USING X-RAY DIFFRACTION TO MEASURE CHANGES IN UNIT CELL DIMENSIONS DUE TO ALLOYING

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Abstract
Vergard's law is often used to relate changes in unit cell dimensions to the concentration of impurities or alloying elements. Employing it requires accurate measurements of d-spacings which in turn requires a well aligned and characterized diffractometer and internal (preferred) or external standards. This can be a bit overwhelming for students in an introductory structure of materials course, so a simpler experiment that demonstrates this using brass and copper was developed. It involves placing strips of the copper and brass in the instrument at the same time and recording the diffraction patterns for both simultaneously. When students see the peaks for the copper and brass on the same plot, the concept behind the experiment becomes very clear and the students can analyze the data to see if Vergard's law applies in this case.

Keywords: x-ray diffraction, solid solutions, brass, Vergard’s law

Prerequisite Knowledge: basic crystallography, principles of x-ray diffraction, substitutional solid solutions

Objectives: To gain an understanding of how subtle variations in the positions of the diffraction peaks can tell us about minor changes in the structure and chemistry of materials.

Equipment and Materials: x-ray powder diffractometer, ICDD’s PDF database, small squares of annealed copper and brass

Introduction: In a third-year course on the structure and characterization of materials half is devoted to x-ray diffraction methods of characterizing materials. These diffraction lessons consist of four experiments, each dealing with a different features of the diffraction pattern, and different applications of x-ray diffraction. These experiments are:

- Introduction – The basics of data collection and interpretation, including peak positions, intensity and counting statistics, background and k^-2 stripping, and the possibilities of peak overlap
- Phase ID – Whole pattern interpretation, including search-match phase identification and quantitative analysis
- Crystallite Size – Peak shape interpretation, particularly Scherrer and Warren-Averbach crystallite size determination techniques
- Residual Stress – Peak-shift interpretation
The residual stress experiment can be troublesome and it may not be an available option at other schools unless the goniometer can operate in 2-32 mode and the software can perform the data collection and most of the analysis. Instrument alignment is also critical and was causing us many problems. Being our only peak-shift experiment, a replacement had to be found. The experiment I came up with, described in this paper, looks at the shifts in peak position due to changes in lattice parameters caused by the presence of impurities, in this case zinc in copper. Normally this type of experiment requires a well-aligned and characterized instrument, care in sample preparation, and corrections for small instrument errors and specimen displacement in particular. To be an effective experiment in a class setting many of these difficulties had to be removed from the procedure. The result is an experiment that can be performed on practically any powder diffractometer with a minimum of difficulty.

Vergard’s law is often used to estimate the effect of substitutional impurities on the lattice parameters. It states that there is a linear relationship between substitutional impurity concentration and the lattice parameter in cases where the solute and solvent have similar bonding properties. In these cases the lattice parameter is influenced only by the relative sizes of the atoms and has been shown to be valid in ionic salts and compounds such as CdSe where sulfur substitutes for the selenium [1]. Vergard’s law does not apply in the cases of interstitial solid solutions and in cases where the bonding in the solute and solvent are different. Positive and negative deviations from Vergard’s law may be seen in fcc and hcp metals [2]. Note that pure copper has the fcc structure and zinc the hcp structure.

**Procedure:** The solubility of zinc in copper can be as high as 39 weight percent. There are many brasses within this range and a common one is the C26000 alloy, or as it is more commonly known, 70/30 or cartridge brass. It is a single phase "brass which should be an excellent candidate for investigating the effects of impurity content on changes in the lattice parameter of pure copper and to experiment with Vergard’s law.

The procedure has two parts:

1. modeling and feasibility
2. laboratory measurements and analysis

In the modeling phase students are asked to perform a number of calculations designed to improve their understanding of the subject and, in a sense, to gain a measure of experience with this subject. By doing these calculations they can investigate the basis of Vergard’s law and can see if experiment will require more precision than our instrument can provide. Specifically, the students are asked to obtain the PDF files for copper and any brasses found in the ICDD database then use spreadsheets, Math Lab, Mathematica, or similar software to do the following:

- Calculate and plot the density and lattice parameters of copper as a function of zinc content.
- Calculate and plot the diffraction angles for all peaks in copper’s diffraction pattern as a function of zinc content.
- Finally, determine the peak shifts, ) 22, one can expect to measure in the upcoming
From this they should be able to see clearly what the experiment is all about and they can see if Vergard’s law applies in this case.

During the previous experiments done in this course the students learned that:

- The 2\(^2\) error of our diffractometer is within 0.01 degrees 2\(^\theta\) from 20 to 90 degrees when performing very careful scans of NIST standards.
- The 2\(^2\) error is generally closer to ±0.04 degrees 2\(^\theta\) for routine experiments.
- Peak widths (FWHM) can range from 0.2 to 0.5 degrees 2\(^\theta\).

Knowing this they can determine if our instrument, and this technique, is up to the job.

The experimental phase is very straight-forward. Students already know where they can expect to find the diffraction peaks (2\(^\theta\) positions) so selecting the starting and ending 2\(^\theta\) positions for the scan is more a matter of deciding how many, and which, peaks they want to measure. The students discuss their options, taking into consideration the time it takes to obtain a high-quality and complete diffraction pattern as opposed to scanning only selected peaks, or sacrificing quality (counting statistics) by increasing the scan rate.

The scan procedure itself is a normal 2-2 scan of the 2\(^\theta\) range or ranges the students agree on.
They might settle on a scan rate after performing a couple of scans of only one peak, or a quick scan of the whole pattern to see what the peak intensities will be in the final scan, or from their experience analyzing other materials and consulting the \(I/I_c\) value for copper. Their constraints are simply getting everything done within the allotted 3 hour-long laboratory session.

The samples used in this experiment are simply small pieces of brass and copper strip (1.6 mm thick) that were annealed at 500°C for one hour to affect recrystallization and limited grain growth. They were then cut into 15 mm x 30 mm pieces and mounted side-by-side on a 30 mm x 30 mm plexiglass substrate using double-sticky tape. The mounted sample was sanded using 600 grit SiC paper to remove oxides and to ensure that the tops of the samples were in the same plane. Figure 1 shows these samples after mounting them in the diffractometer.

Figure 2 shows the diffraction pattern obtained after scanning the all the major peaks of copper and brass. Note the excellent separation in the peaks. The peak positions and intensities were determined by profile fitting using the Pearson profile.

The results of the analysis of the diffraction data are summarized in tables 2 and 3 while the agreement between the reference, calculated, and measured densities and peak positions are shown in figure 3. These results show that there is excellent internal agreement in the data (low standard deviations) and with the densities and lattice parameters from the literature \([3,4,5]\). It also shows a clear deviation from the calculated lattice parameters, and therefore with Vergard’s law.
To improve the results the student have the option of correcting for absorption errors. The different mass absorption coefficients of the copper and brass means that x-rays will penetrate the two samples to different depths, resulting in errors similar to those caused by sample displacement. The correction is simply:

\[ \Delta 2\theta = \frac{180 \sin(\theta)}{\pi} \frac{2\mu R}{\text{cm}^2} \]  

(1)

where \( \Delta 2\theta \) is the peak shift in degrees, \( R \) is the goniometer radius, and \( \mu \) is the linear absorption coefficient. This correction is not essential, but it does provide an example of one of the many sources of error in making precision diffraction measurements.

The thorough investigator might notice that the relative intensities of the peaks for the copper do not match those of the PDF file. This might cause some concern until the possible reasons for this are considered. The same can also be seen for the brass.
Table 1. Summary of the results from the analysis of the diffraction data. ($\lambda=0.1540562$ nm)

<table>
<thead>
<tr>
<th>Peak Nr.</th>
<th>Position</th>
<th>Intensity</th>
<th>Relative Intensity, %</th>
<th>d-spacing, nm</th>
<th>Indices</th>
<th>Lattice Parameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Brass</td>
<td>Copper</td>
<td>0.2127</td>
<td>h</td>
</tr>
<tr>
<td>1</td>
<td>42.46</td>
<td>410.0</td>
<td>93.9</td>
<td>100.0</td>
<td>0.2127</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>43.28</td>
<td>1738.0</td>
<td>45.3</td>
<td>32.6</td>
<td>0.1843</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>49.42</td>
<td>198.0</td>
<td>100.0</td>
<td>38.8</td>
<td>0.1303</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>50.38</td>
<td>566.4</td>
<td>34.3</td>
<td>22.0</td>
<td>0.1111</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>72.48</td>
<td>436.8</td>
<td>9.2</td>
<td>0.1044</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>74.08</td>
<td>675.2</td>
<td>9.2</td>
<td>0.1044</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>87.76</td>
<td>150.0</td>
<td>9.2</td>
<td>0.1044</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>89.86</td>
<td>382.0</td>
<td>9.2</td>
<td>0.1044</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>95.10</td>
<td>159.6</td>
<td>9.2</td>
<td>0.1044</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Maximum:</td>
<td>1738.0</td>
<td>436.8</td>
<td>1738.0</td>
<td>0.3685</td>
<td>0.3618</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Comparison of reference, calculated and measured densities and lattice parameters. The measured density is based on the measured lattice parameter and assumes nominal compositions for the copper and brass.

<table>
<thead>
<tr>
<th>Sample</th>
<th>w% Zn</th>
<th>Reference</th>
<th>Density, Mg/m³</th>
<th>Lattice Parameter, nm</th>
<th>Difference in Lattice Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Reference</td>
<td>Calculated</td>
<td>Measured</td>
</tr>
<tr>
<td>Copper</td>
<td>0</td>
<td>04-0836 [3]</td>
<td>8.950</td>
<td>8.934</td>
<td>8.915</td>
</tr>
<tr>
<td>Brass</td>
<td>30</td>
<td>ASM [5]</td>
<td>8.530</td>
<td>8.679</td>
<td>8.504</td>
</tr>
</tbody>
</table>
When analyzing the results the students can take advantage of the spreadsheet they created in the modeling phase of the experiment. For instance, it is very easy to modify it to plot measured and expected peak positions and to cut and paste tables of calculations into their reports. It is also easy to add the absorption error correction to this spreadsheet.

**Comments:** The experiment works very well, the measurements can be completed within one laboratory session, and it costs only $60 (based on 3 hours of instrument time recharged at a rate of $20/hour). Sample preparation and out-of-class preparation are minimal and the results obtained are very close to those reported in the literature. In the future I will try to get samples of the other brasses listed in table 3 so that small teams of students can analyze each and compile the results. This experiment can also be used to analyze other materials such as solders, nickels and other materials that are relatively inexpensive and easy to find.

This experiment contains three essential elements which I am trying to incorporate into all of the experiments I teach in upper division courses. They are:

- Modeling which forces the student to not only prepare to do the experiment but also to learn how to design their own experiments and interpret the results.
- The students’ independence in selecting key parameters for the experiments.
- The opportunity to critically analyze, and even disagree with, established principles.

Modeling provides an opportunity to basically rehearse the whole experiment in one’s mind and on paper before being presented with the practical issues and complexity of preparing samples and operating the laboratory instruments. Even the simplest modeling requires using a systematic approach to defining and solving the problem, or in this case, posing the appropriate questions. Hopefully the students will learn that they should never just show up in the laboratory without first thinking things through carefully and knowing well in advance that the experiment has a reasonable chance of being successful.

The second element may play out as the classic struggle between the tendency to “find fastest possible way to get out of here” and the need for quality and completeness of results on which they would be willing to base their grades, and in many respects, their professional reputations.

Next year I plan to add one new component to each of our x-ray experiments – budgeting and cost accounting. The students will be given the instrument’s recharge rate and told to decide how much their time is worth, then add it all up, and finally add overhead at a rate of 48.5%, the current NUD rate at U.C. Davis. In their final report they must include this budget and a summary of the costs associated with the their time spent on this project and the instrument time actually used, plus the NUD. This will help teach another important aspect of engineering and science and will get the students to start thinking in terms of the personal and institutional resources required to do this type of work, and the need to set and then stay within their budgets.
Table 3. Data for other brasses that could be used in this experiment [5].

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Zinc Content (w%)</th>
<th>Density (Mg/m³)</th>
<th>Lattice Parameter (nm)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>C21000</td>
<td>5</td>
<td>8.86</td>
<td>0.3627</td>
<td>Gilding metal, 94.0-96.0% Cu Single phase microstructure, &quot; (fcc)</td>
</tr>
<tr>
<td>C22000</td>
<td>10</td>
<td>8.80</td>
<td>0.364</td>
<td>Commercial bronze Single phase microstructure, &quot; (fcc)</td>
</tr>
<tr>
<td>C22600</td>
<td>12.5</td>
<td>8.87</td>
<td>-</td>
<td>Jewelry bronze Single phase microstructure, &quot; (fcc)</td>
</tr>
<tr>
<td>C23000</td>
<td>15</td>
<td>8.75</td>
<td>-</td>
<td>Red brass Single phase microstructure, &quot; (fcc)</td>
</tr>
<tr>
<td>C24000</td>
<td>20</td>
<td>8.67</td>
<td>0.366</td>
<td>Low brass Single phase microstructure, &quot; (fcc)</td>
</tr>
<tr>
<td>C26000</td>
<td>30</td>
<td>8.53</td>
<td>0.3684</td>
<td>Cartridge brass, 70-30 brass, spinning brass, spring brass Single phase microstructure, &quot; (fcc)</td>
</tr>
<tr>
<td>C26800</td>
<td>34</td>
<td>8.47</td>
<td>-</td>
<td>Yellow brass Single phase microstructure, &quot; (fcc)</td>
</tr>
<tr>
<td>C27000</td>
<td>35</td>
<td>8.47</td>
<td>-</td>
<td>Yellow brass Single phase microstructure, &quot; (fcc)</td>
</tr>
<tr>
<td>C28000</td>
<td>40</td>
<td>8.39</td>
<td>-</td>
<td>Muntz metal Two phase microstructure consisting of &quot; (fcc) and $ (bcc)</td>
</tr>
</tbody>
</table>

The parallels between budgeting/accounting and modeling/executing an experiment should be obvious. Hopefully the students will learn that they should never just show up in the laboratory without first considering well in advance how much everything will cost and that the experiment has a reasonable chance of being successful in economic terms.

References:
3. ICDD Powder Diffraction Files, file number 04-0831 (zinc, syn.).
4. ICDD Powder Diffraction Files, file number 04-0836 (copper, syn.).

Biography:
Michael L. Meier received his B.S. in Materials Engineering from North Carolina State University in 1979 and his M.S. (1986) and Ph.D. (1991) in Materials Science and Engineering from the University of California, Davis. After a two-year post-doctorate position at the Universität Erlangen-Nürnberg in Erlangen, Germany he returned to UC Davis where he is now the director of Materials Science Central Facilities and is also developing the laboratory teaching program.