Determination of the Odd Part of the Texture Function by Anomalous Scattering

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Dedicated to the memory of Professor J. M. Bijvoet

Abstract

The texture function \( f(g) \) of a polycrystalline material may be split into two parts \( \tilde{f}(g) \) and \( \bar{f}(g) \), where the first one contains the terms of even order \( l \) in the series expansion, whereas the second one consists of the odd-order terms. In the case of centrosymmetric crystals, or by virtue of Friedel's law in noncentrosymmetric crystals, the contribution of \( \bar{f} \) to experimental pole figures is identically zero. Hence it is impossible to determine \( \bar{f} \) from pole figures obtained by 'normal' polycrystal diffraction experiments. It is suggested therefore that anomalous scattering of X-rays or neutrons should be used to determine \( \bar{f} \) from pole figure measurements directly and the corresponding formulae are given.

Introduction

The orientation distribution of crystallites in a polycrystalline material, i.e. the texture, can be described by a function \( f(g) \) where the rotation \( g \) describes the crystal orientation (Bunge, 1969). In the case of enantiomorphic crystals, two such functions are needed which refer to the right- and left-handed crystal forms (Bunge, Esling & Muller, 1980; Esling, Bunge & Muller, 1980). The texture function may be developed into a series of generalized spherical harmonics which are symmetrized with respect to crystal and sample symmetry [or more strictly speaking to the corresponding subsymmetry of rotations only (Bunge, 1969)].

\[
f(g) = \sum_{l=0}^{\infty} \sum_{\mu=1}^{M(l)} \sum_{\nu=1}^{N(l)} C_l^{\mu \nu} \bar{T}_l^{\mu \nu}(g) .
\]

This sum may be split into two parts corresponding to even and odd values of the index \( l \) (Matthies, 1979):

\[
f(g) = \bar{f}(g) + \tilde{f}(g) .
\]

It has been shown (Bunge, Esling & Muller, 1980; Matthies, 1979) that it is impossible to determine \( \tilde{f}(g) \) from 'normal' polycrystal diffraction experiments. This is because experimental pole figures are always the superposition of the figure belonging to the crystal direction \([hk\ell]\) and the one belonging to \([\bar{h}k\ell]\). These two directions are indistinguishable in 'normal' polycrystal diffraction experiments. This indistinguishability may, however, be due to different reasons:

1. in centrosymmetric crystals it is due to crystal symmetry;
2. in noncentrosymmetric classes it is due to Friedel's law which requires \( F_{\bar{h}k\ell} = F_{hk\ell} \)

in diffraction experiments carried out with 'normal' wavelengths.

Violation of Friedel's law by anomalous scattering

Friedel's law may be broken, however, in certain cases of anomalous scattering in the vicinity of an absorption edge (Coster, Knol & Prins, 1930; Bijvoet, 1949). It will be shown in the following that in these cases it should be possible to determine the contribution of the odd-order terms \( \tilde{f}(g) \) from polycrystal diffraction experiments.

Noncentrosymmetric crystals may belong to two different kinds of symmetry groups, namely the enantiomorphic groups containing rotations \( g_b \) only, and groups containing inversion axes, i.e. symmetry elements of the second kind \( I_g \), where \( I \) is the inversion centre, (but of course not the inversion centre itself). In the enantiomorphic groups an additional difficulty may arise if both right- and left-handed crystals are present in the polycrystalline sample at the same time. Polycrystal X-ray diffraction cannot distinguish between these two forms. This problem has been dealt with in the work of Bunge, Esling & Muller (1980). In the non-enantiomorphic groups containing mirror planes, or an inversion axis \( 4 \) (but not \( I \)), in addition to Friedel's law, other symmetry restrictions occur which will be dealt with in another paper (Bunge, Esling & Muller, 1981). Hence, in the present paper, we restrict ourselves to enantiomorphic crystals with only one of the two crystal forms present in the polycrystalline sample. The considerations can, however, with the
appropriate adaptations, also be applied to non-centrosymmetric crystals in general.

Texture analysis with non-superposed pole figures
The pole figure of the \([hkl]\) direction can be expressed by a series of surface spherical harmonics \(K_i(\alpha \beta)\) in the form

\[
P_{hkl}(\alpha \beta) = \sum_{i=0}^{\infty} \sum_{v=1}^{N(i)} \lambda_{i,v} K_i(\alpha \beta).
\] (4)

The coefficients \(\lambda_{i,v}\) are to be distinguished from the structure factors \(F_{hkl}\) in (3). (For both of these quantities the letter \(F\) is usually used.) The coefficients \(\lambda_{i,v}\) can be obtained from the pole-figure values by

\[
\lambda_{i,v} = \frac{4\pi}{2l+1} \sum_{\mu=1}^{M(i)} C_{i,v}^{\mu} K_{i,v}^{\mu}(\theta_{hkl}, \varphi_{hkl}).
\] (5)

They are related to the coefficients \(C_{i,v}^{\mu}\) by

\[
K_{i,v}^{\mu}(\theta_{hkl}, \varphi_{hkl}) = \frac{1}{2l+1} \left[ F_{i}(hkl) - \left( \frac{1}{2l+1} \sum_{\mu=1}^{M(i)} C_{i,v}^{\mu} K_{i,v}^{\mu}(\theta_{hkl}, \varphi_{hkl}) \right) \right].
\] (6)

With the relation

\[
K_{i,v}^{\mu}(\theta_{hkl}, \varphi_{hkl}) = (-1)^l K_{i,l}(\theta_{hkl}, \varphi_{hkl}),
\] (10)

this reads

\[
F_{i}(hkl) = \frac{4\pi}{2l+1} \left( \sum_{\mu=1}^{M(i)} C_{i,v}^{\mu} K_{i,v}^{\mu}(\theta_{hkl}, \varphi_{hkl}) \right) \times \left[ \frac{1}{2l+1} \sum_{\mu=1}^{M(i)} C_{i,v}^{\mu} K_{i,v}^{\mu}(\theta_{hkl}, \varphi_{hkl}) \right].
\] (11)

The complete orientation distribution function \(f(g)\) is in (2), then one easily finds

\[
\frac{1}{2l+1} \left[ F_{hkl}(\alpha \beta) + F_{hkl}(\pi - \alpha, \pi + \beta) \right] = F_{hkl}(\alpha \beta)
\] (12)

and

\[
\frac{1}{2l+1} \left[ F_{hkl}(\alpha \beta) - F_{hkl}(\pi - \alpha, \pi + \beta) \right] = \frac{1}{2} F_{hkl}'(\alpha \beta),
\] (13)

where \(r = 2(\varphi_{hkl} - \varphi_{hkl}')\) is the Bijvoet ratio (Ramachandran & Srinivasan, 1970).

Hence, the pole figure corresponding to the true texture is obtained by

\[
P_{hkl}(\alpha \beta) = \frac{1}{2} \left[ P_{hkl}(\alpha \beta) + P_{hkl}(\pi - \alpha, \pi + \beta) \right] + \frac{1}{2} \left[ P_{hkl}(\alpha \beta) - P_{hkl}(\pi - \alpha, \pi + \beta) \right].
\] (15)

To these pole figures the usual texture analysis process (including even and odd terms) can be applied according to (5), (6), (1), in order to obtain the complete orientation distribution function.

It is, however, necessary that only such pole figures be used for the determination of the odd part of the texture function for which \(F_{hkl} \neq F_{hkl}'\) (Bijvoet pairs), i.e. the direction \([hkl]\) must not be perpendicular to a mirror plane or a twofold axis of crystal symmetry.

Values of the Bijvoet ratio \(r\) have been reported to vary in the range from a few percent up to about 0·9 (Ramachandran & Srinivasan, 1970) and may be even higher with a suitable choice of wavelength in the vicinity of an absorption edge (International Tables for X-ray Crystallography, 1974). Anomalous scattering has also been observed in neutron diffraction. In the case of cadmium tartrate pentahydrate a mean value of the Bijvoet ratios of 0·177 has been found, whereas the maximum value was 0·56 (Sikka & Rajagopal, 1975). These ratios are assumed to be sufficient to apply the method described above.

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References


