

The contribution to asymmetry from  $hQ_x$  terms can be calculated analytically from the coefficients obtained in step 1 using B-S analysis (§ 3.1). These coefficients are not affected in the present scheme of separating thermal and static components.  $f(\mathbf{q})$  can then be obtained from the experimentally observed asymmetry of diffuse scattering. In a similar manner  $f(\mathbf{q})$  and hence  $I_{\text{TDS}}$  can be evaluated in different directions of reciprocal space. In this way the contribution from TDS can be obtained in a straightforward manner without actually computing mode frequencies using elastic constants. This method has the further advantage of yielding  $I_{\text{TDS}}$  over a range of temperatures, and an additional knowledge regarding the temperature dependence of various physical parameters is no longer required.

Once the contribution from TDS has been subtracted, the remaining diffuse intensity can be reanalysed using the method outlined in step 1 (§ 3.1). The coefficients thus obtained will have contributions only from static displacements.

#### Concluding remarks

Hayakawa, Bardhan & Cohen (1975) suggest the inclusion of higher powers of  $\mathbf{u}$  in the expansion of  $\exp(i\mathbf{K} \cdot \mathbf{u})$  for observing the direct effect of temperature factors, common to all contributions of diffuse scattering. This is not strictly true [see equation (7)] as  $\delta^2$  terms due to thermal vibrations suffice to produce the above mentioned effect and higher powers are not in general required.  $u^2$  terms included in the present formalism correspond to static distortions and they are expected to yield information about the strongly distorted neighbourhood around the core of the SRO domain/cluster.

We should also note a basic difference between static and dynamic Debye-Waller (DW) factors. Static distortions attenuate atomic form factors only near fundamental reflections and do not modify scattering elsewhere in the reciprocal space (Khanna, 1984). On the other hand, the dynamic DW factor, in addition to affecting Bragg peaks, attenuates diffuse scattering from other sources as well. This result has an important implication. According to (7) the experimental diffuse scattering data have to be weighted by the thermal DW factor  $\exp[-\omega_k(\mathbf{Q})]$ . Since it is rather difficult to calculate  $\exp[-\omega_k(\mathbf{Q})]$  accurately, Bardhan & Cohen (1976) employed the ratio  $I(100)/I(300)$  (for f.c.c. crystals) to obtain  $\exp[-2\omega(\mathbf{Q})]$ . Their claim, that the DW factor thus obtained contains both static and dynamic contributions, is however not correct.  $I(100)/I(300)$ , the ratio of scattered intensity at superlattice reflections, contains only dynamic contributions and yields the correct DW factor needed to reduce the experimental diffuse scattering data.

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## On the Effective Physical Properties of Polycrystalline Materials

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#### Abstract

An iteration method is presented for calculation of the gross physical properties of polycrystals in terms of the physical properties of the crystals. No assumptions are made concerning the shape or behaviour of

the crystallites. The only mathematical condition to be fulfilled is that the product of the matrix of a gross physical property with its inverse must give a unit matrix if the same is valid for the crystals. The method is demonstrated by the calculation of the effective elastic tensor of a hypothetical texturized polycrystal

consisting of Cu crystallites. The calculated upper and lower bounds of the Young modulus are extremely close to each other.

### Introduction

Let  $P$  denote the matrix representation of a physical property of a single crystal. We are concerned with properties for which

$$PP^{-1} = P^{-1}P = I \quad (1)$$

where  $P^{-1}$  is the inverse of matrix  $P$  and  $I$  denotes the unit matrix.

A polycrystalline material consists of a great number of crystallites with orientation  $g$ .  $g$  is defined by the rotation which transforms the coordinate system  $K_A$  fixed to the polycrystalline material into system  $K_B$  fixed to a crystallite (Fig. 1). The basic domain of orientations, containing only one of the symmetrically equivalent orientations, will henceforth be denoted by  $G$ .

The distribution of orientations is described by the density function  $f(g)$  defined by (Bunge, 1969, p. 26)

$$\Delta V(g)/V = f(g) dg \quad (2)$$

where  $\Delta V(g)$  is the volume of all crystallites having orientations in the range  $dg$  around  $g$  and  $V$  means the volume of the polycrystal.  $f(g)$  is generally determined from the measured pole figures in an indirect way using the series expansion method of Bunge (1969). In our work we use a hypothetical function  $f(g)$  abstracted from a number of functions actually determined by Matthies & Vinel (1983). A standard model function  $f(g)$  would be useful in the future to compare different calculation methods of gross physical properties.

The matrix of the physical property of the polycrystal corresponding to  $P$  of the crystallites is denoted by  $\tilde{P}$ . In the case of fulfilment of relation (1) an analogous relation is required of the corresponding gross properties, *i.e.*

$$\tilde{P}\tilde{P}^{-1} = \tilde{P}^{-1}\tilde{P} = I. \quad (3)$$

$\tilde{P}$  relates the gross physical properties  $\tilde{X}$  and  $\tilde{Y}$  by the linear relation

$$\tilde{Y} = \tilde{P}\tilde{X}. \quad (4)$$

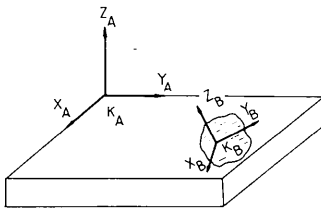


Fig. 1. Coordinate systems  $K_A$  and  $K_B$  fixed to the polycrystal and a crystallite, respectively.

The inverse relation is

$$\tilde{X} = \tilde{P}^{-1}\tilde{Y}. \quad (5)$$

### The model

The problem is the determination of the gross matrices  $\tilde{P}$  and  $\tilde{P}^{-1}$  of a polycrystalline aggregate in terms of the matrices  $P$  and  $P^{-1}$  of the constituent crystallites. We are looking for solutions under the assumption that  $P$  depends on the orientation of the crystallite only, *i.e.*

$$P = P(g). \quad (6)$$

The mean of the matrices  $P(g)$  is defined by

$$\bar{P} = V^{-1} \int P(g) dV. \quad (7)$$

The integration can be performed in two steps: first over all volume elements with orientation  $g$  and then over all orientations (Bunge, 1969, p. 178):

$$\bar{P} = V^{-1} \int_G P(g) \int_{V(g)} dV. \quad (8)$$

With the help of definition (2)

$$\bar{P} = \int_G P(g)f(g) dg. \quad (9)$$

Analogously

$$\overline{P^{-1}} = \int_G P^{-1}(g)f(g) dg. \quad (10)$$

Generally  $\bar{P}$  and  $\overline{P^{-1}}$  do not fulfil the condition (3), and consequently  $\bar{P}$  and  $\overline{P^{-1}}$  are not solutions of the problem. To find the correct solutions let us write the inverse relation (5) in the form

$$\tilde{P}^{-1}\tilde{Y} = P^{-1}(g)P(g)\tilde{X} \quad (11)$$

and multiply the definition (4) by  $P^{-1}(g)$ ,

$$P^{-1}(g)\tilde{Y} = P^{-1}(g)\tilde{P}\tilde{X}. \quad (12)$$

The sum of these two equations is

$$[\tilde{P}^{-1} + P^{-1}(g)]\tilde{Y} = P^{-1}(g)[P(g) + \tilde{P}]\tilde{X} \quad (13)$$

from which

$$\tilde{Y} = [\tilde{P}^{-1} + P^{-1}(g)]^{-1}P^{-1}(g)[P(g) + \tilde{P}]\tilde{X}. \quad (14)$$

A comparison with definition (4) gives

$$\tilde{P} = [\tilde{P}^{-1} + P^{-1}(g)]^{-1}P^{-1}(g)[P(g) + \tilde{P}]. \quad (15)$$

On the other hand, if we write definition (4) in the form

$$\tilde{P}\tilde{X} = P(g)P^{-1}(g)\tilde{Y} \quad (16)$$

and multiply the inverse relation (5) by  $P(g)$ ,

$$P(g)\tilde{X} = P(g)\tilde{P}^{-1}\tilde{Y}, \quad (17)$$

then upon taking the sum of (16) and (17) we get

$$\tilde{X} = [\tilde{P} + P(g)]^{-1}P(g)[P^{-1}(g) + \tilde{P}^{-1}]\tilde{Y}. \quad (18)$$

A comparison with the inverse relation (5) leads to

$$\tilde{P}^{-1} = [\tilde{P} + P(g)]^{-1} P(g) [P^{-1}(g) + \tilde{P}^{-1}]. \quad (19)$$

We take into account all crystallites by taking the average of both sides of (15) and (19):

$$\tilde{P} = \int_G [\tilde{P}^{-1} + P^{-1}(g)]^{-1} P^{-1}(g) [P(g) + \tilde{P}] f(g) dg \quad (20)$$

$$\tilde{P}^{-1} = \int_G [\tilde{P} + P(g)]^{-1} P(g) [P^{-1}(g) + \tilde{P}^{-1}] f(g) dg. \quad (21)$$

The required  $\tilde{P}$  and  $\tilde{P}^{-1}$  are the limit values of the following series

$$\begin{aligned} \tilde{P}^{(N+1)} &= \int_G [\tilde{P}^{-1(N)} + P^{-1}(g)]^{-1} P^{-1}(g) \\ &\quad \times [P(g) + \tilde{P}^{(N)}] f(g) dg \end{aligned} \quad (22)$$

$$\begin{aligned} \tilde{P}^{-1(N+1)} &= \int_G [\tilde{P}^{(N)} + P(g)]^{-1} P(g) \\ &\quad \times [P^{-1}(g) + \tilde{P}^{-1(N)}] f(g) dg. \end{aligned} \quad (23)$$

Thus, knowing the matrices  $P(g)$  and  $P^{-1}(g)$  and the distribution of crystallite orientations described by  $f(g)$  we can calculate the effective matrices  $\tilde{P}$  and  $\tilde{P}^{-1}$  of the polycrystalline material by successive approximation. The initial functions  $\tilde{P}^{(0)}$  and  $\tilde{P}^{-1(0)}$  are chosen to be the mean values  $\bar{P}$  and  $\overline{P^{-1}}$  calculated from (9) and (10), respectively, i.e.

$$\tilde{P}^{(0)} = \bar{P} \quad (24)$$

and

$$\tilde{P}^{-1(0)} = \overline{P^{-1}}. \quad (25)$$

### Elasticity of crystallites

We shall apply the model to the calculation of elastic tensors of polycrystals. First we must control the relation (1).

For small deformations the stresses  $\sigma_{ij}$  depend linearly on the strains  $\epsilon_{kl}$  (Hooke's law):

$$\sigma_{ij} = c_{ijkl} \epsilon_{kl} \quad (i, j, k, l = 1, 2, 3). \quad (26)$$

The matrix  $C$  of elastic coefficients  $c_{ijkl}$  is  $9 \times 9$ , relating the nine elements  $\sigma_{ij}$  to the nine elements  $\epsilon_{kl}$ . The inverse relation reads

$$\epsilon_{mn} = s_{mnop} \sigma_{op} \quad (m, n, o, p = 1, 2, 3). \quad (27)$$

We denote the  $9 \times 9$  matrix with the elements  $s_{mnop}$  by  $S$ .

The product of the matrices  $C$  and  $S$  is not an ordinary unit matrix  $I$ , but

$$CS = SC = U \quad (28)$$

with the elements

$$u_{ijj} = 1 \quad (i = j) \quad (29)$$

$$u_{ijj} = \frac{1}{2} \quad (i \neq j) \quad (30)$$

and the other elements which are not symmetrically equivalent to the ones above are zeros.  $U$  can be considered as a definition of a special unit matrix, limited to the  $9 \times 9$  representation of elastic coefficients. Whenever it is multiplied into a complete matrix with the symmetries peculiar to elasticity, it has the same effect as a proper unit matrix (Hirth & Lothe, 1968, p. 403). Thus, if we use the  $9 \times 9$  representation of the elastic coefficients the matrix  $U$  plays the role of  $I$  in the preceding sections.

### Calculations

We applied the model to the calculation of the effective elastic tensor of a polycrystal consisting of Cu crystallites. The elastic constants for Cu crystals on the basis of data given by Hirth & Lothe (1968, p. 762) in units of  $10^{13}$  Pa are ( $i \neq j, i, j = 1, 2, 3$ )

$$c_{iiii} = 1.684 \quad c_{ijj} = 1.214 \quad c_{ijj} = 0.754. \quad (31)$$

The elastic compliances in units of  $10^{-13}$  Pa<sup>-1</sup> are

$$s_{iiii} = 1.498 \quad s_{ijj} = -0.629 \quad s_{ijj} = 0.332. \quad (32)$$

The distribution of orientations of the Cu crystallites was chosen according to the model function  $f(g)$  (Fig. 2) constructed by Matthies & Vine (1983) often used for examinations of theoretical problems in texture analysis (e.g. Esling, Bunge, Philippe & Muller,

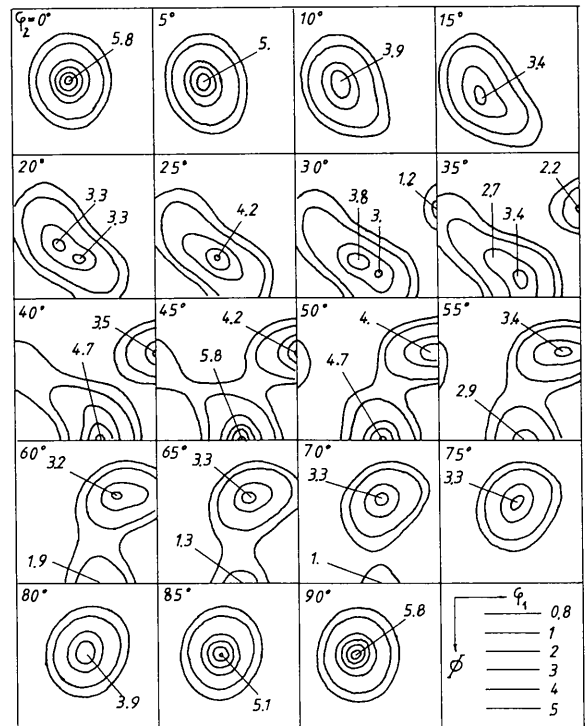


Fig. 2. Three-dimensional orientation density function  $f(g)$  represented by its two-dimensional sections. (Courtesy of Professor S. Matthies.)

Table 1. Results for the example discussed in the text

N	Coefficient	ijkl								
		1111	2222	3333	1122	1133	2233	1212	1313	2323
0	$\tilde{P}^{(0)}: \overline{c_{ijkl}^A}$	2.149	2.161	2.132	0.968	0.997	0.985	0.525	0.537	0.508
	$\tilde{P}^{-1(0)}: \overline{s_{ijkl}^A}$	0.845	0.828	0.869	-0.282	-0.323	-0.306	0.655	0.638	0.679
	$\tilde{u}_{ijkl}^{(0)} (\tilde{P}^{(0)} \tilde{P}^{-1(0)} = \tilde{u}^{(0)})$	1.221	1.215	1.229	-0.110	-0.124	-0.118	0.688	0.685	0.690
1	$\tilde{P}^{(1)}: \overline{c_{ijkl}^{A(1)}}$	2.047	2.059	2.029	1.022	1.052	1.040	0.448	0.459	0.433
	$\tilde{P}^{-1(1)}: \overline{s_{ijkl}^{A(1)}}$	0.743	0.731	0.761	-0.237	-0.267	-0.255	0.560	0.546	0.579
	$\tilde{u}_{ijkl}^{(1)} (\tilde{P}^{(1)} \tilde{P}^{-1(1)} = \tilde{u}^{(1)})$	0.998	0.998	0.998	-0.006	-0.007	-0.006	0.502	0.501	0.501

1987). The function is represented by its two-dimensional sections in the shape of Eulerian angles  $\varphi_1, \phi, \varphi_2$  (Bunge, 1969).

For the calculations the basic domain  $G$  of the Eulerian space was divided into cells with  $\Delta\varphi_1 = \Delta\phi = \Delta\varphi_2 = 5^\circ$ . The transformed values  $c_{ghmn}^A$  and  $s_{ghmn}^A$  were calculated according to

$$c_{ghmn}^A = a_{ig} a_{jh} a_{km} a_{ln} c_{ijkl}^B \quad (33)$$

where the superscripts  $A$  and  $B$  refer to the coordinate systems  $K_A$  and  $K_B$ , respectively, and  $c_{ijkl}^B$  and  $s_{ijkl}^B$  are the values listed in (31) and (32), respectively.  $a_{jh}$  means the direction cosines of the  $j$ th axis of  $K_B$  with respect to the  $h$ th axis of  $K_A$ .  $c_{ghmn}^A$  and  $s_{ghmn}^A$  are the components of matrices  $P(g)$  and  $P^{-1}(g)$ , respectively.

### Results

The function  $f(g)$  possesses an orthorhombic sample symmetry. Table 1 therefore contains the nine independent constants only. The product

$$\tilde{P}^{(N)} \tilde{P}^{-1(N)} = U^{(N)} \quad (34)$$

for  $N=0$  differs considerably from the unit matrix

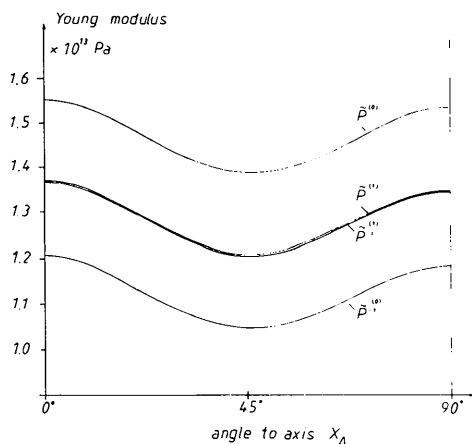


Fig. 3. The Young modulus for a polycrystal consisting of Cu crystallites with the orientation density function  $f(g)$ . The zero approximations  $\tilde{P}^{(0)}$  and  $\tilde{P}^{-1(0)}$  are equivalent to the Voigt and Reuss bounds, respectively. After one iteration step (30 min CPU, IBM 360) the new bounds are very close.

(29), (30). Already one iteration step leads to such satisfying results that further iteration is practically unnecessary.

Fig. 3 shows the anisotropy of the Young modulus in the  $(X_A, Y_A)$  plane of the polycrystal calculated from  $\tilde{P}^{(0)}$ ,  $\tilde{P}^{-1(0)}$ ,  $\tilde{P}^{(1)}$  and  $\tilde{P}^{-1(1)}$ . The difference between the Young moduli derived from  $\tilde{P}^{(1)}$  and  $\tilde{P}^{-1(1)}$  is approximately a constant value of  $2.2 \times 10^{10}$  Pa.

### Discussion

$\tilde{P}^{(0)}$  corresponds to the Voigt (1928) approximation which is appropriate for a polycrystal in which the grains have the same state of strain.  $\tilde{P}^{-1(0)}$  corresponds to the Reuss (1929) approximation with the assumption that the grains have the same stress. The advantage of the Voigt and Reuss treatment is that they do not make any assumptions concerning crystal behaviour or shape. This advantage was also retained by Hashin & Shtrikman (1962) using a variational method for the derivation of new lower and upper bounds for the effective elastic moduli. The bounds obtained by Bunge (1974) are also closer than the Voigt and Reuss bounds. Bunge's approximation is based on the assumption of minimum elastic energy under the condition of constant mean strains or stresses.

Our model belongs also to those in which no assumptions concerning shape or behaviour of the crystals are involved, but the fulfilling of the condition (3) established by Alexandrow & Aisenberg (1966) was aimed at. The resulting two bounds are already extremely close to each other after one iteration step.

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## Exact Conditional Distribution of a Three-Phase Invariant in the Space Group $P1$ . I. Derivation and Simplification of the Fourier Series

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### Abstract

An exact expression is derived for the conditional probability density function of a three-phase invariant and the general result is applied to the space group  $P1$ . The expression for the conditional density is given in terms of a sixfold Fourier series. A straightforward numerical evaluation of this series, without further analysis, is extremely time consuming. Much of the present paper is therefore devoted to an exposition of symmetries hidden in the various summations. The computational effort required for the evaluation of the above expression is thereby reduced to manageable proportions in a number of interesting cases. Results of numerical computations of the exact conditional density are given in the second paper in this series. It is also shown that the exact expression for the conditional probability reduces to that given by Cochran [*Acta Cryst.* (1955), **8**, 473-478].

### Introduction

Current approaches to phase determination by direct methods are based on the use of linear combinations of phases invariant under a shift of the origin of the unit cell. Such combinations are generally termed structure invariants (Hauptman & Karle, 1953). Of these, one of the most extensively used is the so-called three-phase structure invariant associated with the product of the three normalized structure factors  $E_h$ ,  $E_k$  and  $E_{-h-k}$ , i.e.

$$\Phi = \varphi_h + \varphi_k + \varphi_{-h-k}. \quad (1)$$

In order to use the three-phase invariant for structure determination one needs to know the conditional probability density function (c.p.d.f.) of  $\Phi$ , where the

conditioning is on the values  $|E_h|$ ,  $|E_k|$  and  $|E_{-h-k}|$ . An approximate form of this c.p.d.f., based on the central limit theorem, was first derived by Cochran (1955). Corrections to this result were subsequently calculated by a number of investigators in terms of Gram-Charlier, Edgeworth, or exponentiated series [e.g. Naya, Nitta & Oda (1965); Hauptman (1971); Karle (1972); Karle & Gilardi (1973); Giacovazzo (1974); Peschar & Schenk (1986); a rich source of references is the book by Giacovazzo (1980)]. As in the above studies we shall assume that the primitive random variables of the problem are the atomic coordinates, which vary independently and uniformly over the (0, 1) range. However, none of the approximate c.p.d.f.'s have been compared with exact results to assess their accuracy. Such an assessment is the motivation for the present study.

We have recently developed methods, not involving the approximations based on the central limit theorem, for calculating exact representations of p.d.f.'s useful in crystallographic applications (e.g. Shmueli, Weiss, Kiefer & Wilson, 1984; Shmueli & Weiss, 1985, 1986). Some of the problems considered include that of finding exact representations of the p.d.f.'s for  $|E|$  in various space groups as well as for joint p.d.f.'s for  $E$  from which exact  $\sum_1$  and  $\sum_2$  relationships can be recovered. In the present two papers we present some analogous results for the p.d.f. of the three-phase invariant  $\Phi$  relevant to the solution of the phase problem in non-centrosymmetric structures. As in the above studies we shall assume that the primitive random variables of the problem are the atomic coordinates which, in the space group  $P1$ , vary independently and uniformly over the (0, 1) range.