Rapid Determination of Polarity Sense by an Energy-Dispersive Diffractometer

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The polarity sense of the non-centrosymmetric GaP crystal has rapidly been determined by use of an energy-dispersive diffractometer by choosing a suitable scattering angle, where the anomalous scattering is heavy, for example for the 333 and 333 reflexions in a pair of measurements. The main merits of this method are: (1) The necessary scaling is easily carried out by use of the intensity of even reflexions observed simultaneously; (2) Unwanted fluorescence contributions can generally be separated. These make the conclusion more reliable. It was thus established that the less shiny surface is the Ga side when a 111 plate of GaP is treated by an etchant (HF:HNO₃ = 5:1).

Introduction

Many years ago, the absolute sense of polarity was determined for ZnS by use of anomalous dispersion (Nishikawa & Matsukawa, 1928); subsequently, more quantitative measurements were carried out (Coster, Knol & Prins, 1930; Geib & Lark-Horowitz, 1932). In these early studies, various characteristic radiations were used while later continuous X-rays were applied to the Laue-photograph method for this purpose (Grenville-Wells & Lonsdale, 1954). More recently, such detection of the difference in the intensities of a pair of h and -h reflexions due to continuous X-rays has been applied to various polar crystals (Cole & Stemple, 1962; Mariano & Hanneman, 1963; Barns, Keve & Abrahams, 1970).

In the present work, a simple and lucid polarity-sense determination is carried out in a more straightforward way by the use of an energy-dispersive diffractometer with a solid-state detector (SSD), where continuous X-rays are fully used. This is demonstrated on a GaP crystal of the zincblende type, but is applicable to various crystals. The merits of this method are summarized in the last section.

Theory

A GaP crystal is of the zincblende type. In the present work, the origin is taken so that Ga atoms are at (0,0,0)+f.c.c. positions and P atoms at (½, ½, ½)+f.c.c. positions based thereon. Then the structure factors \( F(\omega) \) for \( hhh \) (\( h = \text{odd} \)) reflexions are given by

\[
F(\omega)/4 = \left[ f_{Ga} + \Delta f'_{Ga}(\omega) - (1)^{h+1} \Delta f''_{P}(\omega) \right] + i \left[ \Delta f'_{Ga}(\omega) + (1)^{h+1/2} \Delta f''_{P}(\omega) \right],
\]

(1)

where \( \omega \) is energy and otherwise the ordinary notation is used. Therefore, the ratio between intensities of a pair of 333 and 333 reflexions is given by

\[
\frac{I_{333}}{I_{333}} = \frac{\left[ f_{Ga} + \Delta f'_{Ga}(\omega) - (1)^{h+1} \Delta f''_{P}(\omega) \right]^2 + \left[ \Delta f'_{Ga}(\omega) + (1)^{h+1/2} \Delta f''_{P}(\omega) \right]^2}{\left[ f_{Ga} + \Delta f'_{Ga}(\omega) + \Delta f''_{P}(\omega) \right]^2 + \left[ \Delta f'_{Ga}(\omega) - f_{P} + \Delta f''_{P}(\omega) \right]^2},
\]

(2)

where \( \Delta f'_{P}(\omega) \) and \( \Delta f''_{P}(\omega) \) are rather small for the X-ray energy near the absorption edge of Ga (10.368 keV). The calculated values for \( \Delta f'_{Ga}(\omega) \), \( \Delta f''_{Ga}(\omega) \), \( \Delta f'_{P}(\omega) \) and \( \Delta f''_{P}(\omega) \) are shown in Tables 1 and 2.

The Bragg condition is expressed as

\[
\omega_h = 6.199 (d_h \sin \theta)^{-1}
\]

(3)

where \( \theta \) is the Bragg angle and \( 2\theta \) is the scattering angle, \( d_h \) in \( \text{Å} \) is the relevant interplanar distance for a net plane with an index \( h \) and \( \omega_h \) is in keV. Therefore, the X-rays with desired energy can be reflected for a particular \( d_h \) value by choosing a suitable \( \theta \) value.

Table 1. Measured intensity ratios for the third-order reflexion compared with calculations

For GaP, \( a = 5.4506 \text{ Å} \) (Giesecke & Pfister, 1958), \( \omega_k = 10.368 \).

<table>
<thead>
<tr>
<th>( h )</th>
<th>( \omega ) (keV)</th>
<th>( \omega/\omega_k )</th>
<th>( \Delta f' )</th>
<th>( \Delta f'' )</th>
<th>( \Delta f' )</th>
<th>( \Delta f'' )</th>
<th>I_{333}/I_{333}</th>
<th>cal.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>72.94</td>
<td>9.94</td>
<td>0.959</td>
<td>-2.96</td>
<td>0.29</td>
<td>0.22</td>
<td>0.27</td>
<td>0.97</td>
<td>1.01 ± 0.05</td>
</tr>
<tr>
<td>69.94</td>
<td>10.31</td>
<td>0.995</td>
<td>-5.10</td>
<td>0.27</td>
<td>0.21</td>
<td>0.25</td>
<td>0.98</td>
<td>1.09 ± 0.05</td>
</tr>
<tr>
<td>68.94</td>
<td>10.44</td>
<td>1.007</td>
<td>-4.65</td>
<td>3.75</td>
<td>0.21</td>
<td>0.24</td>
<td>1.66</td>
<td>1.79 ± 0.05</td>
</tr>
<tr>
<td>67.94</td>
<td>10.58</td>
<td>1.020</td>
<td>-3.43</td>
<td>3.68</td>
<td>0.20</td>
<td>0.24</td>
<td>1.53</td>
<td>1.49 ± 0.05</td>
</tr>
<tr>
<td>66.94</td>
<td>10.72</td>
<td>1.034</td>
<td>-2.81</td>
<td>3.60</td>
<td>0.20</td>
<td>0.23</td>
<td>1.47</td>
<td>1.47 ± 0.05</td>
</tr>
<tr>
<td>64.94</td>
<td>11.01</td>
<td>1.062</td>
<td>-2.06</td>
<td>3.45</td>
<td>0.19</td>
<td>0.22</td>
<td>1.40</td>
<td>1.42 ± 0.05</td>
</tr>
</tbody>
</table>

* The calculations are based on Hönli's correction for K electrons and Prins's correction for L electrons (James, 1954)
it is possible to cause anomalous scattering for any reflexion as long as the X-rays with the relevant energy are included in the incident beam.

In this measurement, the energy resolution is not limited by the energy-dispersive detector, although every reflexion peak on the display of a multi-channel pulse-height analyser appears wider than it is really. As was reported before (Fukamachi, Hosoya & Terasaki, 1973), if the incident beam is sufficiently limited in angular divergence by use of a Soller slit system, the peak width is mainly limited by the following energy broadening,

\[ \Delta \omega_0 = - \omega_0 \cot \theta \Delta \theta. \]

Therefore the use of a continuous X-ray source and of an SSD enables us to study anomalous dispersion with a narrow energy width \( \Delta \omega_0 \) corresponding to a small \( \Delta \theta \) value.

In general, the fluorescence X-rays from a sample are usually detected separately, but may sometimes overlap Bragg reflexions. When the anomalous scattering is caused by the \( K\alpha \) absorption edge at a certain reflexion, the \( K\beta_1 \) and \( \beta_2 \) fluorescence X-rays appear around that reflexion. For such elements with atomic numbers of about 30 and 70, this \( K\beta_1 \) and \( \beta_2 \) radiation nearly overlaps the relevant reflexion. This is an unfavourable point, but it is very easy to eliminate these fluorescence X-rays as will be shown later.

### Experimental

The outline of the present experimental set-up is shown in Fig. 1. A Soller slit system is indispensable for making \( \Delta \omega_0 \) small, and is also very helpful for suppressing the fluorescence X-rays which radiate in various directions. In the present case, where a pair of Soller slits with a divergence of \( \pm 7' \) are used, the signal-to-background ratio was about \( 10^3 \). The X-ray tube with an Ag target for fluorescence work was operated at 40 kV and 20 mA. The detector used is Ge(Li) with a resolution of about 180 eV at Mn \( K\alpha \).

The GaP single-crystal specimen used for the measurement has been prepared by cutting parallel to the (111) plane, polished and then etched in etchant (HF: \( \text{HNO}_3=5:1 \)) for 3 min. In order to determine the polarity sense, it is sufficient to take a pair of \( \{hnh\} \) diffraction spectra by choosing only one suitable scattering angle so that a pair of reflexions, say 333 and 333, are heavily subject to anomalous dispersion. However, in the present measurement, many other scattering angles were used on both sides of the absorption edge. In Fig. 2, the measured points are indica-

### Table 2. Measured intensity ratios for the fifth-order reflexion compared with calculations

For GaP \( a=5.4506 \) Å (Giesecke & Pfister, 1958), \( \omega_K=10.368 \).

<table>
<thead>
<tr>
<th>( \theta )</th>
<th>( \omega(\text{keV}) )</th>
<th>( \omega/\omega_K )</th>
<th>( \Delta f' )</th>
<th>( \Delta f'' )</th>
<th>( \Delta f' )</th>
<th>( \Delta f'' )</th>
<th>( I_{555}/I_{555} )</th>
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<tr>
<td>72-94</td>
<td>16-57</td>
<td>1-599</td>
<td>0-242</td>
<td>1-72</td>
<td>0-11</td>
<td>0-10</td>
<td>1-25</td>
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<tr>
<td>69-94</td>
<td>17-19</td>
<td>1-658</td>
<td>0-282</td>
<td>1-62</td>
<td>0-11</td>
<td>0-09</td>
<td>1-23</td>
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<td>68-94</td>
<td>17-41</td>
<td>1-679</td>
<td>0-295</td>
<td>1-58</td>
<td>0-11</td>
<td>0-09</td>
<td>1-23</td>
</tr>
<tr>
<td>67-94</td>
<td>17-63</td>
<td>1-700</td>
<td>0-306</td>
<td>1-54</td>
<td>0-10</td>
<td>0-09</td>
<td>1-22</td>
</tr>
<tr>
<td>66-94</td>
<td>17-86</td>
<td>1-723</td>
<td>0-317</td>
<td>1-51</td>
<td>0-10</td>
<td>0-09</td>
<td>1-21</td>
</tr>
<tr>
<td>64-94</td>
<td>18-35</td>
<td>1-770</td>
<td>0-355</td>
<td>1-44</td>
<td>0-10</td>
<td>0-08</td>
<td>1-20</td>
</tr>
</tbody>
</table>

* See footnote to Table 1.
ased together with the calculated values based on Hönl's correction for \( K \) electrons only (James, 1954) in the region of interest. An example of the diffraction spectrum as measured is shown in Fig. 3, where the Ga\( K\alpha \) fluorescence peak appears between reflexions but \( K\beta \) mostly overlaps the 333 reflexion. As far as the polarity sense is concerned, this does not matter much if the geometry is identical for a pair of reflexions. However, these Ga \( K \) radiations were separately measured with the specimen slightly off the Bragg condition as shown in Fig. 4, and then were subtracted from the spectra shown in Fig. 3, after multiplication by a suitable factor scaled with Ga \( K\alpha \). The result is shown in Fig. 5. In the present experiment, a Ge(Li) detector readily available in the laboratory was used and, therefore, the escape peaks due to Ge \( K \) were also recorded, as seen in Fig. 3 and 5 (Fukamachi, Togawa & Hosoya, 1973). This could have been improved by the use of a Si(Li) detector in this energy region.

The numerical results thus obtained are shown in Table 1. The calculations show that the influence of anomalous dispersion on ±555 reflexions is mainly due to \( K \) electrons of Ga. The results are shown in Table 2. As expected from the formulae similar to (1) and (2), the calculated intensity ratio \( I_{555}/I_{555} \) is smaller than unity. For all calculations made in the present work, the atomic scattering factors \( f_{Ga} \) and \( f_{K} \) have been taken from the values by Fukamachi (1971) based on Clementi's wave functions.

**Results and discussion**

As shown in Fig. 6, as well as in Tables 1 and 2, the measured ratios \( I_{333}/I_{555} \) and \( I_{555}/I_{555} \) showed better agreement with the corresponding calculated values than in the earlier measurements (Coster, Knohl & Prins, 1930; Geib & Lark-Horowitz, 1932). In these cases, the measured ratio is nearer to unity than the calculated ratio. This fact probably indicates that these errors were caused by the fluorescence X-rays which could hardly be separated in those days. In this connexion, a favourable point to be noted is that the intensity ratio does not depend on crystal perfection (Cole & Stemple, 1962). Thus the present results have established that the shiny surface is the P side and the matt surface is the Ga side, when GaP is etched as described in the above.

As far as the value of \( \Delta f' \) is concerned, a precise measurement has recently been carried out on Ni by use of an X-ray interferometer with Cu \( K\alpha \) (Bonse & Materlik, 1972). The value obtained is smaller, by about 50%, than any of the calculated values so far published. The present intensity ratios agree with the calculated values within 10%, and the present precision is about ±5%. However, it does not necessarily mean that the present values for both \( \Delta f' \) and \( \Delta f'' \) agree with the corresponding calculated values to such an accuracy. The value of \( I_{333}/I_{555} \) varies by 10% either when \( \Delta f_{Ga} \) changes by 50%, or when \( \Delta f_{Ga} \) changes by 20%. Therefore, the present results at least suggest that the value of \( \Delta f_{Ga} \) is fairly well approximated by Hönl's value. A further check of these values requires absolute measurement or reliable scaling.

The merits of the present method are as follows:

1. The fluorescence X-rays from the sample, if any, can be clearly separated or, at least, be eliminated.

2. The difference between the opposite surfaces in surface treatment or imperfection may not much affect the determination of the polarity sense, because the scaling can reliably be carried out by comparing a pair of reflexions, such as ±222 and ±444, unaffected by the anomalous dispersion.

3. A pair of reflexions with higher indices show an intensity ratio which is on average further from unity. It is possible to cause heavy anomalous scattering for such high-index reflexions by choosing a suitable combination of the voltage supplied to the tube and the scattering angle dependent upon the dispersive atom.

![Fig. 3. Diffraction spectrum from a GaP single crystal. The 333 reflexion is most strongly subject to the anomalous dispersion. The \( \epsilon^{h a h} \)'s indicate escape peaks accompanying \( hha \) reflexions.](image)

![Fig. 4. Fluorescence X-rays due to Ga atoms in the GaP sample.](image)
(4) The radiation with the most suitable energy can be used in order to make the anomalous dispersion most effective in finding an even smaller deviation from Friedel's law, i.e. the present method is applicable to crystals including atoms which have absorption edges far from any common characteristic X-ray wavelength.

By the present method, the polarity sense can be determined rapidly and unambiguously with high reliability and this can be applied to distinguish between an enantiomorphous pair. Moreover, this method will be very useful both in the study of anomalous scattering itself and in its various applications to crystal-structure analysis. Further work is in progress in the authors' laboratory.

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References