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## 1 Anisotropic MSD tensor

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

$$f(\mathbf{e}_z) = e^{-\langle zz \rangle} \quad (1)$$

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

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

the mean square expectation value for any direction  $\mathbf{e}$  is obtained as  $\langle \mathbf{e}^T U_{msd} \mathbf{e} \rangle$  or equivalent by rotation  $R(\phi, \theta)$  of the z-axis to the  $\mathbf{e}$ -direction and taking the  $\langle zz \rangle$  element:  $(R U_{msd} R^{-1})_{zz}$ .

The symmetric tensor has a principal axis system  $S_{msd}$  and eigen values  $U_{xx}, U_{yy}, U_{zz}$ .

Subtraction of the trace  $Tr(U_{msd})/3 = (U_{xx} + U_{yy} + U_{zz})/3$  the Tensor can be written as:

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

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

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

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 contributions 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]).

$$T_{zz} = \sqrt{\frac{2}{3}} \cdot T_{20} \quad (5)$$

Instead of changing the direction  $\mathbf{e}$ , the spherical tensor components are transformed to a coordinate system with  $\mathbf{e}$  parallel to the z-axis.

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

with the rotation matrices  $D_{mn}^L$ .

$$\begin{aligned} D_{00}^2 &= \frac{1}{2}(3\cos\theta - 1) \\ D_{\pm 20}^2 &= e^{\mp 2i\phi} \sqrt{\frac{3}{8}} \sin^2\theta \end{aligned} \quad (7)$$

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

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

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

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

Expanding the e-function

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

$$\eta^k 3^j (\cos 2\phi)^k (\sin\theta)^{2k} (\cos\theta)^{2j} \quad (11)$$

The integrations can be carried through.

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

These formula have been coded in the program msd-powder. The sum has been extended to n=18. Input parameters are  $T_{zz}$  and  $\eta$ . 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].

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

where  $f_s$  and  $f_a$  are the f-factors of source and absorber, respectively,  $n$  [ $\text{cm}^{-3}$ ] the number of Mossbauer nuclei per volume,  $\beta$  the abundance of resonant isotope,  $d$  the thickness,  $\sigma_0$  the cross section, and  $J_0$  the zero Bessel function.

EFFI defines the thickness of the absorber by  $mg(nu)/\text{cm}^2 \cdot f_a$  of the nucleus  $nu$ , which is multiplied by the constant  $uthick\_w = \sigma_0 \beta 6.022 \cdot 10^{23} / \text{atomic\_weight}$  which has the dimension [ $\text{cm}^2/\text{mg}$ ].

The dimensionless exponent  $t_{eff}/2$  in Eq. 13 is the product  $t_{eff} = uthick\_w \cdot mg(nu)/\text{cm}^2 \cdot f_a$ . The numerical integration of the convolution integral, the accuracy of which depends on the integration boundaries, the constants `vm_SC` and `i_conv`, can be tested by Eq. 13. With  $f_s = 1$  the position of the maximum  $Z_0/Z_\infty$  is

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

For a very thin absorber  $Z_0/Z_\infty = 1 - t_{eff}/2$ . For 0.1  $\text{mg}/\text{cm}^2$  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<sup>2</sup>* 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).