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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 $\langle zz \rangle$ 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} ($u_{zz} = \langle zz \rangle$, $u_{ik} = u_{ki}$)

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

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.

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

with the rotation matrices D_{mn}^L .

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

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

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

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

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

The integrations can be carried through.

$$\int_0^{2\pi} (\cos 2\phi)^k d\phi = \frac{k-1}{k} \frac{k-3}{k-2} \cdots \frac{1}{2} \cdot 2\pi \quad (12)$$

$$\int_0^{\pi} (\sin \theta)^{2k+1} (\cos \theta)^{2j} d\theta = \frac{2j-1}{2k+2j+1} \frac{2j-3}{2k+2j-1} \cdots \frac{1}{2k+3}$$

$$\cdot \frac{2k}{2k+1} \frac{2k-2}{2k-1} \cdots \frac{2}{3} \cdot 2$$

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].

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

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 isotope, 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 $uthick_w = \sigma_0 \beta 6.022 \cdot 10^{23} / atomic_weight$ 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_conv`, can be tested by Eq. 13. With $f_s = 1$ the position of the maximum Z_0/Z_∞ is

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

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/cm²* 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).