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THE COMBINED EFFECT OF ACCELERATION VOLTAGE AND INCIDENT BEAM ORIENTATION ON THE CHARACTERISTIC X-RAY PRODUCTION IN THIN CRYSTALS

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ABSTRACT

A systematic experimental study has been carried out to determine the combined effect of acceleration voltage and incident beam orientation on the characteristic x-ray production in thin crystals. For MgAl₂O₄, it has been shown that the voltage dependence of the orientation dependence undergoes a reversal in character above a particular voltage labelled as the "inversion" voltage. This "inversion" voltage has been experimentally determined to be ~270kV for MgAl₂O₄ compounds with a spinel structure. A physical interpretation of this phenomenon in terms of the localization of the Bloch waves in the crystal has been suggested. Further detailed calculations are necessary to understand this behavior and determine its relation to the conventional critical voltage effect. From the microanalysis point of view, it has been experimentally shown that in order to obtain an analysis independent of the incident beam orientation or the acceleration voltage it is essential to systematically tilt the crystal to an orientation whence no lower order Bragg reflections are excited.

INTRODUCTION

One of the principal products of the interaction of a fast electron (an electron accelerated through a potential of 100kV or more) with a crystalline solid in the form of a thin film is characteristic x-ray emission. These x-ray photons with energies characteristic of the elements constituting the crystalline solid and peak intensities proportional to their concentrations in the material can then be detected by standard energy dispersive x-ray spectrometers to give a chemical microanalysis of the sample (Goldstein, 1979). However, the precise interpretation of these x-ray intensities in terms of their concentrations in the solid (chemical microanalysis) in an analytical transmission electron microscope is limited by a number of instrument and specimen related factors (Zaluzec,
In general for crystalline materials, an incident plane wave of electrons under conditions of strong dynamical scattering sets up a standing wave within the crystal. The intensity modulations of this standing wave within the crystal unit cell are a function of the incident beam orientation and the acceleration voltage. As the scattering events (like inner shell excitations) that lead to characteristic x-ray production are highly localized, the x-ray intensities in turn, are strongly determined by the orientation and the acceleration voltage. For a given acceleration voltage or wavelength of the incident wave, it has been shown that this orientation dependence of the characteristic x-ray emission, termed the "Borrmann (1941) effect," can also be used as a probe for determining specific site occupations of elemental additions in single crystals (Spence and Tafto, 1983; Krishnan, Rabenberg, Mishra and Thomas, 1984; Krishnan and Thomas, 1984; Krishnan, Rez and Thomas, 1985). The implications of this orientation dependence of the x-ray productions on energy dispersive x-ray microanalysis in a transmission electron microscope have also been briefly discussed (Cherns et al., 1973). However, an interesting voltage dependence of this orientation dependence has also been suggested earlier (Krishnan, Rez and Thomas, 1983). In this paper we present the result of a systematic experimental investigation of the combined effect of the orientation and the acceleration voltage on characteristic x-ray production in thin crystals and discuss its ramifications with respect to conventional energy dispersive x-ray microanalysis.

EXPERIMENTAL DETAILS AND RESULTS

Experiments were performed on single crystal MgAl₂O₄ with a spinel (Fd3m) structure. The single crystal was oriented and thin slices with a [100] normal were cut using a diamond wafering saw. They were mechanically thinned to a thickness of 35-50 microns
and then ion-milled to perforations using argon ions accelerated through a potential of 5-6kV. This gave uniformly thin electron transparent regions of the specimen for TEM observations.

Experiments were performed on the Osaka analytical atomic resolution electron microscope fitted with a LaB₆ filament and a Tracor Northern energy dispersive x-ray analyser and capable of operating over an acceleration voltage range up to 400kV. A standard type two-axis side entry holder was used in all experiments. A specimen thickness that indicated a strong dynamical scattering condition judged by the appearance of the Kikuchi line pattern was selected.

The spinel crystal structure is a layered one, for in the [100] projection, it can be resolved into alternating layers of parallel non-identical [004] planes. One of these planes is composed of the octahedrally coordinated Al³⁺ ions and the other of the tetrahedrally coordinated Mg²⁺ ions. In this crystallographic projection, if one sets up a two-dimensional diffraction condition by exciting a $\vec{g} = 004$ systematic row, then the standing wave that is set up in the crystal under strong dynamical scattering conditions can be preferentially localized on one of these two planes with varying intensities by suitably altering the specimen tilt along the $\vec{g} = 004$ direction with concomitant changes in the characteristic x-ray emissions (Spence and Tafto, 1983).

Hence a strong $\vec{g} = 004$ systematic row was excited and spectra collected at five different orientations of the incident beam (specimen tilt/excitation errors):

1. First order Bragg diffraction with large negative excitation error ($s < 0$)
2. First order Bragg diffraction with small negative excitation error ($s < 0$)
3. Exact first order Bragg diffraction condition ($s = 0$)
4. First order Bragg diffraction condition with small positive excitation error ($s > 0$)
5. First order Bragg diffraction condition with large positive excitation error ($s > 0$)
Apart from this, spectra were also collected at a symmetric [100] zone axis pattern orientation (a reference orientation which would lend itself naturally to computation of the x-ray intensities) and at an orientation in which no lower order Bragg diffraction vectors were excited. The specimens were oriented using the Kikuchi line method.

At any particular acceleration voltage, spectra were collected at each of the above orientations for a period of approximately 300-600 seconds at a counting rate of ~500 cts/sec in order to ensure proper statistics. Parallel illumination was used throughout the experiment. It was also ensured that the specimen thickness remained uniformly constant for the different spectral acquisitions. This entire experimental procedure was repeatedly carried out at the following acceleration voltages: 125kV, 175kV, 225kV, 270kV, 300kV, 350kV and 400kV.

The overall results of the experiment are shown in Table 1. At each orientation and acceleration voltage the ratio of the intensities of aluminum to magnesium, i.e. \( r = \frac{N_{Al}}{N_{Mg}} \), is shown. This ratio is a convenient measure as it eliminates any dependence on all other experimental parameters like specimen thickness, counting time, beam spreading, etc. However, it is impossible to reproduce the orientations of the incident beam accurately at each acceleration voltage. Further, it is also likely that in some cases the incident beam orientation corresponding to the first order Bragg diffraction condition with large positive excitation errors (\( s \gg 0 \)) might have been very close to the second order Bragg diffraction condition (\( g = 008 \)) with small negative excitation errors. These might explain some of the fluctuation in the data.

Figure 1 is a typical set of EDS x-ray spectra collected at an acceleration voltage of 300kV. The accompanying diffraction patterns show the precise orientation of each acquisition.
DISCUSSION

The integrated elemental intensity ratios show a clear variation with the orientation of the incident beam (specimen tilt) at each acceleration voltage and with acceleration voltage for each orientation (except for the case in which no lower order diffraction vectors are excited); further these variations are statistically significant. However, in order to interpret the data and be able to compare spectra collected at different acceleration voltages, it is essential to normalize the data. We define a normalized measure of the orientation dependence at each acceleration voltage \( R \) as

\[
R = \frac{r_s - r_{zap}}{r_s + r_{zap}}
\]

where all terms have been defined earlier. Any variation in the value of \( R \) would then indicate an orientation dependence attributed to the preferential localization of the standing wave on the distinct plane within the crystal unit cell. The effect of voltage can be isolated by comparing values of \( R \) at a specific orientation (specimen tilt) specified by the excitation error \( s \) over the range of acceleration voltages.

Values of this normalized measure have been calculated, tabulated in Table 2 and plotted in Figure 2.

It can be seen that this orientation dependence of the characteristic x-ray emission exhibits an interesting reversal in character for negative excitation errors of the first order Bragg diffraction conditions. Above some voltage (~270kV) which we term the "inversion voltage" the value of \( R \) undergoes a change in sign. Physically, this could be interpreted as follows. Below the "inversion voltage" one observes a particular localization behavior of the standing wave within the crystal unit cell. It is known that for negative excitation errors the Bloch wave is localized primarily in the octahedrally coordinated aluminum sites (Spence and Tafto, 1983). However, above the inversion voltage, for negative excitation errors, the Bloch wave is localized on the tetrahedrally
coordinated magnesium site leading to a significant reduction in the value of $r_s$. This observation of the "inversion voltage" behavior might have some relation to the critical voltage behavior observed for a centro-symmetric crystal set at the symmetric Laue position for the second order Bragg diffraction condition and attributed to the degeneracy of the eigenvalues of the Bloch waves (Lally et al., 1972). Preliminary attempts to gain a theoretical understanding of this phenomenon based on a simple model have been futile (K. M. Krishnan, P. Rez and G. Thomas, 1983). However, the experimental observation of this "inversion voltage" behavior increases the need for a detailed theoretical understanding of this phenomenon.

From the microanalysis point of view it can be seen from Table 1 that only in the case in which no lower order Bragg diffraction vectors are excited is there no statistically significant variation with voltage of the characteristic x-ray intensities. This should be borne in mind when performing routine microanalysis of crystalline materials and the crystal systematically tilted to obtain such a diffraction condition before collecting energy dispersive x-ray spectra to avoid artifacts due to this kind of diffraction effects.

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G. Borrmann, Phys. Z. 42, 157 (1941).


TABLE 1

Integrated elemental intensity ratio $r = \frac{N_{Al}}{N_{Mg}}$

<table>
<thead>
<tr>
<th>Acceleration Voltage</th>
<th>$s&lt;&lt;0$</th>
<th>$s&lt;0$</th>
<th>$s=0$</th>
<th>$s&gt;0$</th>
<th>$s&gt;&gt;0$</th>
<th>zap</th>
<th>No Bragg</th>
</tr>
</thead>
<tbody>
<tr>
<td>125kV</td>
<td>4.54</td>
<td>4.55</td>
<td>3.49</td>
<td>3.43</td>
<td>3.42</td>
<td>5.59</td>
<td>3.83</td>
</tr>
<tr>
<td>175kV</td>
<td>4.55</td>
<td>4.13</td>
<td>3.78</td>
<td>3.47</td>
<td>3.59</td>
<td>5.77</td>
<td>3.87</td>
</tr>
<tr>
<td>225kV</td>
<td>5.61</td>
<td>5.83</td>
<td>3.19</td>
<td>3.17</td>
<td>3.48</td>
<td>6.11</td>
<td>3.78</td>
</tr>
<tr>
<td>270kV</td>
<td>4.45</td>
<td>4.63</td>
<td>4.45</td>
<td>3.23</td>
<td>3.42</td>
<td>4.37</td>
<td>3.71</td>
</tr>
<tr>
<td>300kV</td>
<td>5.07</td>
<td>4.51</td>
<td>3.50</td>
<td>3.18</td>
<td>3.45</td>
<td>4.32</td>
<td>3.82</td>
</tr>
<tr>
<td>350kV</td>
<td>5.47</td>
<td>5.39</td>
<td>4.61</td>
<td>3.24</td>
<td>3.38</td>
<td>4.29</td>
<td>3.77</td>
</tr>
<tr>
<td>400kV</td>
<td>5.00</td>
<td>5.07</td>
<td>3.89</td>
<td>3.14</td>
<td>3.41</td>
<td>4.27</td>
<td>3.72</td>
</tr>
</tbody>
</table>
### TABLE 2

Normalized measure of orientation dependence -- $\mathcal{R}$

Orientation (Specimen tilt/excitation errors)

<table>
<thead>
<tr>
<th>Acceleration</th>
<th>s&lt;&lt;0</th>
<th>s&lt;0</th>
<th>s=0</th>
<th>s&gt;0</th>
<th>s&gt;&gt;0</th>
</tr>
</thead>
<tbody>
<tr>
<td>125kV</td>
<td>-0.10</td>
<td>-0.10</td>
<td>-0.23</td>
<td>-0.24</td>
<td>-0.24</td>
</tr>
<tr>
<td>175kV</td>
<td>-0.12</td>
<td>-0.17</td>
<td>-0.21</td>
<td>-0.25</td>
<td>-0.23</td>
</tr>
<tr>
<td>225kV</td>
<td>-0.04</td>
<td>-0.02</td>
<td>-0.31</td>
<td>-0.32</td>
<td>-0.27</td>
</tr>
<tr>
<td>270kV</td>
<td>0.01</td>
<td>-0.11</td>
<td>0.01</td>
<td>-0.15</td>
<td>-0.12</td>
</tr>
<tr>
<td>300kV</td>
<td>0.08</td>
<td>0.02</td>
<td>-0.01</td>
<td>-0.15</td>
<td>-0.11</td>
</tr>
<tr>
<td>350kV</td>
<td>0.12</td>
<td>0.11</td>
<td>0.04</td>
<td>-0.14</td>
<td>-0.12</td>
</tr>
<tr>
<td>400kV</td>
<td>0.08</td>
<td>0.09</td>
<td>-0.05</td>
<td>-0.15</td>
<td>-0.12</td>
</tr>
</tbody>
</table>
Fig. 1
\[ \mathcal{A} = \frac{r_s - r_{zap}}{r_s + r_{zap}} \]
Fig. 1. A typical set of energy dispersive x-ray spectra as a function of orientation of the incident beam at an acceleration voltage of 300kV. Parallel illumination conditions were used. In the insets the precise orientation of each acquisition is shown.

Fig. 2. Characteristic x-ray production intensities in \( \text{MgAl}_2\text{O}_4 \) (spinel) as a function of acceleration voltage and incident beam orientation. The normalized measure \( R \) (see text for definition) is defined such that any non-zero value indicates an orientation dependence.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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