average) absorp-
tion parameter \( \mu_0 = 0.001 \, \text{Å}^{-1} \). Instead of the in-
tensity difference at the two types of sites shown in
Fig. 1, the variation of the intensity with incident beam direction will be as shown in Fig. 7 for a spinel
with extinction length 700 Å. From this curve we find
\( R(\text{Al}/\text{Mg}) = 2.8 \) for the natural \( \text{MgAl}_2\text{O}_4 \) spinel which is
known to be normal and \( R(\text{Fe}/\text{Ti}) = 0.65 \) for
\( \text{TiFe}_2\text{O}_4 \) which is inverse. The observed ratios were
between 2 and 3 for \( \text{MgAl}_2\text{O}_4 \) and between 0.65 and
0.75 for \( \text{TiFe}_2\text{O}_4 \). In the \( \text{ZnCr}_{x}\text{Fe}_{2-x}\text{O}_4 \) spinels
\( R(\text{Cr}/\text{Zn}) \) and \( R(\text{Fe}/\text{Zn}) \) are very similar to \( R(\text{Al}/\text{Mg}) \)
in \( \text{MgAl}_2\text{O}_4 \). We can therefore conclude that most of
the Cr and Fe atoms are in the octahedral positions
and the Zn atoms at the tetrahedral positions. We
notice, however, that \( R(\text{Cr}/\text{Fe}) \) is somewhat higher
than 1 (see Table 1). This would be the case if there
were more spurious X-rays from Fe than from Cr. As
was mentioned in the experimental section the amount of Cr and Fe signal was negligible when the
electron beam was placed outside the specimen.
Therefore \( R(\text{Cr}/\text{Fe}) > 1 \) suggests that Cr has a slightly
higher octahedral preference than Fe. It is probable
that all the Cr atoms are at the octahedral positions
and all the Zn atoms at the tetrahedral positions.
Under this assumption the ratio of the changes of the
electron intensities at the octahedral and tetrahedral
sites with incident beam direction can be deduced and
an estimate for the tetrahedral occupancy of the Fe
atoms can be made. Typically \( \delta^o \) of the Fe atoms
seem to be in the tetrahedral positions. This indicates
a deficiency of Zn probably due to the presence of a
small fraction of \( \text{ZnO} \).
The results are in agreement with the site preference
calculations of Verwey & Heilmann (1947), and Miller
(1959). According to their works, Zn has the strongest
tetrahedral and Cr the strongest octahedral preference
of these three cations.

V. Conclusion

For the channeling effect in electron-induced X-ray
emission to be a quantitative method for the de-
termination of atomic site occupancy, the crystal
thickness and the absorption parameters have to be
known accurately. But the three models of normal,
random and inverse \( XY_2O_4 \) spinel can easily be
distinguished. In spinels containing more than two
types of cations the succession with respect to site
preference (e.g. on the tetrahedral sites) can be
determined with a high degree of certainty. This is
expected to be the case even when many different
cations are involved. In view of the technological
importance of spinels containing many types of ca-
tions and the fact that this is a rapid method which
can be used on small crystal areas, down to about
100 Å in diameter, the method may be a useful
supplement to the established methods for the deter-
mination of atomic site occupancy in some cases.

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