Application of group theory

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1 Powder average

An efficient average of Mossbauer spectra of randomly oriented single crystals (powder samples) was described in the thesis of Katja Knese,Leipzig 1994, Fachbereich Physik Universität Leipzig, based on the work of Hasselbach and Spiering from 1980 [2]. The figures are copied from the thesis.

1.1 The choice of grid points

The average $\overline{f}$ of a function $f(\Omega)$ over the unit sphere given by the integral

$$
\begin{aligned}
\overline{f} &= \frac{1}{4\pi} \int_{\Omega} f(\Omega) d\Omega \\
&= \frac{1}{4\pi} \sum_{i=1}^{N} f(\Omega_i) \Delta\Omega_i \\
1 &= \frac{1}{4\pi} \sum_{i=1}^{N} \Delta\Omega_i
\end{aligned}
\tag{1}
$$

is replaced by a sum over N directions $\Omega_i = (\theta_i, \phi_i)$ with weighting factors $\Delta\Omega_i$ which are normalized to 1 (Eq. 1). Numerical calculation requires the selection of the N directions and solid angle segments $\Delta\Omega_i$ of the sphere. The choice of Alderman et al. [1] uses $\Delta\Omega_i$ depending on the direction Ω_i as illustrated in Fig. 1.

Earlier in 1980 Hasselbach et al. developed a numerical solution which best fits to problems where an expansion of $f(\Omega)$ in a series of spherical harmonics is meaningful from the physical properties of f. The directional dependence of intensities of multipole radiation is a typical example. The average value of f of the expansion series with coefficients A_{lm}
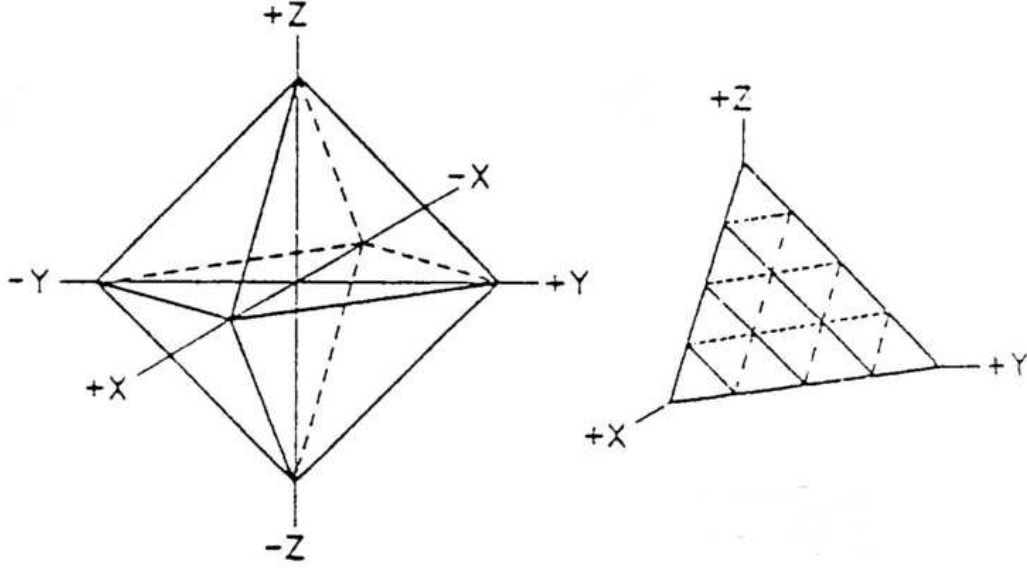
Figure 1: The 6 vertices of the octaedron lie on the x,y,z-axes of the coordinate system and its 8 faces belong to the octants. The equilateral triangular faces are partitioned as shown for the triangle in (111)-direction on the right side. The center of (sub) triangles in the plane serve as the directions on the sphere. The solid angle belonging to the sub-triangles depends on their distance to the surface of the sphere [1]

$$f(\Omega) \;=\; \sum_{l=0}^{\infty}\sum_{m=-l}^{l} A_{lm}Y_{lm}(\theta,\phi)$$

is just proportional to A_{00} according to the property of the spherical harmonics (Eq. 2).

$$\int_{\Omega} Y_{lm}(\Omega)d\Omega \;=\; 0 \quad for \quad l \neq 0 \qquad (2)$$

$$\overline{f} \;=\; \frac{1}{\sqrt{4\pi}}A_{00}$$

The aim is the minimization of each spherical harmonic (the $S(l,m)$ of Eq.3) by the choice of directions and solid angle segments $\Delta\Omega_i$. In the thesis of Knese following the ideas from 1980 the $\Delta\Omega_i$ were restricted to be of equal size. The minimization procedure, however, was completely changed. The calculation of spherical harmonics and minimization of the sum over ϵ_{lm} (Eq. 3) by variation of Ω_i has been avoided and instead the function $V(N)$ of Eq. 4 was used.

$$S(l,m) \;=\; \frac{1}{4\pi}\sum_{i=1}^{N} Y_{lm}(\theta_i,\phi_i)\Delta\Omega_i \qquad (3)$$

$$\epsilon_{lm} \;=\; |S(l,m)|$$

$$\Delta\Omega_i \;=\; \frac{4\pi}{N}$$

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The idea behind is that this Coulomb potential of equal charges bound to the surface of the sphere will have its minimum 'energy' if the points $\vec{r}_i$ ($r_i = 1$) on the sphere have equal distances to each other.

$$V(N) \quad = \quad \sum_{\substack{i=1 \\ k>i}}^{N} \frac{1}{|\vec{r_i} - \vec{r_k}|} \tag{4}$$

The development of computer capabilities (1980 to 1994) allowed to extend the number of grid points on the sphere in the minimization procedure considerably, from 6 to 128 grid points in 1/48 of the sphere shown as hatched part in Fig. 2. Fig. 3 shows the projection of the 1/8 sphere on the equilateral triangular faces of the octahedron. The projection of the hatched part in Fig. 2 is the upper left triangle, the two others filled with 32 cirles are obtained by a C3, $C3^2$-rotation. The circles have a diameter calculated from the area $4\pi/48$ of the unit sphere. Their different size in the figure makes evident, that the choice of Alderman et al. of equal triangles on this equilateral triangular faces leads to increasing weights to the center (C3-axis) of the figure.

1.2   Quality of data sets

The quality of the data sets dependent on the number of grid points is shown in Fig. 4. The sum over i of the spherical harmonics for l values up to l=100 are plotted. In the range from l to l+1 all sums at l and m with values different from zero are equidistantly plotted, such that with increasing l the number of points per interval becomes larger. Appreciable deviations from the exact average value of zero start at some order l of the spherical harmonics. As expected l increases with increasing number of grid points. For l=6 (the solution of [2]) the average value itself was minimized up to l=18 and the scattering of the sum from zero starts just at l=18. Minimizing with the potential function of Eq. 4 the scattering starts more smoothly and requires more grid points for the quality obtained for l=18 in [2](a number n between 8 and 16).

The average $\bar{\epsilon}$ (Eq. 5) of the absolute deviation from zero, the ϵ-values of Eq. 3, have been plotted in Fig. 5. A comparison with the method of Alderman et al. with $26 \cdot 26 = 676$ grid points per 1/8 of the sphere (corresponding to $8 \cdot n$) lies in between the values of the average deviations obtained for n=32 and n=64 for l larger than 50. However, for l< 50 the average comes out to be much higher. The minimized positions of the grid points on the sphere with equal solid angle turns out to be the better choice. However, the extension to much higher densities of grid points (as they are neccessary for NMR Pake-spectra) is reserved to Alderman's method.

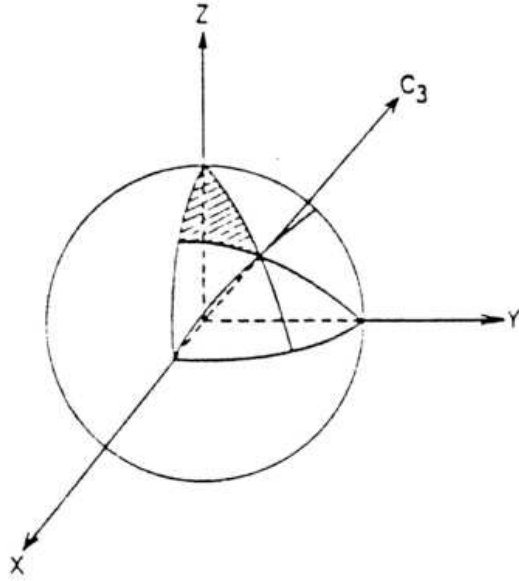$$\bar{\epsilon} \quad = \quad \frac{\sum\limits_{m=-l}^{l} \epsilon_{l,m)}}{2l + 1} \tag{5}$$

Figure 2: The x,y,z-axes as used in Fig. 1 enclose 1/8 of the surface which is subdevided by 6 spherical triangles. Two groups of 3 are related by the 3-fold axis. The mirror plane C3-Z maps the two groups to each other. By the transformations of the cubic group O with 24 elements the hatched triangle is mapped on half of the sphere. The transformations of O_h covers the complete sphere.
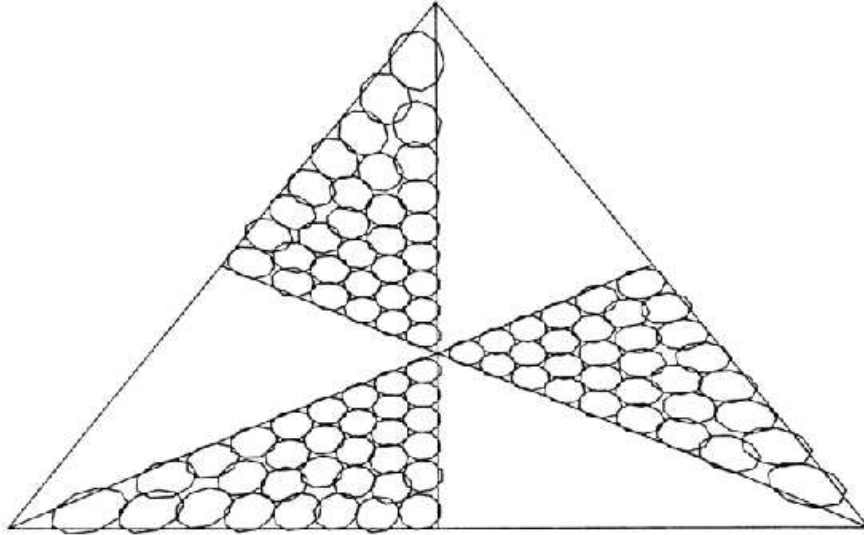

Figure 3: The projection of 1/8 of the surface as shown in Fig. 2 on the equilateral triangle faces of Fig. 1 gives 6 triangles. 3 of them related by the 3-fold axis are filled with 32 cirles each (partly overlapping) of equal area on the surface of the sphere, such that for each direction given by the center of the cirlce the solid angle is the same.
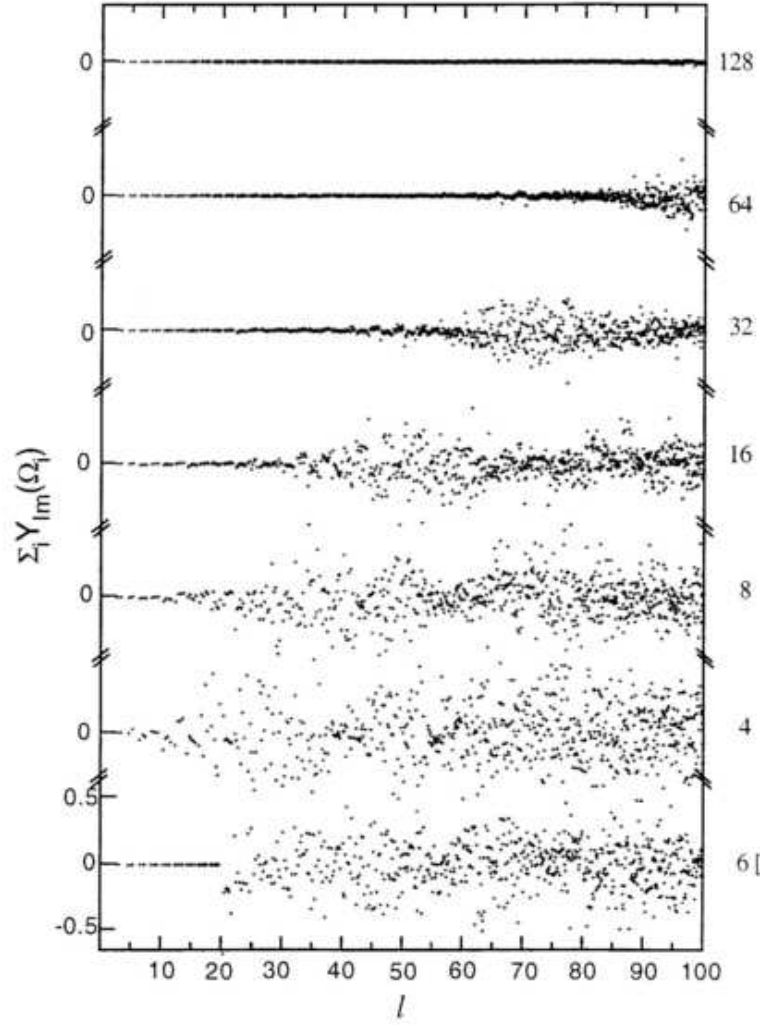
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Figure 4: The sum over n*48 grid points over the sphere (n=4,..., 128) for the sperical harmonics l=0,...,100. The scatter of the sum increases with increasing order l. For n=6 te grid points of the original paper of Hasselbach et al. [2] were used.
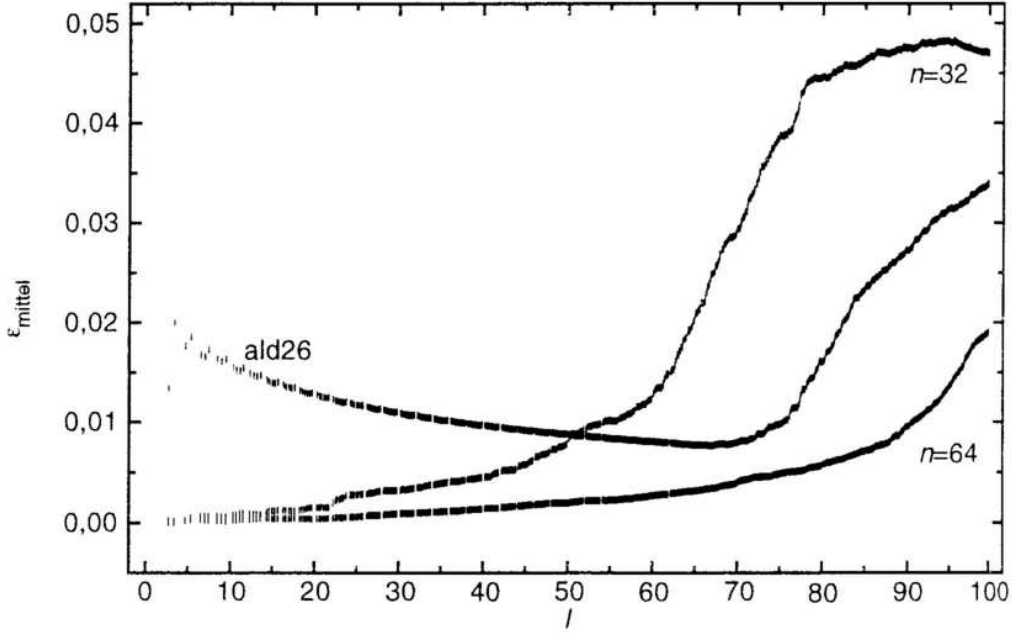
Figure 5: Comparison between optimized (potential function eq. 4) grid points and the fixed choice of grid points according to Alderman et al. [1]. The $\bar{\epsilon}$ values (Eq. 5) for $26 \cdot 26$ sub-triangles inside the equilateral triangle of the octahedron denoted by ald26 ($= 676$ grid points per 1/8 of the sphere) are compared with the optimized values for n=32 and n=64 corresponding to 256 and 512 grid points per 1/8 of the sphere.

1.3 Average of an object with an intrinsic symmetry

The choice of the configuration of the grid points on the sphere is very useful if the function $f(\Omega)$ to be averaged has some symmetry characterized by a symmetry group U which is a subgroup of the cubic group O_h. To begin with the sum over $n \cdot 48$ grid points over the sphere is written as

$$\overline{f} \;=\; \sum_{k=1}^{48} \left(\sum_{i=1}^{n} f(T_k \Omega_i) \right)$$

where the set $\{E = T_1, T_2, ..., T_{48}\}$ denote the 48 symmetry transformations of the group O_h. Be T_1 the identity element E then the inner sum of Eq. 6 represents the integral over the hatched spherical triangle in Fig. 2 and the outer sum the integral over the 48 triangles. It is obvious that in the case of an invariant f with respect to a subset of transformations the outer sum can be restricted to transformations which are effecting f. Group theory has an answer to this problem. The subgroup $U = \{E, U_2, ..., U_M\}$ of order M_U (M_u is a divisor of $M_{O_h} = 48$) has $L_U - 1$ cosets ($L_U \cdot M_U = M_{O_h}$) such that the set $\{O_h\}$ can be written as ($E = S_1$):

$$\{O_h\} \;=\; \{\{U\}, \{U\} \cdot S_2, ..., \{U\} \cdot S_{L_U}\} \tag{6}$$

$\{U\} \cdot S_i$ are right cosets. The outer sum is now written as a double sum

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$$\overline{f} \;=\; \sum_{k=1}^{M_U}\sum_{j=1}^{L_U}\left(\sum_{i=1}^{n} f(U_k \cdot S_j\Omega_i)\right)$$

Invariance of f does mean that $f(U_k\Omega_i) = f(\Omega_i)$. Since $f(S_j\Omega_i) = f(\Omega_{ij})$ with ij one of the 48 elements, the value of $f(U_k \cdot S_j\Omega_i)$ is equal to $f(S_j\Omega_i)$. The sum in Eq. 7 gives the same value for all k.

$$\overline{f} \;=\; M_u \cdot \sum_{j=1}^{L_U}\left(\sum_{i=1}^{n} f(S_j\Omega_i)\right)$$

The set of elements $\{E = S_1, S_2, ..., S_{L_U}\}$ generating the right cosets may be different from the set generating left cosets. If we have the left cosets $\{E = T_1, T_2, ..., T_{L_U}\}$ the transformations have to defined as invers transformations. Since with U_j also U_j^{-1} is an element of U the sum can be written step by step:

$$\overline{f} \;=\; \sum_{k=1}^{M_U}\sum_{j=1}^{L_U}\left(\sum_{i=1}^{n} f((T_j \cdot U_k \cdot)^{-1}\Omega_i)\right) \tag{7}$$

$$=\; \sum_{k=1}^{M_U}\sum_{j=1}^{L_U}\left(\sum_{i=1}^{n} f(U_k^{-1}T_j^{-1}\Omega_i)\right)$$

$$=\; M_u \cdot \sum_{j=1}^{L_U}\left(\sum_{i=1}^{n} f(T_j^{-1}\Omega_i)\right)$$

Wether the transformations of the right or left coset have to be used depends on the code of the program, on the definition of the transformation matrices. It turns out that the transformation of tensor components $t(n)$ by sequence of multiplication: t_lab(k)= Sum t(n)*Dcpt(n,l)*Dslt(l,k) in the subroutines th_hdeqf() and th_hdeq() (file th_22nuclear.f) requires the right cosets as defined in the routine **group** available in the directory effi/helproutines/Octahedral. The tensor t(n) may have its own symmetry like the D2 symmetry of an 2. rank tensor in its PAS or the sum over jloop eqivalent sites t(m)*d1(m,n,jloop), jloop=1,...,nloop as a whole expression become invariant with respect to a subgroup of O. For several subgroups the right cosets as obtained from the program **group** are implemented and are called by a constant named isymmetry in the subroutine sphere().

2 Equivalent sites of single crystals

The situation of symmetry-related equivalent sites of a crystal (despite translational symmetry) requires the transformations (rotations/reflections) to generate the orientations of the fields at each site. If the point group symmetry of the crystal is G and the number of eqivalent sites is less than the order of G then the site itself has a symmetry, it takes a special position in the unit cell.

The general answer for all point groups to the number of equivalent sites and their symmetry has been published by Weil et al. [3]. The program **group** has an entry

point: { Tensor T: $R * T * R^\dagger$ with R(U)} which gives an answer to this problem.
A standard second rank tensor (at present) is transformed with all group elenents of the choosen subgroup U of the octahedral goup O (at present) and equal results are grouped together. From each list of equal tensors one of the transformations is taken to generate an equivalent site. The subroutine {sym_equiv(ncase,timeinvers,nloop,ctimeinv,d1,d2)} has data statements for integer arrays iO3a,...,iO3d and iO4a,...,iO4e. O stands for the group and 3 and 4 for the PAS with z-axes $C3\|z$ and $C4\|z$, respectively. The array elements are the numbers of the transformations (all 24 are defined in another data statement) and as a first integer the number of transformations. Example: {data iO4c/5,2,5,7,8,10/ } lists the five transformations 2,5,7,8,10 which can be found for the full octahedral group U=O and the symmetry elements $C2z = C4z^2$ (denoted by C4z*) and C2-xy, which are compatible with the 2. rank tensor $\eta = 0.5(\neq 0)$ and the Euler angle ($\phi = 135^o, \theta = 0, \psi = 0$). The example is met for the cubic crystal of Almandine (see project directories) which has six equivalent sites.

References

[1] D. W. Alderman, M. S. Solum and D. M. Grant, J. Chem. Physics **84**, 3717–3725 (1986).

[2] K. M. Hasselbach and H. Spiering, Nucl. Instr. Methods **176**, 537–541 (1980).

[3] J A Weil, T Buch and J E Clapp, Adv. Magn. Resonance **6**, 183–257 (1973).