X-Ray Diffraction Profiles of Inhomogeneous Binary Solids

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Z. Naturforsch. **33a**, 693–696 (1978); received April 5, 1978

A general expression for x-ray interference profiles of a binary alloy showing crystals of different concentration and thus different lattice dimensions is deduced. This expression contains previously reported relations as special cases, which are discussed briefly. It is not restricted to systems of total solid solubility or cubic lattice.

1. Introduction

A special application of x-ray diffraction is the evaluation of concentration spectra in a mixture of substitutional crystals [1–14]. Such information is of practical importance for sinter and diffusion technologies. As non destructive methods x-ray techniques have the advantage that the same sample can be examined in several steps of homogenisation or precipitation.

Since several contributions, as for instance crystal size, lattice distortion, constitution etc. usually affect the diffraction profile, the analytical problem of their separation has to be solved. Two different conceptions can be applied:

Based on diffraction theory an equation for the angular intensity distribution of the scattered radiation is established which is then solved with respect to the quantity in question [2, 4, 15, 16]. In general, however, such a straight-forward treatment is rather difficult because of the complexity of equations and the number of parameters involved. Several assumptions are necessary in order to obtain at least an approximate solution. The most sophisticated procedure in reaching this goal is Fourier analysis [4, 5, 19].

In order to overcome the difficulties mentioned above the other possibility is to compare computer synthesized diffraction profiles with those obtained experimentally. From the best match the desired parameters can be determined [10–14]. Although becoming more and more popular, such trial and error methods cannot provide evidence as to whether the solution obtained is unambiguous.

Since both conceptions require an equation for the diffraction profile one should aim at a minimum of approximative assumptions in the formulae used. With this in mind we deduce an expression for the intensity of the scattered radiation by successive inclusion of all influences resulting from the experiment. Starting with the scattering unit cell we generalize the expressions for the intensity of the detected radiation discussing the following items: crystal with uniform concentration, polycrystal consisting of such crystallites in random or preferred orientation, polycrystalline mixture of crystals showing a concentration spectrum. Finally the instrumental function is accounted for.

2. Theory

We shall consider a sample irradiated by monochromatic x-rays in a focusing diffractometer. It is thought to consist of crystals of a binary alloy system. Furthermore let these crystallites, showing different atomic concentration c and consequently different lattice dimensions $\boldsymbol{a}_j(c)$, be the smallest units scattering the x-rays coherently. Their lattice is assumed to be free of defects.

2.1. Scattering on a Single Elementary Cell

In the Fraunhofer approximation the amplitude of the wave scattered by an atom located at the point of the vector $\boldsymbol{r}$ is given by

$$A = f \exp(i \boldsymbol{K} \boldsymbol{r}) . \tag{1}$$

$\boldsymbol{K}$ is the difference of the wave vectors of incident ($\boldsymbol{k}_0$) and scattered radiation ($\boldsymbol{k}$), related to the scattering angle ϑ by $K = 2k \sin\vartheta$. f is the atomic scattering factor.

The elementary cell, characterized by the three (not necessarily cubic) axes $\{\boldsymbol{a}_j\}$, contains N atoms at sites $\boldsymbol{d}_n(c)$, $(1 \leqq n \leqq N)$. $\boldsymbol{d}_n$ are expressed in units $\boldsymbol{a}_j$. We then obtain for the superposition of all N scattered waves i.e. for the wave scattered by the unit cell

$$A = \sum_{n=1}^{N} f_n(K) \exp[i \boldsymbol{K} \boldsymbol{d}_n(c)] \times \exp\left[2\pi i \sum_{j=1}^{3} h_j m_j \frac{a_j(c)}{a_j}\right], \quad a_j = a_j(c=0) . \tag{2}$$

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Here we used the coordinates h_j along the directions $\boldsymbol{b}_j$ in reciprocal space ($\boldsymbol{K} = 2\pi \sum h_j \boldsymbol{b}_j$); m_j are integers assigned to the translations $m_j \boldsymbol{a}_j$ of the unit cell under consideration, with respect to an arbitrarily chosen origin within the crystal.

2.2. *Intensity of the Radiation Scattered by a Crystallite*

Summing up the amplitudes resulting from all $M_1 M_2 M_3$ unit cells of the crystal yields

$$A = \sum_{n}^{N} \sum_{m_1, m_2, m_3}^{M_1, M_2, M_3} f_n(K) \exp[i\, \boldsymbol{K}\, \boldsymbol{d}_n(c)] \times \exp\left[2\pi i \sum_{j=1}^{3} h_j\, m_j \frac{a_j(c)}{a_j}\right]. \tag{3}$$

If we assume the N atoms of type A or B in the unit cell to be randomly distributed at the sites $\boldsymbol{d}_n$, then a mean scattering factor

$$f(c, K) = f_{\mathrm{A}} + c(f_{\mathrm{B}} - f_{\mathrm{A}})$$

may be introduced*. Then the intensity of the scattered wave can be written as

$$I(c, h_j) = A A^* = f^2(c, K) \sum_{n, n'}^{N} \exp[i\, \boldsymbol{K}(\boldsymbol{d}_n - \boldsymbol{d}_{n'})] \times \sum_{m_j, m_j'}^{M_j} \exp\left[2\pi i \sum_{j=1}^{3} h_j (m_j - m_j') \frac{a_j(c)}{a_j}\right]. \tag{4}$$

The first sum normalised to one atom is the structure factor

$$G(c, h_j) = \frac{1}{N} \sum_{n, n'}^{N} \exp\{i\, \boldsymbol{K}[(\boldsymbol{d}_n(c) - \boldsymbol{d}_{n'}(c)]\}\,. \tag{5}$$

We further write l_j for $m_j - m_j'$ and obtain

$$I(c, h_j) = f^2(c, K)\, P(K)\, G(c, h_j) \times \prod_{j=1}^{3} \left\{ \sum_{l_j=1}^{M_j} \left(\frac{1}{2} - \frac{l_j}{M_j} \right) \exp 2\pi i\, h_j\, l_j \frac{a_j(c)}{a_j} \right\} \tag{6}$$

for the intensity of radiation scattered by the crystal per atom. (As we shall see later it is convenient to consider all atoms of the crystal to be identical and to be of imaginary concentration c). The polarisation factor $P(K)$ had to be introduced in order to account for the unpolarised incident radiation.

2.3. *Radiation Scattered by a Polycrystal*

The sample consists of a large number of crystals as described above, which are randomly oriented with respect to the vector $\boldsymbol{K}$. In order to calculate the intensity of the radiation scattered by such a sample we have to scan the sphere $\boldsymbol{K}^2 = \text{const}$ with the vector $\boldsymbol{K}$ and sum up the contributions to the intensity in every position. In the reciprocal space this sphere is given by

$$4\pi^2 \sum_{j=1}^{3} (h_j\, \boldsymbol{b}_j)^2 = \boldsymbol{K}^2\,. \tag{7}$$

In each position (h_1, h_2, h_3) the intensity (6) has to be weighted with the probability for a crystal to be found with such an orientation. Let this probability be $W(c, h_j)$ with

$$\iint_{2\pi |\sum h_j \boldsymbol{b}_j| = K} W\, \mathrm{d}f = 4\pi\, \boldsymbol{K}^2\,. \tag{8}$$

Replacing the sum by an integral we obtain for the intensity per atom

$$I_{\mathrm{p}}(c, K) = \frac{1}{4\pi K^2} \iint_{2\pi |\sum h_j \boldsymbol{b}_j| = K} I(c, h_j)\, W(c, h_j)\, \mathrm{d}f\,. \tag{9}$$

The range of integration is the area of the sphere (7).

2.4. *Instrumental Function*

Here we only outline the way in which instrumental influences are accounted for. A detailed derivation is found in [17].

The beam divergence is given by fixed solid angles of the incident and the scattered bundle. The vector $\boldsymbol{K}$ thus varies within a small region. Since all operations are carried out in reciprocal space, we express this range in coordinates h_j. For the inclusion of all contributions to the scattered intensity we again have to integrate over this region. It is to be noted, however, that the transformation of the angular variables into h_j leads to a factor $1/V$, where V is the volume of the region covered by $\boldsymbol{K}$ in reciprocal space [18]. It can be shown that this region is a parallelepiped with $V \propto \sin 2\overline{\vartheta}$. $\overline{\vartheta}$ is the nominal diffraction angle. I_{p} in (9) is integrated over the angular variables in spherical coordinates yielding a factor $\sin \overline{\vartheta}$ and K as the remaining variable. Further we may consider an intensity profile in the incident bundle and a nonuniform sensitivity within the area of the detector. This gives a weighting function which approximately depends upon $(K - K_0)/k \cos \overline{\vartheta}$. $\boldsymbol{K}_0$ is the

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* If the atoms are regularly positioned in the unit cell (ordered phases) no mean scattering factor can be defined. In this case we have to include the individual scattering factors f_n into the structure factor (5).

mean position of $\boldsymbol{K}$, thus corresponding to the nominal angular position $\overline{\vartheta}$ of the diffractometer. We obtain (per atom)

$$I_n(c, K_0) = \frac{B}{\cos\overline{\vartheta}} \int_0^\infty \mathrm{d}K \, I_\mathrm{p}(c, K) \, R\left(\frac{K - K_0}{k \cos\overline{\vartheta}}\right). \tag{10}$$

R is the instrumental function. It is significantly different from 0 only in a small region around $\boldsymbol{K}_0$. If this function is known (e.g. as an experimental result) near one particular diffraction angle, then it can be stated for the whole range since we know it's argument. B is a constant containing the dimensions of the beam slits in the diffractometer. The length of the sample, over which we also have to integrate, only alters the constant B if the diffraction angle is the same for all parts of the sample, i.e. if a focusing method (Bragg-Brentano-, Seeman-Bohlin-geometry) is used.

Finally we introduce the wavelength spectrum of the radiation by $L(k)$ which leads to

$$I_\mathrm{g} = \frac{B}{\cos\overline{\vartheta}} \int_0^\infty \mathrm{d}k \, L(k) \int_0^\infty \mathrm{d}K \, I_\mathrm{p}(c, K) \, R\left(\frac{K - K_0}{k \cos\overline{\vartheta}}\right). \tag{11}$$

Expressing I_p in (11) by (9) we may combine $\mathrm{d}K$ with $\mathrm{d}f$ yielding the volume element $\mathrm{d}V$ of the reciprocal space. The substitution $x_j = h_j a_j(c)/a_j$ gives

$$\mathrm{d}V = \frac{1}{V(c)} \prod_{j=1}^{3} 2\pi \, \mathrm{d}x_j \tag{12}$$

($V(c)$ ... volume of the elementary cell of concentration c) and furthermore

$$I_\mathrm{g}(c, K_0) \propto \frac{B}{V(c)\cos\overline{\vartheta}} \int_0^\infty \mathrm{d}k \, L(k) \iiint_{-\infty}^{\infty} \mathrm{d}x_j \frac{1}{K^2} \times I(c, h_j) \, W(c, h_j) \, R\left(\frac{K - K_0}{k \cos\overline{\vartheta}}\right). \tag{13}$$

2.5. Concentration Spectrum

We now consider the sample to be a general mixture of binary crystals. It is described by a concentration spectrum, being defined as the number of crystals per concentration interval. We also may express it by number of elementary cells or, as mentioned above, as the number of atoms $\mathrm{d}M$ with imaginary concentration in $[c, c + \mathrm{d}c]$. The latter we write

$$H(c) = \frac{\mathrm{d}M(c)}{\mathrm{d}c}. \tag{14}$$

Hence the intensity (13) must be weighted with $H(c)$ yielding

$$I = \int_0^1 \mathrm{d}c \, H(c) \, I_\mathrm{g}(c, K_0) \, A(c, K_0). \tag{15}$$

$A(c, K_0)$ includes the influence of absorption, if the crystals with composition c are not arbitrarily distributed, as for instance in a diffusion zone. For a mixed powder sample it becomes independent of c.

The number M of scattering atoms depends upon the diffraction angle if only a part of the sample is covered by the incident beam. The irradiated area of the sample changes with $1/\sin\overline{\vartheta}$ because of the inclined incidence. In such a case we obtain for the detected intensity per atom

$$I(K_0) \propto \frac{B}{\cos\overline{\vartheta}\sin\overline{\vartheta}} \int_0^1 \mathrm{d}c \frac{AH}{V} \int_0^\infty \mathrm{d}k \, L \iiint_{-\infty}^{\infty} \mathrm{d}x_j \frac{1}{K^2} \times RWG f^2 P \prod_{j=1}^{3} I_{M_j} \tag{16}$$

with the symbols listed below.

B constant containing the slit dimensions of the diffractometer
$A = A(c, \overline{\vartheta})$ absorption factor
$H = H(c)$ concentration spectrum Eq. (14)
$V = V(c) = \boldsymbol{a}_1(c) \cdot [\boldsymbol{a}_2(c) \times \boldsymbol{a}_3(c)]$ mean volume of the unit cell
$L = L(k)$ wavelength spectrum of the radiation
$x_j = h_j \cdot a_j(c)/a_j$
$K = 2\pi \left|\sum n_j b_j\right|$
$K_0 = 2k \cdot \sin\overline{\vartheta}$
$R = R([K - K_0]/k \cdot \cos\overline{\vartheta})$ instrumental function
$W = W(c, h_j)$ texture factor
$f = f(c, K)$ mean atomic scattering factor
$P = P(K)$ polarisation factor
$I_{Mj} = \sum_{l_j=1}^{M_j} (\frac{1}{2} - l_j/M_j) \cdot \exp 2\pi i \cdot h_j \cdot l_j \cdot a_j(c)/a_j$ particle size function.

3. Discussion

The relation (16) is an integral equation of the Fredholm type and shows the involvement of the concentration spectrum as well as all "undersired" parameters in the measured x-ray profile. In practice the solution of this equation with respect to one of the functions on the right hand side is required, as for instance to the normalized concentration spectrum or the particle size function.

The question of the existence and the uniqueness of this solution is considered in the theory of linear integral equations which also provides analytical methods for the solution of the Fredholm type integral equation. But since most of the functions in (16) are not analytically defined, we confine ourselves a priori to the numerical aspect of the solution. For the same reason no strict treatment can be found in the literature. It deals mainly with simplified formulae adapted to the particular experimental problems and the method of solution.

Thus the question arises, as to which of the simplifications lead to the relations in use and under which conditions they are justified. An answer to this question requires a detailed calculation and an estimation of errors in each particular case. In most cases we find that all effects increasing the line breadth are neglected, which means that the corresponding functions in (16) are replaced by the Dirac δ-function. By means of such approximations the function to be evaluated can be separated explicitely. We obtain for instance Rudman's [2] expression if we do so with L, R and I_{M_j}. Furthermore in this formula $V(c)$ was neglected. The first simplification might be tolerated if the dispersion of the line profile arises from a large difference of the lattice parameters rather than from the instrumental and from particle size broadening. But just in this case $V(c)$ varies strongly so that the expression should be considered with caution [16].

In any other cases the integral equation (16) is simplified to a convolution [4, 5, 19] by the assumption that the arguments in the respective functions are linear combinations. This approximation is allowed when the breadth of the profile is determined mainly by one single effect. In such a case the solution is obtained by a Fourier-transformation or (with respect to a better handling) a Fourier-development. This procedure is a well established method for the determination of particle size and lattice distortion in homogeneous polycrystals [19]. If more than one line broadening effect is substantially present then the above approximation is worse and the accuracy of the results has to be estimated for each case.

An essential restriction of most methods is that they are suitable only for binary systems without any miscibility gaps, sometimes even only for cubic lattices. In the equation reported in this paper, however, none of these restrictions is included, thus permitting a uniform treatment of general mixtures of crystals, provided the lattice dimensions correspond uniquely to the concentration. Of course approximations cannot be totally avoided in the numerical application, but restrictions are no longer necessary in the theory. Numerical aspects will be the subject of a further paper.

Acknowledgements

This work was sponsored by the Austrian Fonds zur Förderung der Wissenschaftlichen Forschung, Project Nr. 2152.

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