Contents

1 Anisotropic MSD tensor

In the harmonic approximation for the lattice vibration the f-factor in the direction of the γ radiation $\mathbf{e}_z$ is described by the thermal average of the expectation value of the square of the projection of the atom displacement $< zz >$ on the direction $\mathbf{e}_z$.

$$f(\mathbf{e}_z) = e^{-<zz>} \tag{1}$$

By means of the symmetric mean square displacement tensor U_{msd} ($u_{zz} = < zz >$, $u_{ik} = u_{ki}$)

$$U_{msd} = \begin{matrix} \\ \langle x| \\ \langle y| \\ \langle z| \end{matrix} \begin{matrix} \begin{matrix} |x\rangle & |y\rangle & |z\rangle \end{matrix} \\ \begin{pmatrix} u_{xx} & u_{xy} & u_{xz} \\ u_{yx} & u_{yy} & u_{yz} \\ u_{zx} & u_{zy} & u_{zz} \end{pmatrix} \end{matrix} \tag{2}$$

the mean square expectation value for any direction $\mathbf{e}$ is obtained as $< \mathbf{e}^T U_{msd} \mathbf{e} >$ or equivalent by rotation $R(\phi, \theta)$ of the z-axis to the $\mathbf{e}$-direction and taking the $< zz >$ element: $(R u_{msd} R^{-1})_{zz}$.
The symmetric tensor has a principal axis system S_{msd} and eigen values U_{xx}, U_{yy}, U_{zz}.
Sutraction of the trace $Tr(U_{msd})/3 = (U_{xx} + U_{yy} + U_{zz})/3$ the Tensor can be written as:

$$U_{msd} = \frac{1}{3} Tr(U_{msd}) \cdot \mathbf{1} + (U_{zz} - \frac{1}{3} Tr(U_{msd})) \begin{pmatrix} \frac{1}{2}(1-\eta) & & \\ & \frac{1}{2}(1+\eta) & \\ & & 1 \end{pmatrix} \tag{3}$$

where $\eta = (U_{xx} - U_{yy})/U_{zz}$.
The exponential $f_{isotropic} = exp(-\frac{1}{3} Tr(U_{msd}))$ represents the isotropic part of the f-factor and

$$f_{ani} = exp\left(-T_{zz} \cdot \begin{pmatrix} \frac{1}{2}(1-\eta) & & \\ & \frac{1}{2}(1+\eta) & \\ & & 1 \end{pmatrix} \right) \tag{4}$$

with $T_{zz} = (U_{zz} - \frac{1}{3}Tr(U_{msd}))$ the anisotropic part referred to the system S_{msd}.

2 The average f-factor of a random powder

Since f_{ani} has no tensor properties (the exponential of a tensor is no longer a tensor) there are also contibutions of f_{ani} to the average f-factor.
In order to calculate the average, the standard tensor of Eq. 3 is expressed by spherical coordinates (see [1]).

$$T_{zz} = \sqrt{\frac{2}{3}} \cdot T_{20} \tag{5}$$

Instead of changing the direction **e**, the spherical tensor components are transformed to a coordinate system with **e** parallel to the z-axis.

$$\begin{aligned} T_{20}(\phi,\theta) &= T_{20}D^2_{00}(\phi,\theta) + T_{22} * D^2_{20}(\phi,\theta) + T_{2-2} * D^2_{-20}(\phi,\theta) \quad (6)\\ T_{2\pm2} &= \frac{\eta}{2}T_{zz} \end{aligned}$$

with the rotation matrices D^L_{mn}.

$$\begin{aligned} D^2_{00} &= \frac{1}{2}(3cos\theta - 1) \quad (7)\\ D^2_{\pm20} &= e^{\mp 2i\phi}\sqrt{\frac{3}{8}}sin^2\theta \end{aligned}$$

Inserting Eqs. 7 and using Eqs. 5,6 gives

$$T_{zz}(\phi,\theta) = \frac{1}{2}T_{zz}\left((3cos\theta - 1) + \eta sin^2\theta cos2\phi\right) \tag{8}$$

the exponential of which has to be averaged over the sphere:

$$\overline{f_{ani}}^{\phi,\theta} = \frac{1}{4\pi}\int_\Omega e^{-T_{zz}(\phi,\theta)}d\Omega \tag{9}$$

Expanding the e-function

$$\begin{aligned} e^{-T_{zz}} &= 1 + \sum_{n=1}^{\infty}\frac{1}{n!}(-T_{zz}/2)^n\left((3cos\theta - 1) + \eta sin^2\theta cos2\phi\right)^n \quad (10)\\ &= 1 + \sum_{n=1}^{\infty}\frac{1}{n!}(-T_{zz}/2)^n\sum_{k=0}^{n}\sum_{j=0}^{n-k}\binom{n}{k}\binom{n-k}{j}(-1)^{n-k-j}\\ &\qquad \eta^k 3^j (cos2\phi)^k (sin\theta)^{2k}(cos\theta)^{2j} \quad (11) \end{aligned}$$

The integrations can be carried through.

$$\begin{aligned} \int_0^{2pi} (cos2\phi)^k d\phi &= \frac{k-1}{k}\frac{k-3}{k-2}...\frac{1}{2}\cdot 2\pi \qquad (12) \\ \int_0^{pi} (sin\theta)^{2k+1}(cos\theta)^{2j} d\theta &= \frac{2j-1}{2k+2j+1}\frac{2j-3}{2k+2j-1}...\frac{1}{2k+3} \\ &\cdot\frac{2k}{2k+1}\frac{2k-2}{2k-1}...\frac{2}{3}\cdot 2 \end{aligned}$$

These formula have been coded in the program msd-powder. The sum has been extended to n=18.Input parameters are T_{zz} and η. For $T_{zz} = 1$ (standard traceless tensor) the expansion converges already for n=6 (1.1136 ($\eta = 0$)) with 4 digits.

3 Lorentzian resonance absorption line

The resonance absorption of source and absorber of Lorentzian line shape is again a Lorentzian in the limit of an infinite thin absorber. For absorbers of finite thickness the maximum of the line has an analytical solution [2].

$$\frac{Z_\infty - Z_0}{Z_\infty} = f_s \left[1 - e^{\left(\frac{n\beta d f_a \sigma_0}{2}\right)} \cdot J_0\left(i\frac{n\beta d f_a \sigma_0}{2}\right)\right] \qquad (13)$$

where f_s and f_a are the f-factors of source and absorber, respectively, n $[cm^{-3}]$ the number of Mossbauer nuclei per volume, β the abundance of resonant isotop, d the thickness, σ_0 the cross section, and J_0 the zero Bessel function.
EFFI defines the thickness of the absorber by $mg(nu)/cm^2 \cdot f_a$ of the nucleus nu, which is multiplied by the constant $uthick\_w = \sigma_0\beta\, 6.022\, 10^{23}/atomic\_weight$ which has the dimension $[cm^2/mg]$.
The dimensionless exponent $t_{eff}/2$ in Eq. 13 is the product $t_{eff} = uthick\_w \cdot mg(nu)/cm^2 \cdot f_a$. The numerical integration of the convolution integral, the accuracy of which depends on the integration boundaries, the constants vm_SC and i_convol, can be tested by Eq. 13. With $f_s = 1$ the position of the maximum Z_0/Z_∞ is

$$\frac{Z_0}{Z_\infty} = e^{\left(\frac{t_{eff}}{2}\right)} \cdot J_0\left(i\frac{t_{eff}}{2}\right) \qquad (14)$$

For a very thin absorber $Z_0/Z_\infty = 1 - t_{eff}/2$. For 0.1 mg/cm**2 of iron and $f_a = 1$ the effective thickness is $t_{eff} = 0.0589$ (see effi/nucleus.hdb).

The infinite thin approximation is $Z_0/Z_\infty = 0.97055$ to be compared with the exact value of 0.97119, a deviation of 2.2%. From effi a value of 0.97112 is obtained ($f_s = 1$ and background=0) from the plot {pl si} by the mouse click for the position of the maximum. This is a deviation of 0.25%. For larger $weights/cm^2$ the deviations are of the same order. They increase with decreasing velocity range (to be compared with the natural linewidth) and integration boundaries.

A Fortran program taken from the numerical recipes (Bessel functions) is available here (bessj0) calculating BESSJ0(X) and EXP(-X)*BESSJ0(X).

References

[1] A. J. Stone, Molecular Physics **29**, 1461–1471 (1975).

[2] H. Wegener, *Der Mössbauereffekt und seine Anwendungen in Physik und Chemie*, (Bibliographisches Institut (Mannheim), 1965).