Differential X-ray Diffraction: a Theoretical Basis for a Technique Based on Wavelength Variation

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Abstract
Differential diffraction is an extension of spectrum-subtraction techniques of spectroscopy to X-ray powder diffraction. In differential diffraction two patterns are taken for the same material under different conditions. The patterns are then subtracted to obtain information helpful in characterizing the material. Examples of exploitable effects are density, magnetism, particle size, preferred orientation and absorption. One application of differential diffraction is the identification of phases in mixtures. If differential diffraction techniques could be used to label each diffraction line in a pattern with the elements of the compound giving rise to that particular line, phase characterization of mixtures would be greatly simplified. One possible way to accomplish this labeling is to take advantage of the pronounced change in absorption that occurs near the absorption edge of an element. A theory is presented for a differential diffraction technique based on wavelength variation that will allow diffraction peaks to be labeled with elemental information. Patterns are calculated for a binary mixture of CuO and NiO using wavelengths chosen to straddle an absorption edge for Ni. The absorption effects make it easy to use the difference pattern to separate and identify the two phases present. Extension of this method to more complex multiphase mixtures would necessitate additional patterns and require solution through factor analysis.

In difference spectroscopy, two spectra are recorded under different conditions and subtracted. This seemingly trivial process results in a difference spectrum that contains information extremely useful in understanding changes in materials. For example, spectra of an organic molecule recorded before and after heat treatment provide a difference spectrum that may contain information useful in determining how heat degrades that molecule. Hirschfeld (1976) notes that difference methods depend on very exacting conditions of high signal-to-noise ratios and excellent wavelength repeatabilities. Although X-ray diffraction patterns typically do not have signal-to-noise ratios comparable to state-of-the-art Fourier transform infrared (FTIR) spectroscopy, it is beneficial to consider extensions of this idea to X-ray diffraction. Such extensions result in a number of possible methods called differential X-ray diffraction (DXD).

One of the more useful applications of DXD may be in the identification of phases in a complex mixture. In powder diffraction experiments involving mixtures of compounds, identification of each individual phase is complicated by the presence of other phases. If two or more patterns are obtained using conditions that increase or diminish the contribution of certain phases in a mixture, difference patterns could be obtained for possibly identifying those phases. As the patterns of identified phases are subtracted from the mixture pattern, the residual pattern may become simple enough to unravel by more conventional techniques. With the lower signal-to-noise ratio characteristic of X-ray diffraction patterns, methods that do not require sample handling are especially desirable because they do not introduce additional data scatter due to differences between samples.

Several of the ways individual differences in physical or chemical properties may be exploited to obtain a difference pattern are density or magnetic separation, solvent action, particle size differences, preferred
orientation effects, thermal treatment, anomalous dispersion or absorption effects.

As an example, consider the case of preferred orientation, an effect the analyst usually tries to minimize. Deliberate enhancement of differences in the nature or degree of preferred orientation may produce exploitable differences. If one sample is randomized and another is purposely oriented by pressing, packing, vibrating, settling, smearing or other methods, the resulting difference pattern should show strong peaks derived from the changing intensities for the phase that undergoes preferred orientation.

In the case of absorption, samples show marked differences in scattering power depending on the nature of the sample and the X-ray wavelength used. Difference patterns that result from using different wavelengths, especially in the vicinity of the absorption edge for one of the elements, should show enhanced peaks from those compounds that contain the element whose absorption edge has been spanned by the wavelengths used.

It should be pointed out that of all the methods mentioned above only the anomalous dispersion and absorption cases to be discussed here do not require permanent alteration or remounting of the unknown sample. In the case of absorption, samples show marked differences in scattering power and absorption as a function of the elements present. Individual elements also show marked absorption differences when different X-ray wavelengths are employed. Difference patterns that result from using different wavelengths should show enhanced peaks from those compounds that contain elements that have the largest absorption changes.

The absorption property probably has the greatest potential for development into a practical DXD method. This potential results because the sample never needs to be disturbed to obtain the multiple patterns required to produce the difference pattern. Consequently, sample-induced scatter caused by the need to use more than one sample does not occur. There are several ways in which absorption can be utilized in DXD. In the principal approach, which we will term DXD by wavelength variation (DXD-WV), a difference pattern would be obtained by subtracting patterns that are produced using different wavelengths. Wavelengths would be chosen to bracket the absorption edge of one of the elements (previously identified using X-ray fluorescence or other techniques) in the mixture. A difference pattern emphasizes the differences between the data and shows which peaks belong to the phase containing the element whose absorption edge was selected. Wavelength selection could be accomplished on a conventional scanning powder diffractometer by adjusting a diffracted beam monochromator or by selecting two channels in an energy dispersive detector, one on each side of the absorption edge for the element under consideration. Multiple patterns taken on either side of a number of absorption edges could be used, coupled with factor analysis, to unravel the complete pattern in terms of the diffraction peaks produced by phases containing certain elements. Using this approach, the fact that the diffraction peaks will move and that their intensities will change in response to the different wavelengths would need to be taken into account by using appropriate normalization methods.

A variation of this method would exploit the anomalous dispersion effects when a strong change in scattering is observed near a resonance wavelength for a particular element. It is probable that this variation would require a synchrotron source, but because a synchrotron source is not generally available to most practicing analysts the anomalous dispersion case will not be treated further here. Another variation utilizing wavelength variation would be to select individual diffraction peaks and scan across the absorption edge of the element under consideration. This experiment could be accomplished by varying the wavelength from one side of the edge in question to the other, while at the same time varying 2θ to maintain a constant d. Intensities of diffraction peaks, resulting from phases containing the element whose absorption edge is being scanned, will exhibit strong discontinuities as the edge in question is traversed. Diffraction peaks due to phases that do not contain the element in question should show minimal and continuous changes as the edge is traversed.

Two absorption effects need to be considered in DXD-WV. The first of these effects, macroabsorption, results in beam attenuation due to passage through separate ‘grains’ of each phase in a homogeneous sample with a ‘grain’ size that is small relative to an infinitely thick sample (generally less than 1 μm). The second effect, microabsorption, results in a modifi-

![Graph](image.png)

**Fig. 1.** The effect of different ratios of mass absorption coefficients in a binary mixture on the intensity contribution of any peak. $N = (\mu/p)/c(\mu/p)_0$ (modified from Klug & Alexander, 1974, p. 535).
cation of beam intensity due to absorption by a sample having a coarse 'grain' size or to an inhomogeneous sample that results in 'large' areas containing predominantly one phase.

The effect macroabsorption has on diffracted intensity, as a function of the weight fraction of phases and on mass absorption ratios, is shown in Fig. 1. It is observed that the intensities of lines in the pattern that stem from the compound having the higher absorption will be enhanced relative to the rest of the mixture. Correspondingly, the weaker absorbing material contributes less intensity.

The predicted effect of microabsorption is exactly the opposite of macroabsorption. Microabsorption does not allow ready analysis, but it is possible to estimate its effect for simple sample configurations.

2. Calculations

2.1. Basic intensity equation

Calculations have been undertaken to determine the magnitude of the intensity differences for selected compounds to verify the feasibility of the method and to examine the potential magnitude of the effect. Owing to the experimental convenience of using Cu Kα and Cu Kβ radiations, and Ni and Cu compounds, initial calculations have been made using the Ni K edge. The K absorption edge for Ni lies between Cu Kα and Cu Kβ. Hence compounds containing Ni should show marked differences in scattering behavior for these wavelengths, and the ratio of mass absorption coefficients of Ni-bearing and non-Ni-bearing phases should be altered significantly. The strongly absorbing phase would be accentuated in mixtures where the mass absorption ratio deviates significantly from unity.

The intensities of a powder diffraction pattern for a given compound may be calculated if the crystal structure is known. The expression for the integrated diffracted beam intensity on the absolute scale (I<sub>abs</sub>) for a flat randomly-oriented diffractometer sample (modified from Warren, 1969) is

$$I_{abs} = \frac{P_p}{16\pi R} \left( \frac{\lambda^4 e^4}{m^2 c^4} \right) \left( M_l |F_T|_l^2 \right) \left( \frac{1 + \cos^2 \theta}{\sin \theta \sin 2\theta} \right),$$

where the subscripts i, x and λ represent the ith diffraction maxima from phase x using a wavelength λ, P<sub>p</sub> is the total power of the primary beam in the irradiated area (A) of the sample, R is the distance from the sample to the detector slit, M<sub>i</sub> is the multiplicity factor, |F<sub>T</sub>|<sub>i</sub> is the structure factor including thermal effects, μ is the linear absorption factor, V is the volume of the unit cell and θ, ω, ε, m and c have their usual meanings. The trigonometric term is the Lorentz–polarization factor, usually abbreviated (L<sub>p</sub>).}

Table 1. The γ and 1/I<sub>c</sub> coefficients for α-Al<sub>2</sub>O<sub>3</sub>, NiO and CuO

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cu Kα</th>
<th>Cu Kβ</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ&lt;sub&gt;α-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;/sub&gt;</td>
<td>0.513 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>0.866 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>γ&lt;sub&gt;NiO&lt;/sub&gt;</td>
<td>0.197 × 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.476 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>γ&lt;sub&gt;CuO&lt;/sub&gt;</td>
<td>0.131 × 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.181 × 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td>(I&lt;sub&gt;c&lt;/sub&gt;/I&lt;sub&gt;NiO&lt;/sub&gt;)&lt;sub&gt;α-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;/sub&gt;</td>
<td>3.655</td>
<td>2.913</td>
</tr>
<tr>
<td>(I&lt;sub&gt;c&lt;/sub&gt;/I&lt;sub&gt;CuO&lt;/sub&gt;)&lt;sub&gt;α-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;/sub&gt;</td>
<td>4.732</td>
<td>5.267</td>
</tr>
</tbody>
</table>

*Data based on structures from Newnham & DeHahn (1962).
†Data based on structures from Shimomora (1955); Tunell, Posnjac & Ksanda (1935).

2.2. Relative absolute intensity scale

For experimental diffraction purposes, intensity comparisons are usually made on a 'relative-absolute' scale (I<sub>ra</sub>), where

$$I_{ra} = \frac{I_{abs}}{K} = \frac{M_o(L_p)|F_T|_l^2}{2\mu V^2}.$$ (2)

The quantity K contains those values that are constant for a given diffractometer system. In this and subsequent expressions, the triple subscript refers to the line in the diffraction pattern, the contributing phase and the selected wavelength, respectively. A double subscript implies only the phase and wavelength. The use of the subscript zero indicates the strongest line in the pattern while the subscript c refers to the standard phase, in this paper, corundum. Tabulated data are most commonly available on the relative scale through the factor γ<sub>x</sub>, where

$$\gamma_x = \frac{I_{ra}}{100} = \frac{M_o(L_p)|F_T|_l^2}{200\mu V^2}.$$ (3)

The γ<sub>x</sub> values calculated in this study using POWDIO (Smith & Nichols, 1981) are listed in Table 1.

2.3. Scaling of intensities

Scaling of intensities is extremely critical to proper interpretation of the difference patterns because the patterns are obtained with radiations having different P<sub>p</sub>'s and λ's (equation 1). Because the sample remains unchanged during the experiment, the measured intensities are proportional to I<sub>abs</sub> and

$$I_{ meas} \propto I_{abs} = P_p^3 K'I_{abs},$$ (4)

where K' = K/(P_p<sup>3</sup>). To compare patterns made using different radiations, α and β, it is necessary to measure the effective P<sub>p</sub> ratio, (P_p<sup>α</sup>)/(P_p<sup>β</sup>). This value can be measured using a standard sample. Choosing corundum, α-Al<sub>2</sub>O<sub>3</sub>, as a standard yields

$$\frac{I_{ meas}}{I_{ abs}} = \frac{I_{ meas}}{I_{ abs}} = \frac{I_{ meas}}{I_{ meas}} = \frac{P_p^3 I_{ meas}}{P_p^3 I_{ meas}} = \frac{(P_p^α)^2}{(P_p^β)^2}.$$

(5)
which, when combined with (2), yields

\[
(P\rho)_{\beta}^{2} = \frac{I_{\text{meas}}(\gamma_{\beta})}{I_{0\beta}^{\text{meas}}(\gamma_{\beta})}.
\]

Intensities can be placed on the relative-absolute scale using

\[
I_{\text{meas}} = \frac{I_{\text{meas}}(L_{\rho})_{\gamma}}{I_{0\gamma}^{\text{meas}}(L_{\rho})_{\gamma}}.
\]

It is also possible to calculate the theoretical ratios of intensities from patterns taken with two radiations, using

\[
I_{\text{mix}} = \frac{I_{\alpha}(L_{\rho})_{\gamma}}{I_{\beta}(L_{\rho})_{\gamma}}.
\]

2.4. Weighting factors for mixtures

X-ray diffraction patterns produced from a mixture of phases will be composites of the patterns from all the individual components. The relative weighting factor for each of the individual component patterns will depend on absorption effects and on the relative amounts of each component present. Klug & Alexander (1974) express this dependence for a binary mixture as

\[
K_{\text{mix}} = X_{x}X_{y}(\mu(\rho)_{\beta} - \mu(\rho)_{\gamma}) + \mu(\rho)_{\gamma}.
\]

For a pure phase, \((I_{\text{mix}})_{\text{pure}} = K_{\text{mix}} \cdot \mu_{\gamma} \cdot \mu_{\alpha} \). The scaling of the component patterns obtained from an ideally prepared mixture sample requires a knowledge of the absorption coefficients or a reference intensity ratio that has been obtained using an external standard.

The reference intensity ratio \((I/I_{c})\) is defined as the ratio of the intensities of the strongest lines in a 1:1 binary mixture (by weight) of the sample of interest and an appropriate standard. It may also be calculated using \(I/I_{c} = \mu_{\gamma}/\mu_{\gamma} \). At present corundum, \(\alpha-Al_{2}O_{3}\), is the most commonly used reference material (Hubbard, Evans & Smith, 1976), but several other materials are currently being certified by the National Bureau of Standards Office of Standard Reference Data (Hubbard, 1981). The \(I/I_{c}\) values can then be used to scale the composite patterns by

\[
\frac{(I_{\text{mix}})_{\text{mix}}}{(I_{\text{mix}})_{\text{mix}}} = X_{x}(I_{\alpha}/I_{c})_{x}X_{y}(I_{\beta}/I_{c})_{y},
\]

where \(X_{x}\) and \(X_{y}\) are the weight fractions of phases \(x\) and \(y\). The reference intensity ratio corrects for macro-absorption effects in a mixture. The appropriate calculated values for this study are included in Table 1.

2.5. Differential X-ray diffraction (DXD-WV) equations

Using the DXD-WV concept, a comparison of two patterns obtained using wavelengths \(\alpha\) and \(\beta\) utilizes the expression

\[
\Delta I_{\alpha}(I_{\beta}/I_{\alpha})_{\text{mix}} - \lambda_{\beta}(I_{\beta}/I_{\alpha})_{\text{mix}}
\]

which may be expanded to

\[
\Delta I_{\alpha}(I_{\beta}/I_{\alpha})_{\text{mix}} = \lambda_{\alpha}(I_{\alpha}/I_{\alpha})_{\text{pure}}(I_{\alpha}/I_{\alpha})_{\text{pure}} - \lambda_{\beta}(I_{\beta}/I_{\beta})_{\text{pure}}(I_{\beta}/I_{\beta})_{\text{pure}}
\]

Substituting (9) and \(N_{\lambda} = (\mu/\rho)_{\lambda,2}((\mu/\rho)_{\lambda})_{\text{pure}} \) yields

\[
\Delta I_{\alpha}(I_{\beta}/I_{\alpha})_{\text{pure}}(N_{2}X_{2}/(N_{2} - 1)X_{2} + 1)
\]

The effect of the macroabsorption factor, \((N_{2}X_{2})/(N_{2} - 1)X_{2} + 1\), is illustrated in Fig. 1. The higher the value of \(N\) for a component of a mixture, the more the intensity of the lines of the component is enhanced in the composite pattern.

Because of the absorption factors, the level of the intensities of the composite \(\alpha\) pattern is significantly higher on the relative-absolute scale than is the \(\beta\) pattern, and the differences will always have the same sign. It has proved more useful to scale the \(\alpha\) and \(\beta\) data differently using reference intensity ratios \((I/I_{c})\). Each pattern is scaled to an \(\alpha-Al_{2}O_{3}\) pattern for the appropriate radiation. This scaling has the effect of using a reference compound that is only slightly affected by absorption variations. The scaling thus defines the working level to be used for pattern comparisons. Then, by definition,

\[
I_{\alpha,\beta}^{\text{scaled}} = X_{x}I_{\alpha,\beta}^{\text{mix}}(I_{\alpha}/I_{c})_{x},
\]

for all \(\alpha\). When the data are scaled in this manner, experience has shown that the DXD-WV pattern yields mostly negative differences for the lines from compounds containing the elements whose absorption edge was bridged, and mostly positive deviations for the remainder of the pattern. This scaling has been used for the calculated examples in this paper.

2.6. Experimental considerations

The scaling of experimental data is more of a problem because it is not known \(a\ priori\) which lines belong to which compounds or even which compounds are present. Scaling using (5) results in \(\alpha\) and \(\beta\) patterns at different levels on the relative-absolute scale. Although scaling can be accomplished by adding \(\alpha-Al_{2}O_{3}\) to the mixture and using its peaks as a reference, it is often not a convenient procedure. However, successful scaling can usually be accomplished by examining the two patterns for a moderate-
to-strong line whose intensity ratios to several nearby lines do not show marked differences in the \( \alpha \) and \( \beta \) patterns. The intensities of this line can then be scaled to be equal in the \( \alpha \) and \( \beta \) patterns. Several trials may be required regardless of the choice of reference line, although the strongly negative peaks usually stand out on inspection.

As seen in (1), several factors are affected when using different radiations near an absorption edge. The most apparent and probably the most sensitive parameter is \( \mu \), the linear absorption coefficient, which influences the relative-absolute scale of the intensity set but does not alter the intra-pattern intensity ratios. Close to the absorption edge of an element, the anomalous dispersion coefficients become significant and measurably affect the atomic scattering factors that contribute to the structure factor \( F_T \). The anomalous scattering alters the intra-pattern intensity ratios for a compound and may have an effect on the absolute intensity. The other factor that changes is \( L_p \). This term is included in the scaling described above and requires no other consideration except where it may change the strong line used to determine \( I/I_T \). This effect occurs for the corundum pattern calculated for Cu \( K\beta \) radiation where the 116 line becomes 0.3% stronger than the 113 line - the most intense line calculated using Cu \( K\alpha \) radiation.

In experimental patterns the nature of the sample also becomes important and the effect of microabsorption must be evaluated carefully. Microabsorption occurs when particles of a strongly absorbing phase only partially screen the diffracted intensity from weakly absorbing phases in a mixture. It is extremely sensitive to the particle size and size differences when two or more phases are present. The theory of Brindley (1945) enables an approximate evaluation of the nature and magnitude of this effect on experimentally measured intensities. According to the theory, intensity ratios are modified by a correction factor based on absorption and size effects. An approximate experimental ratio is given by

\[
I_{ix\lambda}^{\text{rel}} = \frac{f_{ix\lambda}I_{ix\lambda}^{\text{rel}}}{f_{jx\lambda}I_{jx\lambda}^{\text{rel}}},
\]

where \( \tau_x \) is the microabsorption coefficient for phase \( x \). Values for \( \tau \) can be obtained using the tabulated data in International Tables for X-ray Crystallography (1962). It is important to note that the effect of microabsorption is to enhance the intensity of the weakly absorbing phase in a mixture causing the intensities from strongly absorbing phases to appear reduced on a relative basis. The limiting effect of microabsorption can be illustrated by considering the extreme case in which a sample is composed of very narrow strips of each phase oriented parallel to the diffraction plane. In this situation, no phase influences any other phase. The macroabsorption effect of the mixture is eliminated, and the fractional intensity contribution of each phase on the relative-absolute scale will be proportional to the volume fraction, \( f_x \), of that phase. The intensities will be given by

\[
I_{ix\lambda}^{\text{rel}} = \frac{f_{ix\lambda}I_{ix\lambda}^{\text{rel}}}{f_{jx\lambda}I_{jx\lambda}^{\text{rel}}}. \tag{16}
\]

Because the \( I^{\text{rel}} \) scale is the same for all compounds, it must be the \( \gamma \) factor that influences the magnitude of \( I^{\text{rel}} \). Referring to 3, it is apparent that the linear absorption coefficient, \( \mu \), is the dominant factor in \( \gamma \). In the absence of intergrain absorption effects, pattern intensities will vary inversely with \( \mu \).

3. Results

3.1. Implementation of DXD-WV

Several different approaches could be employed whereby the variations in intensity around an absorption edge might be exploited to obtain phase and/or chemical information about individual diffraction peaks. In the first of these techniques, a diffraction peak would be scanned maintaining a constant \( d \) by varying the scan angle as the wavelength is changed. The resulting trace would represent a single diffraction peak scanned over the absorption edge. A significant change in peak intensity at the edge would indicate that the peak contains the element associated with that edge. The magnitude of the change that occurs would depend on the amount of the element present in the compound. As many strong peaks as necessary could be scanned in this way until one of the phases is identified and its pattern subtracted from the composite pattern. In the second, perhaps more straightforward approach, two complete patterns would be obtained using fixed wavelengths on opposite sides of the absorption edge for a given element. By placing the intensities on the same \( d \) and intensity scales, differences between the two patterns would indicate effects due to the absorption edge. This latter approach is more amenable to currently available instrumentation and is outlined below in greater detail.

3.2. Compounds considered

For the purposes of the calculations performed here, compounds of copper and nickel have been used, specifically NiO and CuO. These elements were chosen for initial study because Cu \( K\alpha \) and Cu \( K\beta \) radiations, having reasonable intensity, are readily available using standard laboratory generators and because compounds of copper and nickel should show marked contrast with these radiations. The large difference between the linear absorption coefficients for Ni (See Table 2) accounts for a significant difference in the absolute intensity scale of the Cu \( K\alpha \) vs Cu \( K\beta \) patterns for nickel-bearing compounds and markedly affects the intensities in the patterns of
mixtures. The variation in absorption of these radiations by Cu is small. The fractional contribution to diffraction intensities of each phase in a Cu Kα pattern differs little from the weight fraction because the mass absorption ratio is near unity; but, in a Cu Kβ pattern, the deviation is very large because the mass absorption ratio is now quite large.

The anomalous dispersion coefficients also show significant differences that affect the scattering powers of the individual atoms. As previously indicated, anomalous dispersion will affect the relative intensities within a pattern more than it will the overall scaling. The effect is sufficient to cause perceptible differences between the patterns produced by the two wavelengths. The effect would be more pronounced in patterns from acentric compounds than from centric compounds because the $f''$ term would also become important. The $f'$ terms for Cu and Ni show opposite effects with the Cu scattering power for Cu Kβ, being about 2.5 electron scattering units (e.s.u.) more negative than for Cu Kα, whereas for Ni the scattering power is about 1.0 e.s.u. less negative. This effect enhances differences between the patterns of Cu- and Ni-bearing compounds.

3.3. Macroabsorption effects

Table 3 shows intensities calculated for rhombohedral NiO and monoclinic CuO using the POWD10 program (Smith & Nichols, 1981). Composite patterns were prepared for Cu Kα and Cu Kβ by calculating individual patterns, scaling the patterns by multiplying each data set by its appropriate $I/I_c$ value and adding the patterns. The columns labeled $I'$ contain integrated intensities for a 1:1 mixture by weight scaled to the relative-absolute scale using $I/I_c$ values. These patterns simulate composite experimental data that could be obtained for each radiation. The problem is to reverse the procedure and to use two different experimental patterns to indicate the component phases.

The column labeled $Δ$I in Table 3 shows the difference values obtained by subtracting the $Kβ$ pattern from the $Kα$ pattern when both patterns are on the same relative-absolute scale. It is immediately apparent when looking at the difference pattern that certain peaks may be attributed to the compound containing the element whose absorption edge was bridged. Those differences, which are strongly negative, are all due to the NiO component. The peaks attributable to CuO have differences near zero or distinctly positive. The variations from zero are mostly due to the effect of anomalous dispersion and partly due to the Lorentz–polarization ($L_p$) effect. Some of the weaker high-angle peaks of NiO are not sufficiently distinct from the CuO lines to allow them to be distinguished or tagged. Nonetheless, there are sufficient clearly tagged peaks to allow an identification of the NiO phase. All of the NiO lines can be removed from the pattern and the CuO quickly identified.

3.4. Microabsorption effects

To illustrate the potential magnitude of the effect of microabsorption on the data presented above, consider a sample of CuO–NiO with particle sizes 1 and 10 μm, respectively. The appropriate values of $τ$ (equation 15) are $(τ_{CuO})_x = 0.99$, $(τ_{NiO})_x = 1.02$, $(σ_{CuO})_β = 1.10$ and $(σ_{NiO})_β = 0.35$. These figures indicate that the experimental ratios for intensities in the Cu Kα pattern are little affected, but in the Cu Kβ pattern the CuO intensities will be enhanced by a factor of three with respect to the intensities of the NiO. This change is opposite to the macroabsorption effect that has been discussed above. In the extreme case where microabsorption completely cancels the absorption factor, the magnitudes are further enhanced. The column labeled Microabsorption case in Table 3 shows the intensities that would be obtained in the extreme case typified by the striped sample described previously. Not only have the signs of the differences reversed compared to the results from the macroabsorption case of Table 3, but the magnitudes of the CuO and NiO differences have been enhanced.

3.5. Separation methods

One way to separate a composite pattern into its components is to compare the patterns collected using different wavelengths on a plot of scaled intensity versus $d$. Scaling using experimental $I/I_c$ ratios compensates for differences in the incident beam power, $P_p$, that exist for Cu Kα and Cu Kβ. The intensity correction ratio $I/I_c$ should be measured experimentally to avoid system-dependent parameters, such as detector quantum counting efficiencies. Proper scaling gives intensity values comparable to those shown in Table 3. The plot is similar to what can be accomplished on split-screen video terminals, which are becoming more and more commonly used with modern diffraction systems.
Table 3. Calculated diffraction patterns for NiO and CuO using $\lambda = \text{Cu } K\alpha$ and $\lambda = \text{Cu } K\beta$ with intensities calculated on the relative-absolute scale ($I^{\text{ra}}$)

Values based on:
NiO: $a_0 = 2.954$, $c_0 = 7.236$ Å, SG = $R3m$;
CuO: $a_0 = 4.653$, $b_0 = 3.410$, $c_0 = 5.108$ Å, $\beta = 99^\circ29'$, SG = $C2/c$.

<table>
<thead>
<tr>
<th>Contributing phase (x)</th>
<th>$d$(Å)</th>
<th>hkl</th>
<th>$I_{\text{rea}}$</th>
<th>$I_{\text{red}}$</th>
<th>$\Delta I_{\text{rea-red}}$</th>
<th>$I_{\text{rea}}$</th>
<th>$I_{\text{red}}$</th>
<th>$\Delta I_{\text{rea-red}}$</th>
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<tr>
<td>NiO</td>
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4. Discussion

4.1. General

It has been shown in the theoretical development of the DXD-WV concept that differences will occur between diffraction patterns obtained with different radiations. These differences are enhanced when marked absorption differences exist for the different radiations employed. In powdered samples the effect of microabsorption also becomes significant when absorption differences become large. It may prove advantageous to accentuate the microabsorption by deliberately using coarse-grained samples rather than preparing an ideally fine-grained sample. The magnitude of the microabsorption effect can be so large that micronized samples would be required in order to observe the idealized macroabsorption effects. The coarse-grained specimen will also be advantageous as it will show minimum peak broadening and overlap. As long as the grains are small enough to ensure adequate particle statistics, these ‘coarser’ samples will result in better resolved peaks that can be more accurately tagged.

4.2. Potential applications

To utilize the DXD-WV approach for actual samples, with or without microabsorption effects, it will be necessary to modify a diffractometer or X-ray source in order to select different wavelengths. Using Cu K$\alpha$ and Cu K$\beta$ radiation will limit experiments to only those involving Ni compounds. Sealed X-ray tubes employing other targets would also be limited to detecting one or two elements. There are, however, several other experimental approaches that could extend the utility of the concept to many other elements.

One way to allow elemental labeling of diffraction peaks from compounds containing other elements would be to employ a synchrotron source. Such a source of X-rays would allow the selection of an intense beam of almost any wavelength desired, but would not be routinely available.

Although in the general case not all diffraction peaks for a given phase may be equally affected by this differential wavelength technique, the bulk of the intense peaks will be changed in the manner suggested by this paper. These changes in the intensities of the major peaks could then be used in conjunction with existing search/match procedures to identify phases containing the elements spanned by the edge in question. The peaks affected by this change in $\lambda$ are, to first order, those peaks in the phases containing the element whose edge has been spanned in the difference process. Armed with this information, most search/
match techniques would be in a position to provide an identification for the phase containing the element in question and would have received valuable negative information regarding the peaks that did not change as the edge was crossed.

Although the equipment requirements seem to be elaborate, the method may prove to be very useful. Using this technique, two patterns could be obtained from a multiphase sample without removing the sample from the diffractometer. The 'same' crystalline grains would then contribute to each pattern and the patterns would be directly comparable. Even if preferred orientation exists, differences observed may be sufficient to allow the diffraction lines to be labeled as to the elements present in the compounds. This information could greatly facilitate the identification of phases for complicated mixture problems. Computer graphical display and stripping algorithms already exist that, with modification, could be used to analyze the data.

We would like to acknowledge assistance received during the course of the work. Thanks are due to J. Mansfield and C. L. Bisson for computational assistance and advice, to H. L. Willyard for help in the preparation of the illustrations, to N. A. Sabo for editorial advice and to B. G. Nichols for proof reading and other assistance.

We acknowledge earlier work for the manner in which absorption effects may be useful in distinguishing phases; in particular a study of nickel inclusions in diamonds (Grenville-Wells & Lonsdale, 1959). The thrust of that study was to determine the approximate size and number of nickel inclusions present in artificial diamond crystals by utilizing the 'differential absorption' effects that resulted when a contaminated Cu X-ray tube was used to produce Weissenberg rotation photographs. By contrast, the efforts here explored the possible development of a differential technique that could be expanded to allow elemental labeling of major diffraction lines and thereby serve as a 'routine' analytical tool.

References


