



Kontrym-Sznajd, G., & Dugdale, S. B. (2015). How to estimate isotropic distributions and mean values in crystalline solids. *Journal of Physics: Condensed Matter*, 27, [435501]. DOI: 10.1088/0953-8984/27/43/435501

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How to estimate isotropic distributions and mean values in crystalline solids

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Abstract: The concept of special directions in the Brillouin zone and the applicability of Houston's formula (or its extended versions) to both theoretical and experimental investigations are discussed. We propose some expressions to describe the isotropic component in systems having both cubic and non-cubic symmetry.

This results presented have implications for both experimentalists who want to obtain average properties from a small number of measurements on single crystals, and for theoretical calculations which are to be compared with isotropic experimental measurements, for example coming from investigations of polycrystalline or powder samples.

Keywords: isotropic average, Debye temperature, specific heat, Compton scattering

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1. Introduction

Many of the physical properties of crystalline solids have the full symmetry of the Brillouin zone (BZ), i.e. they are invariant under all symmetry operations of the point group. Examples include the Fermi surface, effective mass, the electron momentum density (and associated quantities such as Compton scattering spectra [1-3]) and frequency distribution [4]. Such *anisotropic* quantities, denoted here as $f(\mathbf{p})$, which describe many electronic and thermodynamic properties of crystals, could be expressed as a series of lattice harmonics $F_{l,v}(\theta,\varphi)$ of an appropriate symmetry [4]:

$$f(\mathbf{p}) = \sum_{l,v} f_{l,v}(p) F_{l,v}(\Theta, \varphi). \quad (1)$$

The index v distinguishes harmonics of the same order, (Θ, φ) are the azimuthal and polar angles of the direction \mathbf{p} with respect to the reciprocal lattice coordinate system and $f_{l,v}(p)$ are the radial coefficients of the investigated function $f(\mathbf{p})$.

Such an expansion was proposed by Houston, for determining the frequency distribution $f(\mathbf{v})$ in order to obtain the total distribution

$$N(\mathbf{v}) = \int \int f(\mathbf{v}, \Theta, \varphi) \sin \Theta d\Theta d\varphi = 4\pi f_0(\mathbf{v}), \quad (2)$$

and subsequently the Debye temperature [4]. As an illustration of the applicability of this formula, Houston checked if it were possible (for cubic structures), using only the three first cubic harmonics in Eq. (1) and a knowledge of $f(\mathbf{p})$ along three high symmetry directions (HSD), to get similar results to those obtained by a more laborious method [5]. In order to determine the radial functions $f_{i,j}(p)$ he solved the set of three algebraic equations (Eq. (1)) instead of performing integration over solid angle (Eq. (2)). Such a method, known as Houston's method, can be applied when the number of terms in Eq. (1) equals to the number of sampling directions $f(\mathbf{p})$.

After allowing for a numerical error in Houston's calculations, the formula

$$f_0^a(p) = [10 f_{[100]}(p) + 16 f_{[110]}(p) + 9 f_{[111]}(p)] / 35 \quad (3)$$

was published in Refs. [6, 7]. Note that superscript "a" emphasises that the use of a finite number of harmonics in Eq. (1) always leads to an approximate value.

Eq. (3) has been used extensively in the theory of thermodynamic properties of crystals with cubic symmetry [8-10], the sum of plane waves over the BZ [11] as well as in studies of electronic properties via one-dimensional angular correlation of annihilation radiation [12-15], Compton scattering [16-25] or positron Doppler broadening spectra [26]. In the latter case Eq. (3) was used either to compare some isotropic theoretical quantity with an average computed from several experimental spectra or to compare experimental spectra measured on polycrystalline samples or powders with an average computed from theoretical spectra.

In spite of being able to determine $f_0(p)$ much more precisely, Houston's formula (Eq. 3), which leads to a very approximate description of $f_0(p)$, is still used, even in the case of theoretical calculations. For example, in Refs. [17-20, 25] Compton profiles along three high symmetry directions (HSDs) were calculated and then Houston's formula was applied to compare the theory with a measurement made on a polycrystalline sample. For inexplicable reasons, in almost all papers the formula expressed in (3) or its extended versions (including also 3-HSD) [9-11] is applied instead of using special directions (SDs) which essentially increases the accuracy to which $f_0(p)$ can be estimated. We emphasize that, for example, for cubic crystals, 1-SD is as good as 3-HSDs, and 6-SDs or 10-SDs are as good as 16 or 27 arbitrarily chosen directions, respectively.

In this paper we show how to estimate $f_0(p)$ for objects having cubic, tetragonal and hexagonal symmetries, and compare the results of the commonly used formulae with corresponding results which come from applying the idea of SDs.

The idea of SDs was introduced by Bansil [28] to reduce three-dimensional (3D) integration over the BZ to a one-dimensional (1D) integral. Bansil proposed sets of SDs, which would optimize calculations of the isotropic component, $f_0(p)$. In subsequent papers [29-37], in which (except for [32,33,36]) cubic structures were considered, the authors estimated such sets of SDs which also enabled the determination of anisotropic $f_{l,v}(p)$. To the best of our knowledge, SDs were utilised in theoretical calculations only in a few papers [38-48].

From the many possible sets of SDs for the cubic structure, we select those which should be the most convenient for experimentalists who want to obtain average properties from a small number of measurements on single crystals, and for theoretical calculations which are to be compared with isotropic experimental measurements. Moreover, because the authors of Refs. [28-31, 34] proposed equations for the isotropic average $f_0(p)$ (based on SDs) only for cubic symmetries, here we propose such expressions also for non cubic structures.

Our considerations are also valid in the real space, with the exception of the hcp structures in which the point symmetry group is non-symmorphic (in real space, some elements contain non-primitive translations, i.e. the point group, so also lattice harmonics, are different).

2. Cubic structures

Analysing results for $f_0(v)$ determined from Eq.(3), Houston concluded [4]: “the use of additional terms in the expansion (1) will reduce the overemphasis and the spurious peaks, and will tend to approach the correct distribution”. Therefore, Betts *et al.* [7] studied the effect of applying more (4, 5 and 6) terms in Eq.(1) stating that „the number of terms retained in the expansion (1) corresponds to a certain degree of approximation.” Directions proposed by Betts *et. al* [36] (3-HSD and [210], [221] and [211], denoted as A, B, C, D, E and F, respectively) are displayed in Fig. 1 ((such directions were also proposed by Miasek [11] and the 6 directional set was applied in Refs [49-52]).

While there is no doubt that the number of terms used in Eq. (1) is important, the choice of sampling directions (orientation (Θ, φ)), which are used to determine functions $f_{l,v}(p)$, is

extremely important. As shown in Fig. 6 in Ref. [34], even a single direction, but a very particular single direction, could be better than three HSDs.

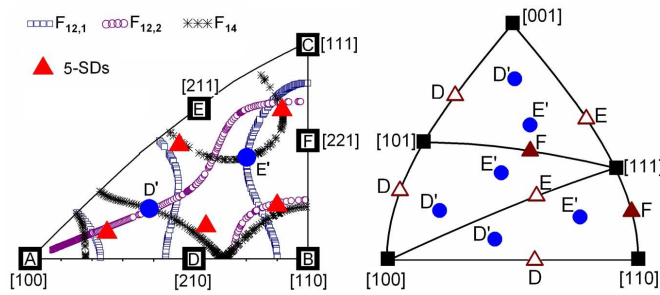


Fig. 1. Stereogram of nonequivalent directions in the BZ for cubic structure (left) with six directions proposed by Betts *at al.* [7], 5-SDs suggested by Bansil and the new D' and E' together with the loci of zeros of cubic harmonics $F_{12,1}$, $F_{12,2}$ and F_{14} . On the right these directions (and equivalent ones) are shown in 1/16 part of the BZ. Angles (Θ, φ) for D' and E' are $(81.76^\circ, 19.30^\circ)$ & $(73.31^\circ, 35.10^\circ)$, respectively.

The quality of each solution can be estimated via d coefficients, which define a deviation of $f_0^a(p)$ from its true value $f_0(p)$:

$$\Delta f_0 = f_0^a - f_0 = \sum_{n,\mu} d_{n,\mu} f_{n,\mu}(p) . \quad (4)$$

The coefficients are calculated in the following manner. Using the expression which defines the isotropic $f_0^a(p)$, the functions $f(\mathbf{p})$ (in the case of Eq. (3), $f_{[100]}(p)$, $f_{[110]}(p)$ and $f_{[111]}(p)$), are expanded into infinite lattice harmonics series according to Eq. (1). After inserting these expansions into Eq. (3) we obtain:

$$f_0^a = f_0 + 1.833 f_8 - 0.254 f_{10} + 0.771 f_{12,1} - 1.869 f_{12,2} + ..$$

As can be seen, in the case of the formula expressed in Eq. (3), the first d coefficient, which distorts $f_0^a(p)$ from its true value $f_0(p)$, is $d_8=1.833$, highlighting the very poor quality of this approach (more details can be found in Ref. [27]).

In Fig. 2 the d coefficients are presented for two sets of sampling directions proposed in Refs [7, 11] and compared with corresponding d for n -SDs with $n = 2, 4, 5$ and 6.

Amongst the five-direction sets proposed by Betts *et. al* [7], the best choice is ABCDE, although the same quality isotropic component can be obtained from only 2-SDs. ABCDF and particularly the ABCEF set, for which $d_{n,\mu}$ have the highest values ($d_{12,1}=2.68$, $d_{12,2}=-4.87$), are unacceptable, which is also evidenced by the negative weights describing corresponding $f_0(p)$ - see Eqs. (2.4.6) and (2.4.7) in Ref. [7]. In view of Eq. (2) negative weights do not make sense. Betts also obtained negative weights for the 9 and 15 sampling directions proposed in Ref. [8]. Furthermore, for 15 directions he obtained weights which were greater than 1; there

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is no justification for such a solution (weights must be positive, and their sum must be equal to one).

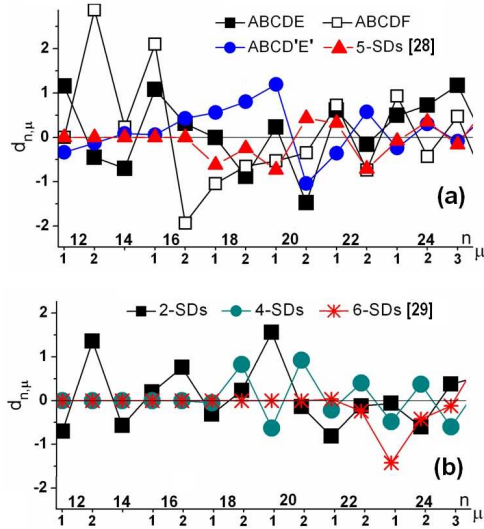


Fig. 2 (a) Comparison of the values of $d_{n,\mu}$ coefficients, defined in Eq. (4), describing deviations of f_0^a from their true values for four sets of sampling directions displayed in Fig.1.

(b). The same comparison for the three sets of SDs proposed by Fehlner *et al.* [29]. Note that for these SDs in all cases $d_{n,\mu} = 0$ for $n < 12$. The highest values of $d_{n,\mu}$ are for ABCEF set ($d_{12,2} = -4.87$), which is not shown in the figure.

When D and E are changed to D' and E' (Fig. 2 (a)), the results radically change, despite the presence of three HSD in the ABCD'E' set. One obvious question is whether this is connected with values of cubic harmonics omitted in the expansion of Eq. (1) (in this case with $l \geq 10$), which influence the values of $d_{n,\mu}$? It seems that it is not the only reason, and if one compares the results for $D \equiv [210]$ and D' in Fig. 3, it can be seen that the division of space and the number of equivalent sampling directions (see the right-hand part of Fig. 1) are also crucial.

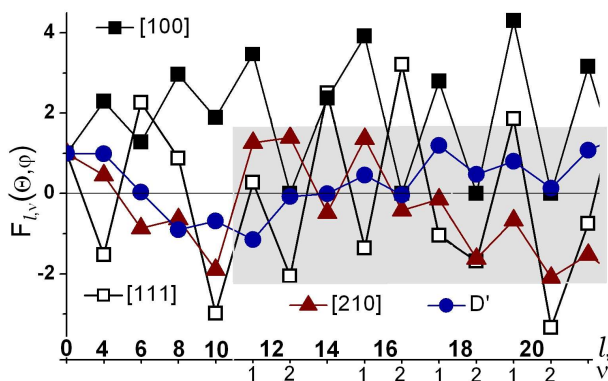


Fig. 3. Values of 15 cubic harmonics for two HSD ([100] and [111]) and directions $D \equiv [210]$ and D' defined in Fig. 1.

Taking into account how unfavourable HSDs are, the ABCD'E' set thus presented is surprisingly good, however it is worse than 4-SDs [29]. Outstandingly good are sets of 6-SDs shown in Fig. 2(b), or 10-SDs, both proposed by Fehlner *et al.* [29].

6-SDs (denoted, respectively, as 1, 2, ..., 6) have the following coordinates (Θ, φ) :

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(60.3793, 41.0942); (69.7400, 36.7174); (82.9974, 37.6583); (70.3745, 21.9485); (83.5528, 22.7359); (82.6351, 7.7063); and the approximation for the isotropic $f_0(p)$ is

$$f_0^a(p) = 0.0722f_1(p) + 0.2170f_2(p) + 0.2367f_3(p) + 0.1154f_4(p) + 0.2276f_5(p) + 0.1312f_6(p) \quad (5)$$

For this set the first non-zero d coefficients are $d_{22,1}=0.0267$ and $d_{22,1}=-0.2365$ (this last one just visible on the scale of Fig. 2b). This means that even when anisotropy is so large that in the Eq. (1) one should apply 15 harmonics, the 6-SD set describes the isotropic $f_0(p)$ perfectly. In an analogous manner one can write an equation for $f_0(p)$ using 10-SDs (see Table 1 in Ref. [29] where their weights, together with those for 4- and 6-SDs, are given with high accuracy). According to our calculations, for 10-SDs [29] all coefficients d up to $n=30$ (not 22 as written in [29]) are equal to zero. It means that for very high anisotropy (where there is the necessity of applying 27 harmonic), 10-SDs again reproduce the isotropic component perfectly.

3. Hexagonal, tetragonal and trigonal structures

For structures with unique R -fold axes ($R = 6, 4$ and 3 for *hcp*, tetragonal and trigonal symmetry, respectively) the lattice harmonics with the full symmetry of the BZ have a very simple form [36]:

$$F_{l,v} = \begin{cases} a_l P_l(\cos\Theta) & l=2 \cdot i \text{ and } i=0,1,2,\dots \\ a_{l,m} P_l^m(\cos\Theta) \cos(m\varphi) & l=R+2 \cdot i \text{ and } m=R+Ri \text{ where } m \leq l \end{cases} \quad (6)$$

where $P_l^{|m|}$ are associated, and a are the normalization constants. As is the case for cubic lattices, for these structures harmonics have the highest values along HSDs, particularly along [0001] and $m=0$ (see Fig. 4).

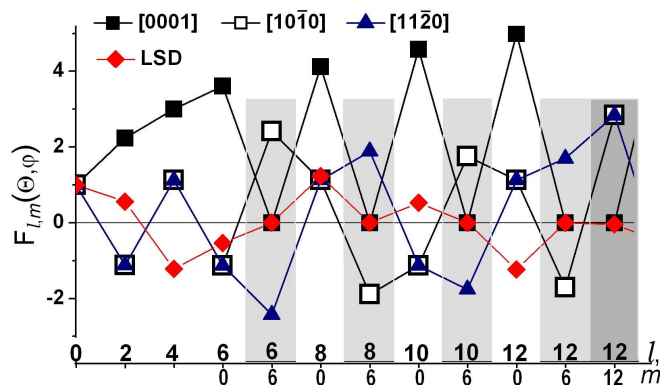


Fig. 4. Values of 12 harmonics for three HSD and a low symmetry direction (LSD). Harmonics with $m=6$ correspond to the hcp lattice.

For these structures, the *SDs* are defined by the positive zeros of the first harmonic $P_l(\cos\Theta)$ omitted in the expansion expressed in Eq. (1), which is analogous to 1D Gauss-Legendre quadrature. Other lattice harmonics containing $\cos(m\varphi)$ are eliminated by the 1D quadrature for trigonometric polynomials $\cos(m\varphi)$ [32, 36]. Below we demonstrate this with the example when the first harmonic, omitted in Eq. (1), is $P_8(\cos\Theta)$.

Each Legendre polynomial $P_l(\cos\Theta)$ has $l/2$ positive zeros, which in the case of $l=8$ are the following: $\Theta_1=16.2008$, $\Theta_2=37.1871$, $\Theta_3=58.2959$ and $\Theta_4=79.4301$ [in degrees]. Because the number of harmonics with $l < 8$ is different (5, 6 and 7 for *hcp*, tetragonal and trigonal symmetry, respectively), the number of *SDs* will also be different, as displayed in Fig.5 (compare it with Fig. 5 in Ref. [35]).

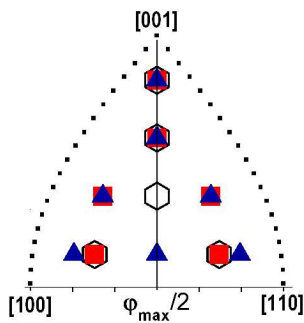


Fig. 5. Three sets of *SDs* for the *hcp* (hexagon), tetragonal (squares) and trigonal (triangles) symmetries (with $\varphi_{\max} = 30^\circ$, 45° and 60° , respectively), determined by zeros of $P_8(\cos\Theta)$.

For such chosen *SDs*, the equations defining the functions $f_{i,\nu}(p)$ can be obtained from the solution of the set of algebraic equations (the orthogonality relation of the lattice harmonics [Eq. (2) in the case of $f_0(p)$] leads to the same solutions).

Because in Refs [28-31, 34], which are devoted to *SDs*, the authors proposed equations for the isotropic average $f_0(p)$ only for cubic structures, here we propose such expressions for non cubic lattices, showing also a very simple way to construct them. Our proposals are diametrically different from those in Ref. [10] (compare Fig. 5 with Fig. 1 in [10]) leading to much better results, – similar to those shown in the previous Section (Fig. 2) for the cubic structures. This will be demonstrated with the example of 4-*SDs* for tetragonal lattices while for the *hcp* symmetry we compare our proposals with those given in Refs [24] and [26].

3.1. Hexagonal structures

In the *hcp* lattice, the first harmonic, which distinguishes directions $[10\bar{1}0]$ and $[11\bar{2}0]$ is the 5th harmonic, $F_{6,6}$. For this reason it is unclear how the isotropic components $f_0(p)$ for the *hcp*

Co and Gd were estimated in Ref. [26] based on 3-HSDs . When $F_{6,6}$ is taken into account, two expressions for the average,

$$f_0^a(p) = [f_{[10\bar{1}0]}(p) + f_{[11\bar{2}0]}(p) + f_{[0001]}(p)] / 3 \quad (7)$$

or

$$f_0^a(p) = 0.380952 f_{[10\bar{1}0]}(p) + 0.380952 f_{[11\bar{2}0]}(p) + 0.238095 f_{[0001]}(p), \quad (8)$$

result from the use in Eq. (1) of 1st, 2nd and 5th (Eq.(7)) or 1st, 4th and 5th (Eq. (8)) harmonics. It is possible that Kawasuso *et al.* [26] (for Doppler broadening of annihilation radiation in Be) used a similar equation to Aguiar *et al.* [24]

$$f_0^a(p) = [3 f_{[10\bar{1}0]}(p) + 3 f_{[11\bar{2}0]}(p) + f_{[0001]}(p)] / 7 \quad (9)$$

where the weights follow from the number of equivalent directions. This last approach reduces the contribution of $f_{[0001]}(p)$ which seems to be very advantageous due to the fact that [0001] direction is the most anisotropic. The corresponding coefficients $d_{n,\mu}$ when using 3-HSDs (Fig. 6 left) and 1-, 2- and 3-SDs (Fig. 6 right), demonstrate that in all cases the application of HSDs is significantly worse than the use of SDs.

In analogy with the results for the cubic structures (Figs. 1 and 2), the $d_{n,\mu}$ coefficients were determined for sets of four and five sampling directions, including both high and low symmetry directions (see Fig. 7).

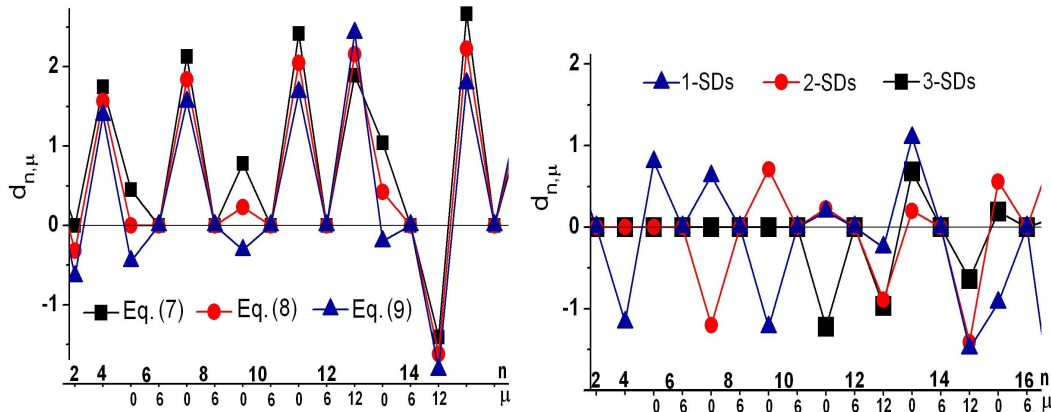


Fig. 6 Coefficients $d_{n,\mu}$ for $f_0(p)$ estimated from 3-HSDs using Eqs. (7 - 9) (left) and 1-, 2- and 3-SDs (right), determined, respectively, by $\varphi=15^\circ$ and by positive zeros of $P_2(\cos\Theta)$, $P_4(\cos\Theta)$ and $P_6(\cos\Theta)$ with Θ equals, respectively: 54.7356° , $(30.5556^\circ \text{ \& } 70.1243^\circ)$ and $(21.1769^\circ, 48.6078^\circ \text{ \& } 76.1949^\circ)$.

It can be seen that when two low symmetry directions ($(30^\circ, 15^\circ)$ & $(60^\circ, 15^\circ)$) were added to 3-HSD (black squares in Fig. 7), facilitating the inclusion of the first five harmonics in Eq. 1 (without omitting any with $l < 6$ as in the case of using 3-HSD), the results change radically,

although not as much as for the cubic ABCD'E' set presented in Figs 1 and 2. Of course, it does not mean that sets containing HSD are recommended, and once again we emphasise that employing SDs is incomparably better.

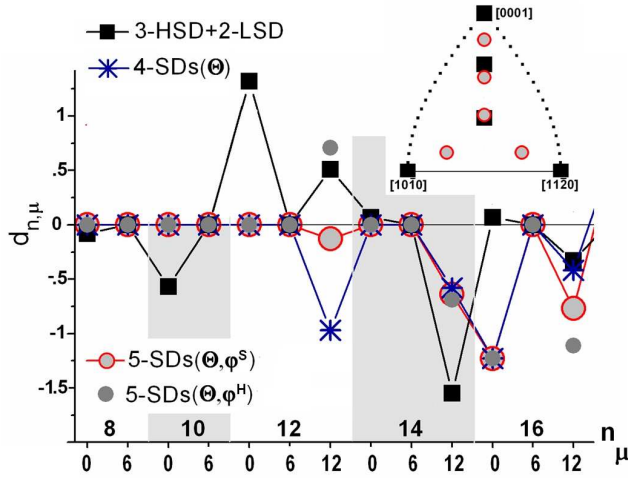


Fig. 7 Values of $d_{n,\mu}$ for f_0^a estimated from sets of four and five sampling directions shown in the stereogram of hcp lattice. For 4- and 5-SDs the angles Θ are defined by the positive zeros of $P_8(\cos\Theta)$ [36]. The notations 5-SDs(Θ, φ^S) and 5-SDs(Θ, φ^H) mean that $\varphi = 7.5^\circ$ & 22.5° (zeros of $\cos(12\varphi)$) and $\varphi = 0^\circ$ & 30° , respectively.

Below we give a formula for $f_0(p)$, when the sampling directions are based on 3-SDs (numbered by 1, 2, 3), with the coordinates given in the description of Fig. 6.

$$f_0^a(p) = \sum_i w_i f_i(p) = 0.1713245 f_1(p) + 0.3607607 f_2(p) + 0.4679147 f_3(p) \quad (10)$$

Weights w_i for sets of 5-, 7- and 12-SDs and their coordinates are presented in Table 1 with illustrating accuracy of proposed sampling directions in Fig. 8.

Table 1. Three sets of SDs in the hcp Brillouin zone. Their coordinates are described by spherical angles (Θ, φ) [in degrees] and weights w (see Eq. (10)) defining the isotropic average $f_0(p)$. When angles 7.5 & 22.5 are replaced by 0 & 30° , weights w are the same.

i	(Θ_i, φ_i)	w_i	(Θ_i, φ_i)	w_i	(Θ_i, φ_i)	w_i
1	16.201 15.0	.1012232	13.118 15.0	.0666747	9.500 15.0	.0351174
2	37.187 15.0	.2223898	30.110 15.0	.1494406	21.808 15.0	.0801636
3	58.296 15.0	.3237013	47.202 15.0	.2190949	34.188 15.0	.1215177
4	79.430 7.5	.1813429	64.317 7.5	.1346318	46.584 7.5	.0786013
5	79.430 22.5	.1813429	64.317 22.5	.1346318	46.584 22.5	.0786013
6			81.438 7.5	.1477632	58.986 7.5	.0927691
7			81.438 22.5	.1477632	58.986 22.5	.0927691
8					71.391 7.5	.1026012
9					71.391 22.5	.1026012
10					83.797 5.0	.0717960
11					83.797 15.0	.0716662
12					83.797 25.0	.0717960

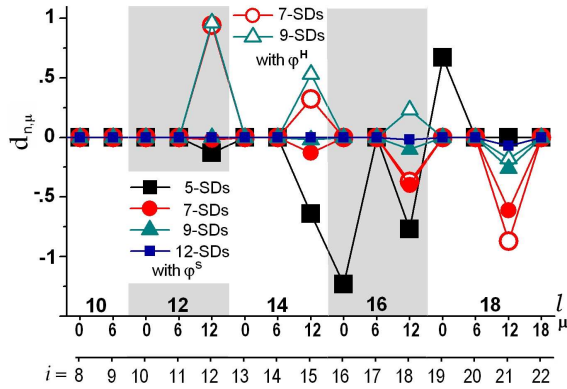


Fig. 8 Coefficients $d_{n,\mu}$ for four sets of SDs in the Brillouin zone of the hcp lattice. ϕ^S denotes angles as given in Table 1, while ϕ^H means that 7.5 and 22.5 are replaced by 0 and 30° , respectively. i denotes the sequence of harmonic in Eq.(1), i.e. i.e. the order in which they appear.

The weights w defining $f_0(p)$ depend on the choice of angles Θ_i , not on ϕ . However, the choice of ϕ strongly influences the quality of $f_0^a(p)$ – there is no doubt that here the best choices are angles ϕ^S corresponding to positive zeros of $\cos(12\phi)$ or $\cos(18\phi)$ in the case of two or three ϕ for a given Θ_i , respectively, which is equivalent to applying Gaussian quadrature in Eq. (2).

The choice of SDs set, of course, depends on the anisotropy. Let us take, for example, the anisotropy of the momentum distribution in Gd, considered in Ref. [26]. Radial functions $f_{l,i}(p)$ for Gd, for one-dimensional angular correlation of annihilation radiation spectra, are displayed in Fig. 1 in Ref. [36]. Functions $f_{12,12}(p)$ is not presented because its absolute values are lower than 0.1% of $f_0(p=0)$, i.e. it is very small. In such a case even 5-SDs may describe isotropic average with good accuracy.

3.2. Tetragonal and trigonal structures

For the tetragonal structure the nonequivalent part of the BZ is 1/16, being 3 and 1.5 times larger than for the cubic and hcp structures, respectively. So, it is understandable that to estimate $f_0(p)$ with similar accuracy, here one needs more SDs.

As an illustrative example, let us take 3-SDs in the hcp structure, defined by angles $\phi=15^\circ$ and $\Theta_1=21.1769^\circ$; $\Theta_2=48.6079^\circ$ and $\Theta_3=76.1949^\circ$. They describe the isotropic component to a particular accuracy:

$$f_0^a(p) = f_0(p) - 1.22 f_{12,0} - 0.97 f_{12,12} + 0.68 f_{14,0} - 0.64 f_{14,12} + \dots \quad (11)$$

The same angles Θ in the tetragonal lattice define 4-SDs with $\phi=22.5^\circ$ for Θ_1 and Θ_2 and two angles $\phi_1=11.25^\circ$ and $\phi_2=33.75^\circ$ for Θ_3 . In this case

$$f_0^a(p) = 0.1713245 f_1(p) + 0.3607607 f_2(p) + 0.2339574 [f_3(p) + f_4(p)] \quad (12)$$

(compare this equation with Eq. (10)) and

$$f_0^a(\mathbf{p}) = f_0(\mathbf{p}) - 0.09 f_{8,8} - 0.52 f_{10,8} - 1.22 f_{12,0} - 0.89 f_{12,8} + 0.68 f_{14,0} - 0.39 f_{14,8} + \dots \quad (13)$$

which is somewhat less accurate than in the case of 3-SDs for the hcp lattice.

Now let us check proposals of Betts and co-authors for the four direction set: 3-HSD and 1-LSD, marked by C in Fig. 1 and described by Eq. (8.1) [10]. In this case

$$f_0^a(\mathbf{p}) = f_0(\mathbf{p}) - 0.50 f_{6,0} + 1.31 f_{6,4} + 1.38 f_{8,0} + 0.73 f_{8,4} + 1.12 f_{8,8} + 0.14 f_{10,0} - 0.19 f_{10,4} + \dots$$

which gives a much worse approximation than 4-SDs described by Eq. (13). However, if the direction C ($\Theta=45^\circ$, $\varphi=0^\circ$) is replaced by C' ($\Theta=45^\circ$, $\varphi=22.5^\circ$), all coefficients $d_{n,\mu}$ are equal to zero. Such a choice (illustrated in Fig. 9 by full squares) is better, although it is nevertheless much worse than for 4-SDs.

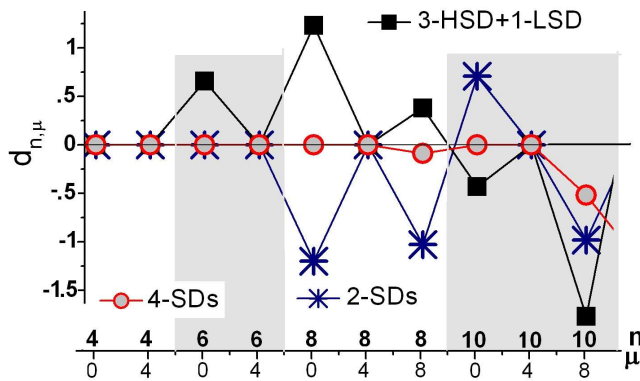


Fig. 9. Values of $d_{n,\mu}$ for tetragonal structures for 2- and 4-SDs with Θ defined by the positive zeros of $P_4(\cos\Theta)$ and $P_6(\cos\Theta)$, respectively. In the case of 4-SDs and for $\Theta=76.1949^\circ$, $\varphi=11.25^\circ$ and 33.75° (zeros of $\cos(8\varphi)$). One low symmetry direction (1-LSD) added to 3-HSD is defined by angles $\Theta=54.7356^\circ$ and $\varphi=22.5^\circ$.

Weighs w_i for sets of 6-, 9- and 12-SDs defining function $f_0(\mathbf{p})$ in the tetragonal lattice and their coordinates are presented in Table 2 and the accuracy of $f_0(\mathbf{p})$ determined by these SDs are show in Fig. 10.

Table 2. Three sets of SDs in the tetragonal Brillouin zone. The notations are the same as for Table 1.

i	(Θ_i, φ_i)	w_i	(Θ_i, φ_i)	w_i	(Θ_i, φ_i)	w_i
1	16.201 22.5	.1012232	13.118 22.5	.0666713	11.02 22.5	.0471754
2	37.187 22.5	.2223898	30.110 22.5	.1494518	25.295 22.5	.1069394
3	58.296 11.25	.1568529	47.202 11.25	.1095431	39.655 11.25	.0800395
4	58.296 33.75	.1568529	47.202 33.75	.1095431	39.655 33.75	.0800395
5	79.430 11.25	.1813429	64.317 11.25	.1346334	54.033 11.25	.1015835
6	79.430 33.75	.1813429	64.317 33.75	.1346334	54.033 33.75	.1015835
7			81.438 7.5	.0987267	68.418 7.5	.0783064
8			81.438 22.5	.0980704	68.418 22.5	.0768808
9			81.438 37.5	.0987267	68.418 37.5	.0783064
10					82.806 7.5	.0828078
11					82.806 22.5	.0835302
12					82.806 37.5	.0828078

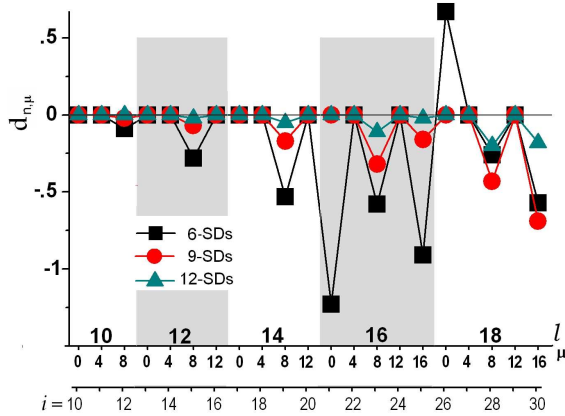


Fig. 10 Coefficients $d_{n,\mu}$ for four sets of SDs for the tetragonal lattice.

Comparing the first five columns of Table 1 with corresponding columns of Table 2 (the same for Eq. (10) with (12)) it is clear that by having equations for the isotropic $f_0(p)$ in the hcp structure, based on SDs, determined by the positive zeros of harmonics $P_l(\cos\Theta)$, one can write (without any further calculation) an equivalent equation for $f_0(p)$ in the tetragonal (or trigonal) lattice. Here a useful diagram is displayed in Fig. 5 in Ref. [36]. As an example, 12-SDs in the hcp Brillouin zone (described in Table 1) are defined by 7 positive zeros of $P_{14}(\cos\Theta)$. The same angles Θ define 16-SDs in the tetragonal lattice (see Fig. 5 in [36]) where, for example, for $l=12$ there are 4, instead of 3, harmonics with $m=0, 4, 8, 12$. So, for 7th angle $\Theta=83.797$ in the tetragonal lattice there will be four sampling directions defined by four angles φ , each with weights $w=0.053847$ ($3 \cdot 0.07179604/4$). Conversely, by having results for 12-SDs in the tetragonal lattice (Table 2), it is possible to construct a corresponding equation for 9-SDs in the hcp Brillouin zone.

The proposed sets of SDs for the hcp and tetragonal structures allow the creation of corresponding sets of n -SDs for the trigonal lattice for $n=4, 7, 10, 14$ and 19. For example, four zeros of $P_8(\cos\Theta)$, which define 5-SDs for the hcp Brillouin zone and 6-SDs for the tetragonal structure, define 7-SDs for the trigonal lattice (see Fig. 5 in [36]). These directions with (Θ, φ) [in degrees] are: (16.201, 30.0); (37.187, 30.0); (58.296, 15.0) & (58.296, 45.0); (79.43, 7.5), (79.43, 30) & (79.43, 52.5) with the same weights w for the first four directions as shown in the second column of Table 2 except those for $\Theta=79.43$, which are equal to 0.1208953 (for $\Theta=79.43$ the “total” weight $w=0.3626858$, is distributed between the three angles φ).

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4. Conclusions

There are a few papers [28-37] devoted to determining the isotropic and anisotropic components of some quantities with applying SDs. Unfortunately, they are identified with some particular theoretical calculations and the standard way of determining the isotropic component is still based on papers [4] and [6], and usually employing Eq. (3). However, this equation may be justified only in very particular cases.

Bansil pointed out: “Traditionally, directions of high symmetry have been emphasized in the physics of solids. *Our considerations suggest that calculations as well as measurements along special directions are probably more useful, because these directions represent more accurately the average properties of the solids*” [28]. Furthermore, Fehlnner, Nickerson and Vosko added “Our results go even further and show that information gathered along a set of SDs can reproduce its anisotropic behaviour to any desired degree of accuracy” [29].

Previous considerations [33, 35-37] and those presented in this paper for various symmetries led to similar conclusions, emphasising additionally that HSD are highly unprofitable and the traditional manner of calculating the isotropic average yields incomparably worse results than the use of SDs. Generally, of course, the quality of $f_0^a(\mathbf{p})$ depends on the anisotropy as well as, in the case of experimental investigations, on the statistical precision of the data and the experimental resolution. Owing to this reason in some particular cases (e.g. measuring Doppler broadening spectra) an application of HSDs may be justified. Moreover, they could be justified if one already had experimental results for HSDs (as long as there was some awareness of the approximations and inherent errors). But the use of HSDs is most certainly not defensible in the case of theoretical calculations, where one should use SDs.

Given the large number of papers which have used HSDs to determine average properties, further investigation of this subject is worthy of further attention. The application of the ideas and formulae presented here extend far beyond momentum density spectroscopy (Compton profiles and positron annihilation) and are likely to find much broader application in solid state physics. For example, in a quantum oscillations (e.g. de Haas-van Alphen) experiment the extremal area of the Fermi surface in a plane perpendicular to the direction of an applied magnetic field can be determined, and the cyclotron mass averaged over that orbit obtained from a fit to the temperature-dependence of the oscillations using the Lifshitz-Kosevich formula [53]. The expressions presented here would allow the *average* cyclotron mass over the whole Fermi surface to be approximated from a limited set of temperature-dependencies

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3 measured with the applied magnetic field along some small number of SDs. We also note
4 some recent experimental work on the melting of the crystalline state, and point out that the
5 averaging process would be applicable to liquid metals [54, 55].
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9 **Acknowledgements.** We are very grateful to Professor M. Samsel-Czekala for making available her
10 numerical programs for calculating lattice harmonics and her helpful remarks.
11

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