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Laboratory Experiment

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X-ray Diffraction of Intermetallic Compounds: A Physical Chemistry Laboratory Experiment

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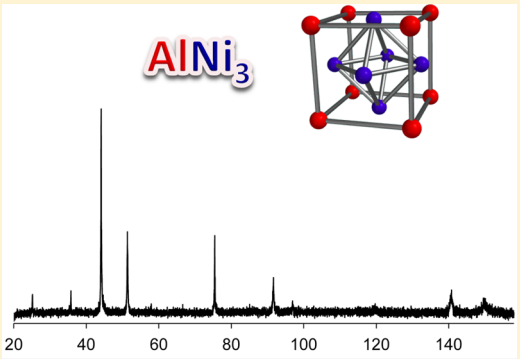
Supporting Information

ABSTRACT: Here we describe an experiment for the undergraduate physical chemistry laboratory in which students synthesize the intermetallic compounds AlNi and $AlNi_3$ and study them by X-ray diffractometry. The compounds are synthesized in a simple one-step reaction occurring in the solid state. Powder X-ray diffractograms are recorded for the two compounds as well as for the elements Al and Ni, all of which have cubic crystal structures. The students analyze the measured spectra to determine both the type of cubic lattice present and the unit cell dimension for comparison with the literature. The experiment demonstrates the utility of X-ray diffraction for structure determination.



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For many years at Macalester College, we have utilized an experiment in our physical chemistry laboratory curriculum that focuses on powder X-ray diffraction. X-ray diffractometry (XRD) is a powerful method of structure determination in chemistry, biology, physics, and materials science, and we want our students to gain some proficiency in the conceptual and experimental aspects of this technique. The theory of X-ray diffractometry is covered in many undergraduate physical chemistry textbooks[1−5] and laboratory manuals.[6,7] In the past, we had students record powder XRD spectra of cubic inorganic compounds (such as alkali and transition metal halides or alkaline earth oxides), index the diffraction patterns, identify the types of cubic lattices present, and determine the cubic lattice constants by a spreadsheet analysis. While this traditional experiment worked well, it was rather contrived, as students were provided samples of commercially available compounds as their unknowns. The high sample purity produced clean XRD spectra that are not so representative of what students will experience in a research setting. We have created a new experiment, described in this paper, in which the students first synthesize their own intermetallic compounds to study and then proceed to analyze them by X-ray diffraction.

We had three pedagogical objectives in developing this experiment. First, we desired to identify compounds that could be synthesized safely, inexpensively, and relatively easily. Second, we wanted to focus on intermetallic compounds of a binary system to display properties of phase diagrams that our students study in the thermodynamics and kinetics course associated with the laboratory. Finally, we desired to synthesize compounds of cubic symmetry, since the XRD patterns produced by cubic systems can be assigned and analyzed by undergraduate students in a straightforward manner using spreadsheet software. After a search of the available literature,[8] we concluded that nickel and aluminum constitute an ideal binary system for such an experiment. These two elements form five different intermetallic compounds, Al_3Ni, Al_3Ni_2, AlNi, Al_3Ni_5, and $AlNi_3$,[9] of which AlNi and $AlNi_3$ have cubic symmetry and can be readily synthesized in the laboratory. Nickel−aluminum (sponge-metal) alloys are important catalysts for hydrogenation reactions, which students may be familiar with from their organic chemistry courses.[10]

This experiment is designed for a 3 h laboratory period. Our students work in teams of two and rotate through a variety of experiments so that typically we have two teams working on the XRD experiment during the same lab period. One team synthesizes AlNi, and the other team synthesizes $AlNi_3$. The synthesis step takes about 45 min, with an additional 15 min required to prepare the samples for XRD analysis by grinding. The remainder of the lab period is spent recording XRD spectra of the two synthesized compounds as well as the pure elements Al and Ni.

Several descriptions of laboratory experiments involving the measurement and analysis of powder XRD diffractograms have been published in this *Journal*, but none includes a student synthesis of intermetallic compounds. Pope[11] has provided an extended discussion of the theory that underlies the powder XRD technique. Rosenthal[12] describes a powder XRD experiment involving several different unknowns, which are provided to the students as commercially available compounds. Butera and Waldeck[13] describe an experiment involving

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transition metal binary systems that form one-phase solid solutions rather than intermetallic compounds so that their experiment does not exhibit the multiple solid phase behavior that we have developed here.

EXPERIMENTAL DETAILS

Each team of students makes up 2.5 g of a mixture of Al and Ni (325 mesh) appropriate to their assigned compound. These mixtures are placed in a capped test tube and mixed thoroughly with a vortexer. Each sample is then transferred into a stainless steel die of the type used for making KBr pellets for infrared spectrometry. The sample is pressurized to 6000 psi in a hydraulic press. For making AlNi, the pressed pellet is placed on a wire mesh square supported by an iron ring attached to a ring stand. In a fume hood, the pellet is heated from below with a Bunsen burner for a few minutes, until the bottom of the pellet begins to turn red. The reaction is exothermic, and within a few seconds, the pellet will glow brightly (and rather dramatically). For synthesizing $AlNi_3$, a hotter temperature is required to ensure complete reaction. The pellet is placed in an alumina crucible and heated for 10 min in a muffle furnace at 1100 °C. In this way, students undertake two different methods of solid-state synthesis.

After cooling in air, each pellet is transferred to a ceramic mortar and ground with a pestle for a few minutes. Both samples are passed through a 60-mesh sieve before the XRD analysis. The XRD spectra are recorded with a PANalytical X'Pert PRO powder X-ray diffractometer that uses a copper anode X-ray tube. The diffraction angle 2θ is scanned from 20–158° in about 6 min. The instrument's software applies a baseline correction and strips the diffraction resulting from the Cu $K\alpha_2$ radiation. The diffraction angles, intensities, and associated d-spacings are then reported in a line list. This experiment should also work with a less expensive, benchtop X-ray diffractometer as long as the instrument is capable of scanning the diffraction angle 2θ out to at least 150°.

Additional experimental notes and suggestions for instructors wishing to adopt this experiment are provided in the Supporting Information.

Data Analysis

We display XRD spectra of the two pure elements Al and Ni and the two synthesized compounds in Figure 1. The pure elements give sparse spectra with no impurity lines. The compounds AlNi and $AlNi_3$ produce diffractograms with broader lines, a lower signal-to-noise ratio, and sometimes the presence of impurity lines arising from other solid phases formed in the reaction. These characteristics make the challenge of correctly assigning the lines a realistic example of an authentic chemical research problem.

The Bragg equation governs the scattering of X-rays from a crystal lattice:[1]

$$d_{hkl} = \frac{\lambda}{2 \sin \theta_{hkl}} \tag{1}$$

where d_{hkl} is the distance between successive planes in the lattice, λ is the X-ray wavelength, and θ_{hkl} is the angle of the scattered radiation. Different sets of planes in the crystal lattice, defined by their Miller indices (hkl), produce the unique pattern of lines diffracted at angles θ_{hkl} for that compound.

Restricting the possible set of compounds or elements to those belonging to one of the three cubic lattice systems—simple (sc), face-centered (fcc), or body-centered (bcc)—simplifies the analysis for the students. With cubic lattices, all three unit cell dimensions (a, b, and c) are identical, and all three unit cell angles (α, β, and γ) are equal to 90°. From a simple geometric analysis of the incident and scattered radiation, it can be shown[1] that

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \tag{2}$$

or

$$\frac{1}{{d_{hkl}}^2} = (h^2 + k^2 + l^2)\left(\frac{1}{a^2}\right) \tag{3}$$

From eq 3, it is clear that the experimental values of $(1/d^2)$ must be integer multiples of the constant $(1/a^2)$, which suggests a method for assigning Miller indices to each line in the diffraction pattern. In a spreadsheet, students create a column that contains the values of $(1/d^2)$ of the observed peaks. In the next column, each value of $(1/d^2)$ is divided by the $(1/d^2)$ value of the first (lowest-angle) diffraction line. Within experimental error, this column of numbers should

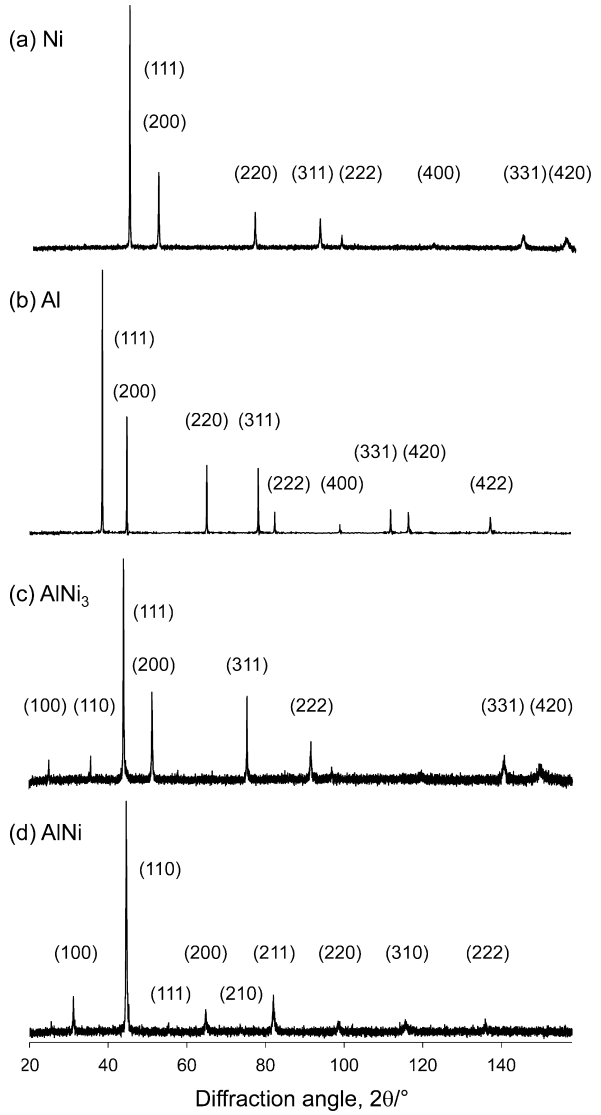

Figure 1. Powder X-ray diffraction spectra of (a) Ni, (b) Al, (c) $AlNi_3$, and (d) AlNi. The assignments of Miller indices (hkl) are shown above each feature.

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contain integers or ratios of small integers. Once the correct pattern of numbers is recognized, students are able to identify which type of cubic crystal (sc, fcc, or bcc) is present by keeping in mind the systematic absences for each of the three cubic lattice types.[1] With correctly assigned Miller indices, a value of the lattice constant a can be determined from each diffraction line using eq 3. From these data, students report the average and standard deviation of a and compare their lattice constants to those available in the literature for the elements and compounds. A typical student's spreadsheet analysis is provided in the Supporting Information. In Table 1, we list values for the lattice constants derived from the XRD spectra displayed in Figure 1 as well as class average values determined by our most recent group of physical chemistry students. We also list literature values for these constants. As can be seen from the class results in Table 1, students can measure the lattice constants with a precision of about 0.1% and an accuracy that places them within three standard deviations of the literature values.

Table 1. Lattice Constants Determined by XRD

Substance	Lattice Type	Measured Lattice Constant (nm)[a]	Class Average Lattice Constant (nm)[b]	Literature Lattice Constant (nm)
Al	fcc	0.4045(3)	0.4046(2)	0.4050[c]
Ni	fcc	0.3520(4)	0.3522(3)	0.3524[c]
AlNi	sc	0.2874(4)	0.2877(2)	0.2884[d]
$AlNi_3$	sc	0.3558(8)	0.3565(6)	0.3568[e]

[a]From analysis of the XRD spectra in Figure 1. Values in parentheses are one standard deviation in units of the last reported digit. [b]From a recent set of 11 student teams at Macalester College. Values in parentheses denote the standard deviation of these results in units of the last reported digit. [c]Value from ref 14. [d]Value from ref 15. [e]Value from ref 16.

In our physical chemistry laboratory, we have the students present their results each week in either written or oral form. We expect written reports to follow the format of a research article such as one might submit to the *Journal of Physical Chemistry A*. Students present their work orally in a 15 min format, as if they were giving a talk at a scientific conference. In either form, the reports include an introduction, an experimental section, and a presentation and discussion of the results, which include comparisons to the literature.

HAZARDS

When handling the aluminum and nickel powders, students should wear gloves and avoid breathing dust from the powdered metals. Sample heating over a Bunsen burner should take place in a chemical fume hood. Students should not look directly at the pellet once it begins to glow, as the reaction produces very bright light for a period of several seconds. Care should be taken when cracking the $AlNi_3$ pellets with pliers, as small fragments could be projected in the process, which makes appropriate safety eyewear essential.

SUMMARY

In this experiment for the physical chemistry laboratory, students synthesize two intermetallic compounds, AlNi and $AlNi_3$, via a one-step, solid-state reaction. The students record powder X-ray diffraction spectra of the two synthesized compounds and their constituent elements aluminum and nickel. All four substances have cubic crystal structures, which make their X-ray diffractograms amenable to an assignment and quantitative analysis using a spreadsheet. Students are able to determine the type of cubic lattice present and the associated lattice constant, which can then be compared to the literature. Through this experiment, they gain an appreciation for the power of X-ray diffractometry for determining accurate solid-state structures.

ASSOCIATED CONTENT

Supporting Information

Laboratory instructions for the students; experimental notes and suggestions for instructors; sample analysis spreadsheet file. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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