User Manual for INES

A program for the Evaluation of Nuclear Inelastic Scattering data

by Luca Pasquini and Alessandro Barla

1. INTRODUCTION

Nuclear Inelastic Scattering (NIS) is a novel technique to study lattice dynamics.[1] It gives direct access to the phonon density of states (DOS) and is therefore complementary to other methods, like inelastic neutron, X-ray and Raman scattering which are meinaly concerned with phonon dispersion relations.

A rapid development set in after the pioneering experiments[2,3,4] thanks to several advantages of the new method. First, the resonance character of the scattering assures high count rates. In combination with the small size of the synchrotron radiation beam, tiny samples such as thin films, materials under high pressure and biological samples are easily accessible. Secondly, NIS can be carried out with any sample, i.e., amorphous, disordered, polycrystalline, single crystalline, and even liquids or gases. Finally, NIS provides directly the phonon DOS by automatically performing integration over all phonon momenta. Therefore, in contrast to other methods, no theoretical models have to be invoked. Furthermore, the instrumental resolution is constant with energy and defined with high precision, allowing one the determine the DOS with a few percent accuracy.

NIS is only sensitive to the vibrations of Mössbauer atoms, i.e. the technique provides a partial density of phonon states. The isotope selectivity simplifies the evaluation of the data and the extraction of the DOS from nuclear inelastic absorption spectra. This manual provides a brief summary of the theory underlying the evaluation of NIS spectra and describes the operation of the INES program, specifically developed for the analysis of such spectra.

2. BASIC THEORY OF NUCLEAR INELASTIC SCATTERING

The treatment of nuclear inelastic scattering data is based on the theoretical works of Singwi and Sjölander[5] and Lipkin.[6] The normalised probability of absorption, $W(E)$, of a photon with energy E_0+E, with E_0 resonance energy of the nuclear transition, can be written as:[5]

$$W(E) = f_{LM}\left(\delta(E) + \sum_{n=1}^{\infty} S^{(n)}(E)\right) \equiv f_{LM}\,\delta(E) + W_{in}(E) \qquad (1)$$

with f_{LM} Lamb-Mössbauer factor. The Dirac delta-function, i.e., the zero-th order term of the expansion, represents elastic nuclear absorption without phonon creation or annihilation. $W_{in}(E)$ is the probability of inelastic nuclear absorption. The first order term $S^{(1)}(E)$ in the sum describes the probability of one-phonon creation/annihilation and is linked to the phonon DOS, $g(E)$, by:

$$S^{(1)}(E) = \frac{E_R\, g(E)}{E(1-\exp(-\beta E))} \qquad (2)$$

with E_R recoil energy and $\beta \equiv 1/k_B T$. The higher order terms, representing multi-phonon creation/annihilation events, obey a recursive relation:[5]

$$S^{(n+1)}(E) = \frac{1}{n+1}\int S^{(n)}(E-E')S^{(1)}(E')dE' \qquad (3)$$

Let us denote the Fourier transforms of the above functions in a τ-space by a tilde superscript. From Eqs. (1),(3) and the properties of Fourier transformations it follows immediately that:

$$\widetilde{S}^{(1)}(\tau) = \ln\left(1 + \frac{\widetilde{W}_{in}(\tau)}{f_{LM}}\right) \tag{4}$$

Another important point is that the energy moments of $W(E)$ are linked with physical quantities as shown by Lipkin's sum rules:[6]

$$\langle W \rangle_0 = 1 \tag{5}$$

$$\langle W \rangle_1 = E_R \tag{6}$$

$$\frac{\langle W \rangle_2 - E_R^2}{4E_R} = \langle T \rangle \tag{7}$$

$$\frac{M(\langle W \rangle_3 - 3E_R \langle W \rangle_2 + 2E_R^3)}{\hbar^2 E_R} = \langle F \rangle \tag{8}$$

where $\langle T \rangle$ is the mean kinetic energy per phonon and $\langle F \rangle$ the mean force constant. In the following, the notation $\langle h \rangle_n \equiv \int E^n h(E) dE$ will be used for the n-th moment of a function $h(E)$. Since the moments of the δ-function satisfy $\langle \delta \rangle_n = 0, n > 0$, Eqs. (6)-(8) hold for the inelastic part of nuclear absorption $W_{in}(E)$ as well.

The actual spectrum measured during an experiment can be written as:

$$I(E) = I_0 \int P(E - E')(b f_{LM} \delta(E') + W_{in}(E')) dE' \tag{9}$$

where $P(E)$ is the instrumental function of the monochromator normalized to unit area, i.e., $\langle P \rangle_0 = 1$. Its energy dependence is known from the measurement in the coherent forward channel and its moments can be calculated independently. I_0 is a scaling factor which depends on the amount of resonant nuclei, the geometry of the experiments, the detector efficiency. The factor b is due to saturation effects occurring in the vicinity of the Mössbauer resonance. In fact, the absorption cross section at E=0 is much larger than for E ≠ 0, resulting in a smaller penetration depth of photons with E=0 and less material contributing to the elastic peak. There is also the possibility that a strong coherent channel influences the spectrum. Since the factor b is unknown, it is not possible to use Eq. (5) to determine the scaling factor I_0. One has to turn to eq. (6) instead. It is easy to show that:

$$\langle I \rangle_1 = \langle I \rangle_0 \langle P \rangle_1 + I_0 \langle W \rangle_1 = \langle I \rangle_0 \langle P \rangle_1 + I_0 E_R \tag{10}$$

The experimental spectrum is then divided by I_0 calculated through Eq. (10). Similar relationships between second and third moments of I and W allow one to calculate the average kinetic energy and force constant from the spectrum. The interested reader is referred to [7].

The elastic peak can be subtracted from the spectrum following the procedure outlined in section 4.6. After this step, the properly normalized inelastic spectrum is determined:

$$I_{in}(E) = \int P(E - E') W_{in}(E') dE' \tag{11}$$

and combination with Eq. 4 yields:

$$\widetilde{S}^{(1)}(\tau) = \ln\left(1 + \frac{\widetilde{I}_{in}(\tau)}{\widetilde{P}(\tau) f_{LM}}\right) \tag{12}$$

Therefore the usual strategy to extract the phonon DOS from the spectrum $I(E)$ is composed of three main steps: (i) normalization using Eq. (10) and subtraction of the elastic peak in order to determine $I_{in}(E)$; (ii) calculation of $\widetilde{I}_{in}(\tau)$ by fast Fourier transform (FFT) and of $\widetilde{S}^{(1)}(\tau)$ through Eq. (12); (iii) back-transformation of $\widetilde{S}^{(1)}(\tau)$ and determination of $g(E)$ from $S^{(1)}(E)$ using Eq. (2).

3. INPUT PARAMETERS FOR THE INES PROGRAM

The INES program makes use of a very simple input file where few parameters describing the structure of the data file(s), the Mössbauer transition parameters and the evaluation procedure must be defined by the user. This input file should have an extension *.in*. The input parameters are subdivided into seven blocks for the sake of clarity. The typical structure of one block is:

- description of the parameter(s); these are comment lines, starting with '*', explaining the meaning of the parameter(s). These lines can also be removed without affecting program execution.
- one line starting with a sequential number in parentheses (e.g., '(01)') followed by the name(s) of the parameter(s). This line should must not be modified by the user.
- one line containing user-defined parameter(s) value(s).

In the following, the parameters used by the INES program are described in detail.

3.1. Data structure (block (01))

These parameters define the structure of the data files. They are:

- *inst_f*: this parameter can assume the following values: 0 if no instrumental function is to be considered; 1 if the instrumental function is listed in the same file as $I(E)$; 2 if the instrumental function is in a separate file.
- *nhr1*: number of header lines in the data file containing $I(E)$.
- *sub1*: the number of the column containing energy values.
- *c1*: the number of the column containing $I(E)$.
- *nhr2*: must be defined only if *inst_f*=2, and represents the number of header lines in the separate file containing the instrumental function.
- *e2*: must be defined only if *inst_f*=2, and is the number of the column containing energy values for the instrumental function. Energy binning for the instrumental function need not to be the same as for the inelastic spectrum.
- *i*: must be defined only if *inst_f*<>0, and is the number of the column containing the instrumental function.

3.2. Energy of γrays (block (02))

This parameters defines the energy (in keV units) of the Mössbauer transition, e.g., 14.4125 for the ^{57}Fe Mössbauer isotope.

3.3. Atomic mass (block (03))

The value of this parameter is the atomic mass of the Mössbauer isotope.

3.4. Maximum energy for data analysis (block (04))

The user can decide that all data points at energies E satisfying the condition abs(E)>*max_en* (in meV) will be neglected in the subsequent analysis, except for the calculation of the background. The region where data points are considered as background is defined only by the parameters in block (05) as explained below. Use *max_en* to exclude from the analysis those region of the spectrum yielding no relevant information and affected by strong statistical fluctuations. If you want to keep all data points, simply put *max_en* > max(abs(E)).

3.5. Energy limits for background subtraction (block (05))

The data points at energies $E<b1$ or $E>b2$ are considered as background and their average is subtracted from the spectrum. In many cases, the user may prefer to determine the

background from the negative energy side only, since the positive side may contain multiphonon contributions up to the maximum energy in the spectrum. In this case, put *b2*>max(*E*). If you do not want to remove background at all, put *b1*<min(*E*) and *b2*>max(*E*). Please note that all data points at energies satisfying the condition *E*<*b1* or *E*>*b2* will be used for background calculation, even if abs(*E*)>*max_en* (parameter defined above). In this way some points can be used to calculate the background without taking them into account for the determination of the DOS.

3.6. Subtraction of the elastic peak (block (06))

This block defines three parameters: *sub1*, *sub2*, and *flag*. The elastic peak will be removed in the region *sub1*<*E*<*sub2*. If you do not want to remove the elastic peak, for instance because you already did so, then put *sub1*=*sub2*=0. *flag* defines how the subtraction has to be carried out. If *flag*=0, a linear interpolation between *sub1* and *sub2* is performed, i.e., the spectrum *I*(*E*) in the region *sub1*<*E*<*sub2* is replaced by *I*(*sub1*)+(*I*(*sub2*)-*I*(*sub1*))*(*E-sub1*)/(*sub2-sub1*). If *flag* <>0, the instrumental function after proper rescaling will be subtracted. This is done interacting with the user and using a criterion that will be explained in section 4.6. Please note that if *inst_f*=0, the program will assume *flag*=0 even if a different value is defined.

3.7. Deconvolution of the instrumental function (block (07))

The user can choose to which extent the deconvolution of the instrumental function is carried out. In fact, the program calculates the one-phonon term both using an iterative procedure and the so-called Fourier-log method, described by Eq. (12). The iterative procedure is performed on the normalised spectrum without any deconvolution. Conversely, the Fourier-log method involves calculation of the Fast Fourier transform (FFT) of the spectrum (see Eq. 4). At this stage, deconvolution is represented by the term P in Eq. 12, where P is the FFT of the instrumental function normalized to unit area. The INES program makes use of the function $\widetilde{P}' \equiv (\widetilde{P} + pif)/(1 + pif)$ instead of $\widetilde{P}$. Since the maximum value of $\widetilde{P}$ is $\widetilde{P}(0) = 1$ (due to normalisation), it is easy to see that $\widetilde{P}' \approx 1$ if *pif* >> 1 whereas $\widetilde{P}' \approx \widetilde{P}$ if *pif* << 1. Therefore, *pif* >> 1 corresponds to no deconvolution, while *pif*<< 1 results in almost complete deconvolution.

4. OPERATION OF THE PROGRAM

This chapter describes the steps performed by the INES program. When the program is launched, a main window with three buttons is displayed: 1) **Start INES** begins data treatment; 2) **Convert ID18 SPEC data** performs conversion from raw experimental data file to energy spectra and 3) **EXIT**. The user interface of the program is very simple. Besides the main window, at each step a small window appears that interacts with the user. Further, one or more graphic windows showing the results of calculations are displayed making use of the XPLOT program (included in the XOP package). The program needs one input file, one file with *I*(*E*), and when necessary a file defining the resolution function of the monochromator. The base name of the file containing *I*(*E*) , *filename*, is used as base name for a set of files with different extensions where the output of the program is saved. The operations performed by INES during data treatment are written step by step both onto the main window and in *filename.out*.

4.1. Reading input and data files

The first step is, of course, reading of the input file where the parameters described in the previous section are listed. The user is prompted with a form of the *open file* type whose

actual appearance depends on the operating system under use. The default extension of the input file is *.in*. Afterwards, the program reads the file containing the spectrum $I(E)$ and, if *inst_f* = 2, the file with the instrumental function. Again, the user is prompted with an *open file* form to select the data file(s). The default extension is *.dat*. Data file(s) are generally obtained from the experimental raw file(s) after summing several scans, converting from motor/encoder steps to energy steps and binning into defined energy intervals. The data file(s) must have a columnar structure. The program assumes a Poisson statistics to calculate the errors, i.e., the errors on the experimental spectrum (and instrumental function, if any) are set equal to the square root of the counts. The parameters defined in section 3.1 serve as a guide for the program to extract the necessary arrays (energy, inelastic spectrum, instrumental function).

4.2. Background subtraction

The program calculates the background as described in section 3.5. The value of the background is subtracted from the whole experimental spectrum. The same is done for the instrumental function, if any. When the instrumental function is in a separate file, it may well be that its energy range is more restricted than for $I(E)$. In this case, if there are no energy values in the file satisfying the condition $E<b1$ or $E>b2$, no background will be removed from the instrumental function.

The spectrum after background subtraction is saved in *filename.bgd*.

4.3. Symmetrization of the spectrum

This step is only performed when abs(min(E)) < *max_en* and abs(min(E)) < max(E). Though not recommended, it may happen that, in order to save time during experiments, the negative energy side is cut to some energy below the elastic peak. The program then uses the detailed balance principle to calculate the missing points from the positive energy side. The user is asked to input the temperature of the experiment in order to extend the negative energy side. Note that this procedure should be viewed with some caution and avoided whenever possible, since the detailed balance equation holds only for the one-phonon term of the spectrum (see Eqs. 2-3).

4.4. Normalisation according to Lipkin's sum rule

The scaling factor I_0 is determined using Eq. (10). If *inst_f*=0, the correction for the asymmetry of the instrumental function is not performed, i.e., I_0 is calculated as $I_0 = \langle I \rangle_1 / E_R$. The spectrum is normalised and the result is saved in *filename.nrm*.

4.5. Calculation of higher order moments

Besides the first moment used to normalise the spectrum, the program calculates the second and third moments as well, from which the kinetic energy per atom and mean force constant are derived.[7]

4.6. Elastic peak subtraction

This step is the only one where some arbitrariness is introduced in the analysis. In fact, subtraction of the central elastic peak is hardly carried out automatically. Recently, a way to solve this problem has been proposed in ref [8]. The author of the present manual however, found that the output of the program described in [8] is strongly sensitive to the values of several user-defined parameters, which do possess some arbitrariness, or at least are not easily chosen in the most proper way by non-expert user. The PHOENIX software[9] assumes a Debye behaviour for the low energy part of the inelastic spectrum below the central peak,

which is again questionable for many samples exhibiting no Debye behaviour or when the shape of the low-energy tail is not known. The INES code gives the user different options, by combination of the parameters *sub1*, *sub2*, and *flag*, and described in section 3.6. Here we explain the elastic peak subtraction for *flag* <> 0 and *sub1* < 0, *sub2* > 0. First, the program displays a picture showing several curves in the region *sub1*<*E*<*sub2*. An example of such a picture is reported in Fig. 1. One curve is the original spectrum. The other curves are obtained after subtracting the instrumental function scaled by different factors *f* in the range $\alpha < f < 1$, with α chosen in such a way that $I(0)-\alpha P(0)=2*I(4*\mathrm{FWHM})$. One can see that, in the central part near zero energy, the subtracted curves depend strongly on *f* and oscillate rapidly up and down. This reflects the fact that *P*(E) measured in the coherent forward channel is not exactly proportional to the *P*(E) function which is convoluted with the inelastic spectrum. The subtraction near *E*=0 leads to strong oscillations because in that region *I-P*<<*I*. Outside a certain interval (*E1*,*E2*) the curves are only weekly dependent on *f* and vary smoothly with the energy.

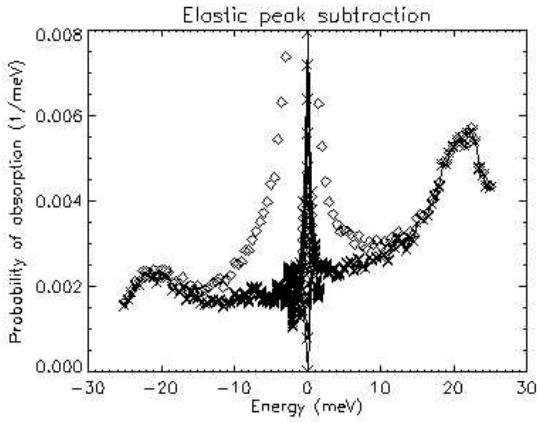

Figure 1

The user is asked to enter *E1*,*E2*. Let us define $I' \equiv I - fP$. The best scaling factor f_{best} is chosen to minimise the absolute value of the function $I'(E) - r(E)$ in the interval (*E1*,*E2*), where $r(E) \equiv I'(E1) + (I'(E2) - I'(E1))(E - E1)/(E2 - E1)$ represents a straight line connecting the points $I'(E1)$ and $I'(E1)$. Finally, the spectrum after subtraction of the elastic peak is defined by:

$I'(E) = I(E)$ *E*<*sub1*, *E* >*sub2* (13-a)

$I'(E) = I(E) - f_{best} P(E)$, *sub1*<*E*<=*E1*, *E2*<=*E*<*sub2* (13-b)

$I'(E) = r(E)$ *E1*<*E*<*E2* (13-c)

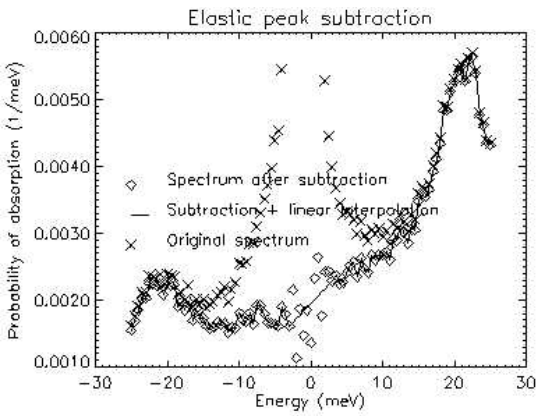

Figure 2

A second picture is displayed showing the original spectrum, the spectrum after subtraction with scaling factor f_{best}, and the spectrum after subtraction plus linear interpolation in the (*E1*, *E2*) interval (see Fig.2). The user has the possibility to try different values for *E1*,*E2* or to confirm the previous choice. Once the user is satisfied with the subtraction procedure, the program continues by displaying a picture of the resulting inelastic spectrum (Fig. 3). The purely inelastic spectrum after elastic peak removal is saved in *filename.sub*.

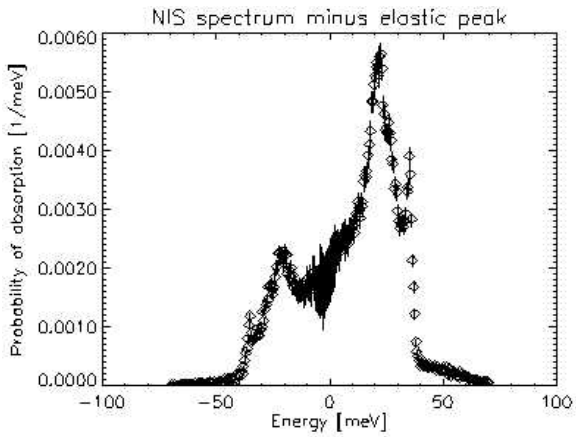

Figure 3

4.7. Determination of Lamb-Mössbauer factor

Eqs. (1) and (4) yield $\langle W_{in} \rangle_0 = 1 - f_{LM}$ and, since $\langle P \rangle_0 = 1$, one also has $\langle I_{in} \rangle_0 = 1 - f_{LM}$. This equation is used to calculate the Lamb-Mössbauer factor. This step raises no particular problems whenever f_{LM} is reasonably high (roughly, when $f_{LM} > 0.2$), but can become critical for very low values because the result depends strongly on the elastic peak subtraction. Small absolute errors in $\langle I_{in} \rangle_0$ turn to quite large relative errors in f_{LM}. A fairly precise calculation of f_{LM} is important for the extraction of the phonon DOS as can be argued from eq. (12). For this reason, INES allows the user to change the value of f_{LM}. It must be kapt in mind that this action is justified only when the calculated f_{LM} deviates significantly from a value known independently with a much better accuracy.

4.8. Calculation of the temperature

The temperature of the experiment is calculated from the inelastic spectrum using the principle of detailed balance expressed by Eq. (2). The first maximum of the spectrum on the positive energy side at *E>sub1* is chosen as reference point. Let's say this point corresponds to energy E^+ and intensity $I(E^+)$. Neglecting multi-phonon contributions, i.e., assuming $I(E) \approx S^{(1)}(E)$, the temperature is derived from Eq. (2) as:

$$T = \ln(I(E^+) / I(-E^+)) / (k_B E) \qquad (14)$$

The temperature derived this way is not reliable if multiphonon terms are not small. The user has the possibility to modify the temperature determined through Eq. (14) and to insert the value measured during the experiment. The automatic determination of *T* via the detailed balance principle can be useful in those cases where uncertainties affect the measured sample temperature, e.g., when the temperature sensor is not close enough to the sample during experiments with cryostats and/or furnaces.

4.9. Extraction of the one-phonon term from the spectrum

The INES code uses two alternative approaches to extract the one-phonon cross-section from the spectrum. The first one is the Fourier-log method, which is fully explained by eq. 12. It performs FFT of the spectrum and instrumental function, applies eq. 12 to calculate $\widetilde{S}^{(1)}(\tau)$ and finally obtains $S^{(1)}(E)$ via back-transformation. Actually, the function $P(\tau)$ in eq. 12 is replaced by $P'(\tau) \equiv (P(\tau) + pif)/(1 + pif)$, as already explained in section 3.7. The *pif* value controls to which degree the deconvolution is performed. The Fourier-log approach thus allows deconvolution of the instrumental function and separation of the multi-phonon term in one single step.

The second method is an iterative approach without deconvolution. The inelastic spectrum $I_{in}(E)$ is used as a starting guess, $S^{(1)}_{guess}(E)$, for $S^{(1)}(E)$. This is obviously an overestimation. The multi-phonon contribution $S^{(n>1)}_{guess}(E)$ (up to the 30th order) is then calculated using Eq. 3 and subtracted from $I_{in}(E)$ to obtain the second guess for $S^{(1)}(E)$, and so on. A graphic window shows the one-phonon and multi-phonon contribution step by step making it possible to follow the convergence process in real time. The convergence criterion is that the sum of the square differences between $S(E)$ and $S^{(1)}_{guess}(E) + S^{(n>1)}_{guess}(E)$ is less than 10^{-8}. If convergence is not reached after 100 iterations, the program asks the user whether to try other 100 iterations or to go on using the results of the Fourier-log method only. When the Lamb-Mössbauer is low, e.g., below 0.5, multiphonon excitation contributes significantly to the spectrum and the initial guess is far from the real one-phonon function, therefore convergence may take long or even never occur. In this last case the user is obliged to go on with the result of Fourier-log calculations only. It is to be pointed out that deconvolution is not performed in the iterative method. It has been extensively checked that, whenever convergence is reached, the two methods yield fully consistent results. The obtained one-phonon functions coincide within the errors if the *pif* parameter is >>1 (i.e., if practically no deconvolution is performed in the Fourier-log method). The one-phonon and multi-phonon terms calculated by Fourier-log and iterative procedure are saved in the files *filename.1ph* and *filename.mph*.

4.10. Determination of the density of states

Once the one-phonon term has been calculated, the determination of the DOS $g(E)$ by Eq. (2) is straightforward. The INES code takes only the positive-energy side of the symmetric curve since this is generally determined with better statistics. Two DOS's, one from Fourier-log and one from iterative method, are calculated. The program also calculates their integrals with the relative error. If the data treatment is correct, these values should be very close to unity. The two functions $g(E)$, already normalized to unit area by the program, are saved in *filename.dos*.

4.11. Calculations of thermodynamic functions from the DOS and consistency check

The program now asks which DOS has to be used to calculate some thermodynamic functions in the 0-500 K temperature interval. These functions and the relative output file extensions are given in Table I. INES also calculates the mean force constant (independent on temperature apart from anharmonic effects) from the DOS.

A consistency check of the whole data treatment is given by those quantities that can be determined both from the moments of the inelastic spectrum and from the density of states. These are: the Lamb-Mössbauer factor, the mean kinetic energy per atom, the mean force

constant. It is clear that the values determined in the two ways should coincide within the errors. A further check is provided by the integral of $g(E)$ before normalization, which should be =1 if normalization of the inelastic spectrum through Eqs. 5-6 and elastic peak is removal have been carried out correctly. The results of these consistency check are saved at the end of the .out file.

Table I

Thermodynamic function	*file extension*
Specific heat at constant volume $C_V(T)$	.cv
Vibrational part of Helmoltz free energy $F_V(T)$	.fv
Mean square displacement	.msd
Lamb-Mössbauer factor	.flm
Mean kinetic energy per atom	.kin
Vibrational entropy	.s
Vibrational part of internal energy	.u

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