

Frequency moments and energy shifts for dilute Mössbauer impurities in metallic solids

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Abstract. Theoretical evaluations of frequency moments and second order Doppler shifts have been made for dilute ^{57}Fe impurities in the high temperature limit for a harmonic solid. The resonant energy shifts have been calculated from the Green's function of the impure crystal containing both mass disordering and force constant change terms in the crystal Hamiltonian. High temperature frequency moments for the impurity in different metallic solids are obtained from Mc-Millan ratios using standard Mössbauer f -values at room temperature.

The effect of mass disordering predominates over the force constant change term in the evaluations of second order Doppler shifts and hence the frequency moments for dilute ^{57}Fe impurities. The variation of frequency moments for the impurity with mass modified Debye-temperature of the hosts is shown for a number of metallic solids.

Keywords. Frequency moments; second order Doppler shift; Mc-Millan ratio; energy shifts.

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1. Introduction

Recently Roy and Bhattacharya (1984) presented an explicit calculation on the effect of finite but small concentration of impurities present in a metallic solid on the Debye-Waller factor under harmonic approximation. We have shown that the Debye-Waller factor is modified mainly due to the presence of potential energy terms in the crystal Hamiltonian containing impurities at the lattice sites. In the present work we evaluate the two other important impurity parameters *viz* the second order Doppler shifts and frequency moments for dilute ^{57}Fe impurities taking the same impurity crystal Hamiltonian and treating both the force constant and mass change terms under separable kernel approximations. The second order Doppler shifts which are evaluated through the (B-B) correlation functions are mainly affected by the presence of mass disordering term in the crystal Hamiltonian. The frequency moments for the impurity are evaluated from the present energy shift values and the Mössbauer f -values already reported by Roy and Bhattacharya (1984) and Grow *et al* (1978). The mass modified Debye-temperatures are obtained from the well-known Debye-relation using standard values of the host Debye-temperatures given by Kittel (1983). The method which we follow here for decoupling the Fourier-transformed imperfect Green's function is similar to that of Maradudin *et al* (1971).

2. Theory

The Hamiltonian of the crystal containing impurities of mass M' occupying the lattice sites replacing the host atoms of mass M can be written in terms of the operators A_k and B_k using suitable normal coordinate transformations (Roy and Bhattacharya 1984)

$$H = \hbar \sum_k w_k (a_k^\dagger a_k + \frac{1}{2}) + \hbar \sum_{kk'} U(kk') B_k B_{k'} + \hbar \sum_{kk'} V(kk') A_k A_{k'}, \quad (1)$$

where the operators A_k and B_k can be represented in terms of phonon creation operator a_k^\dagger and annihilation operator a_k (Roy *et al* 1981) and the kernels can be represented as

$$U(kk') = \left(\frac{\varepsilon}{4N} \right) \sum_l e_\alpha(k) e_\alpha(k') [w_k w_{k'}]^{1/2} \exp[i(k+k')R(l)], \quad (2a)$$

and

$$V(kk') = \left(\frac{\tau}{4N} \right) \sum_{l \neq l'} e_\alpha(k) e_\alpha(k') [w_k w_{k'}]^{1/2} \exp[ikR(l)] \exp[ik'R(l')]. \quad (2b)$$

The kernels in the above equations have the separable form (Tripathi and Behera 1974) and the mass and force constant change parameters are given by,

$$\varepsilon = \left(\frac{M}{M'} - 1 \right) \quad \text{and} \quad \tau = \left(\frac{\phi'}{\phi} - 1 \right). \quad (3)$$

Since in the dilute impurity case the probability of two impurities clustering together becomes negligible (Behera 1979), impurity-impurity interaction terms do not appear in (1).

The evaluation of the second order Doppler shifts for the crystal model Hamiltonian (1) follow from the velocity correlation functions which are related to the Green's function defined in terms of operators A and B .

We use the following double time thermodynamic Green's functions of Zubarev (1960) to evaluate the second order Doppler shift.

$$G_{kq}^{BB}(t) = \langle\langle B_k(t) B_q(0) \rangle\rangle = -i\theta(t) \langle [B_k(t) B_q(0)] \rangle, \quad (4a)$$

and

$$G_{kq}^{AB}(t) = \langle\langle A_k(t) B_q(0) \rangle\rangle = i\theta(-t) \langle [A_k(t) B_q(0)] \rangle. \quad (4b)$$

The equations of motion of the above Green's functions for the given Hamiltonian (1) after Fourier transformations and some rearrangements become

$$G_{kq}^{BB}(E) = -\frac{w_k \delta_{k,-q}}{\pi[E^2 - w_k^2]} + \sum_p \frac{4EV(-kp)}{[E^2 - w_k^2]} G_{pq}^{AB}(E) - \sum_p \frac{4w_k U(-kp)}{[E^2 - w_k^2]} G_{pq}^{BB}(E), \quad (5a)$$

and

$$G_{kq}^{AB}(E) = -\frac{E \delta_{k,-q}}{\pi[E^2 - w_k^2]} + \sum_p \frac{4w_k V(-kp)}{[E^2 - w_k^2]} G_{kq}^{AB}(E) - \sum_p \frac{4EU(-kp)}{[E^2 - w_k^2]} G_{pq}^{BB}(E) \quad (5b)$$

These coupled Green's function equations can be solved in a manner similar to our earlier calculations (Roy and Bhattacharya 1984) to obtain finally the impurity Green's

function as

$$\begin{aligned}
 G_{kq}^{BB}(E) = & -\delta_{k,-q} G_k^{(0)}(E) - \frac{4\pi E^2}{w_k^2} G_k^{(0)}(E) V(-kk) [1 - M_1]^{-1} \\
 & [1 - T_1]^{-1} G_k^{(0)}(E) + 4\pi G_k^{(0)}(E) U(-kk) [1 - L_1]^{-1} \\
 & [1 - T_1]^{-1} G_k^{(0)}(E) + 32\pi^2 \sum_k \frac{E^2}{w_k^2} G_k^{(0)}(E) V(-kk) [1 - L_1]^{-1} \\
 & [1 - M_1]^{-1} [1 - T_1]^{-1} G_k^{(0)}(E) U(-kk) G_k^{(0)}(E), \quad (6)
 \end{aligned}$$

where $G_k^{(0)}(E)$ represents the host crystal Green's function and the matrices L_1 , M_1 , and T_1 , are given by

$$L_1 = -\sum_k \frac{4u(k)w_k u(-k)}{[E^2 - w_k^2]}, \quad (7a)$$

$$M_1 = \sum_k \frac{4v(k)w_k v(-k)}{[E^2 - w_k^2]}, \quad (7b)$$

and

$$T_1 = -\sum_k \frac{16U(-kk)E^2 V(-kk)}{[E^2 - w_k^2]} [1 - L_1]^{-1} [1 - M_1]^{-1}. \quad (7c)$$

The first term on the right side of (6) represents the perfect part whereas the second and third terms represent the contributions due to force constant change and mass disordering terms respectively and the fourth term is the interaction term with two vertices.

3. Averaging of Greens' function for low defect concentration

For randomly distributed non-interaction impurities, the physical properties of the crystal will be independent of the configuration of the impurities. This requires that the Green's function be configurationally averaged. Behera and Deo (1967) dealt with the problem of configurational averaging for very low concentrations following a diagrammatic technique. Here we follow the simple method of Langer (1961) for the averaging of kernels by expansion in powers of concentrations and do not take the multiple occupancy corrections into account as they are important in high concentration theory only.

The averaging of mass disordering kernel is given by

$$\langle U(-kk') \rangle_{av} = \left\langle \frac{\varepsilon w_k}{4N} \sum_{l'} C_\lambda(l') \exp[i(k' - k)R(l')] \right\rangle_{av} \quad (8)$$

The quantity $C_\lambda(l')$ appearing in (8) characterizes the impurity distribution in the crystal. In carrying out the average we use the fact that the probability that a given lattice site is occupied by an impurity atom is $C_d = N_d/N$. Quantities containing $C_\lambda(l')$ after averaging are proportional to C_d in the low defect concentration expansion. Hence (8) can be written as

$$\langle U(-k, k') \rangle_{av} = \frac{1}{4} \varepsilon C_d w_k \delta_{kk'}. \quad (9)$$

Similarly for force constant change one can write

$$\langle V(-k, k') \rangle_{av} = \frac{1}{4} \tau w_k \delta_{kk'} \tag{10}$$

Using (9) and (10) in (6) we get,

$$\begin{aligned} \langle G_{kq}^{pp}(E) \rangle = & -\frac{w_k \delta_{k,-q}}{\pi[E^2 - w_k^2]} - \frac{\pi E^2 \tau w_k}{\pi^2[E^2 - w_k^2]} [1 - M_1]^{-1} [1 - T_1]^{-1} \\ & + \frac{\pi w_k^3 \epsilon C_d}{\pi^2[E^2 - w_k^2]^2} [1 - L_1]^{-1} [1 - T_1]^{-1} \\ & + \frac{2\pi^2 E^2 w_k^5 \epsilon \tau C_d}{\pi^3[E^2 - w_k^2]^3} [1 - L_1]^{-1} [1 - M_1]^{-1} [1 - T_1]^{-1}. \end{aligned} \tag{11}$$

4. Second-order Doppler shift

The shift in the γ -ray energy due to the presence of impurities may be written in terms of Green's function as (Tewari *et al* 1979)

$$\left(\frac{\Delta E}{E}\right) = \frac{\pi}{2M'N\beta c^2} \sum_{kk'} e(k)e(k') [w_k w_{k'}]^{1/2} \sum_{n=-\infty}^{\infty} G_{kk'}(i\omega_n). \tag{12}$$

Using (11) in (12) we can split $(\Delta E/E)$ as

$$\left(\frac{\Delta E}{E}\right) = \left(\frac{\Delta E}{E}\right)_0 + \left(\frac{\Delta E}{E}\right)_1 + \left(\frac{\Delta E}{E}\right)_2 + \left(\frac{\Delta E}{E}\right)_3. \tag{13}$$

The last term in (13) arises because of the interaction of two vertices terms and is negligibly small and hence its contribution to $(\Delta E/E)$ can be neglected. Thus we are left with the mass disordering and force constant change terms in addition to the perfect lattice term with lattice atoms of mass M' .

Using first, second and third terms of the Green's function (11) in (12) one can obtain the energy shift in the high temperature limit as

$$\left(\frac{\Delta E}{E}\right)_0 = \frac{3(k_\beta T)}{2M'C^2} + \frac{\hbar^2 w_D^2}{40M'C^2} (k_\beta T)^{-1} + O(T^{-3}) + \dots, \tag{14a}$$

$$\left(\frac{\Delta E}{E}\right)_1 = \frac{1}{4} \frac{\tau \hbar^2 w_D^2}{M'C^2} (k_\beta T)^{-1} + O(T^{-3}) + \dots, \tag{14b}$$

and

$$\left(\frac{\Delta E}{E}\right)_2 = \frac{3}{2} \frac{\epsilon C_d}{M'C^2} (k_\beta T) + O(T^{-3}) + \dots \tag{14c}$$

The contribution due to $(\Delta E/E)_3$ to the second order Doppler shift is proportional to $O(T^{-3})$ in the high temperature limit and can be neglected.

It may be mentioned that in evaluating (14a), (14b) and (14c) we have replaced the sum over the modes k by the integration

$$\sum_k \rightarrow \frac{3N}{w_D^3} \int_0^{w_D} w_k^2 dw_k \tag{15}$$

The numerical evaluation of $(\Delta E/E)$ are made for ^{57}Fe impurities in different metallic hosts *i.e.* varying the mass and force constant parameters ϵ and τ for the defect concentration $C_d = 0.3$ at room temperature.

5. Impurity parameters and frequency moments

The observed correlations between Mössbauer f -values and thermal shift measurements and also between impurity and host parameters have been discussed by Taylor and Craig (1968) and Craig *et al* (1970). In these papers a key lattice dynamical quantity, known as the Mc-Millan ratio for the impurity has been defined by the thermal averages

$$\left[\frac{\langle w \rangle}{\langle w^{-1} \rangle} \right]^{imp} = \left[\frac{\frac{1}{3} \langle v^2 \rangle}{\langle x^2 \rangle} \right]_{\tau}^{imp} \quad (16)$$

The Mc-Millan ratio defined by (16) approaches $1/\mu'(-2)$ in the high temperature limit, where $\mu'(-2)$ is the impurity frequency moment. Equation (16) can therefore be rewritten as (Grow *et al* 1978)

$$\left[\frac{\frac{1}{3} \langle v^2 \rangle}{\langle x^2 \rangle} \right]_{\text{H.T.}}^{imp} \rightarrow \frac{1}{\mu'(-2)} \quad (17)$$

The numerical evaluations of impurity frequency moments have been made using the high temperature values of the second-order Doppler shift from this work and the Mössbauer f -values already reported (Roy and Bhattacharya 1984; Grow *et al* 1978) for ^{57}Fe impurities in different hosts.

6. Discussion

The second-order Doppler shifts of ^{57}Fe impurities in different metallic hosts are obtained at 300°(K) from (14a)–(14c) using force constant ratios obtained from neutron dispersion data (Grow *et al* 1978). The impurity concentration chosen to evaluate the energy shifts is $C_d = 0.3$ in each case. The values of the force constant change

Table 1. Energy shifts for ^{57}Fe impurities in different metallic solids.

Host	τ	$(\Delta E/E)_1 \times 10^{-12}$	ϵ	$(\Delta E/E)_2 \times 10^{-12}$ for $C_d = 0.3$	$(\Delta E/E) \times 10^{-12}$
Al	-0.375	-0.0049	-0.53	-0.2200	0.9861
Cr	-0.301	-0.0039	-0.30	-0.0367	1.1704
Ni	0.250	0.0032	0.04	0.0146	1.2288
Cu	0.316	0.0041	0.12	0.0500	1.2651
Nb	-0.387	-0.0050	0.63	0.2530	1.4590
Mo	-0.556	-0.0072	0.69	0.2877	1.4915
Rh	-0.457	-0.0059	0.81	0.3379	1.5430
Pd	-0.387	-0.0057	0.87	0.3629	1.5682
Au	-0.329	-0.0043	2.46	1.0262	2.2329
W	-0.587	-0.0076	2.23	0.9302	2.1336

contributions $(\Delta E/E)_1$ and mass disordering contributions $(\Delta E/E)_2$ to the energy shift are given in table 1 along with the τ and ε values, for the host-impurity systems. The variation of $(\Delta E/E)_1$ and $(\Delta E/E)_2$ with τ and ε for ^{57}Fe impurities in different metallic hosts are plotted in figures 1 and 2. The frequency moments of ^{57}Fe impurities in different hosts are obtained from the present values of second order Doppler shifts and the Mössbauer f -values given by Roy and Bhattacharya (1984) and Grow *et al* (1978). Due to the presence of impurity in different hosts of different masses the Debye-temperature of the host is modified as $(1 + \varepsilon)^{1/2}\theta_D$ which we call mass modified Debye-temperature of the hosts. This is the result of the well-known Debye-relation between the host and effective impurity Debye-temperature given by

$$\theta_D^{\text{eff}} = (1 + \varepsilon)^{1/2} \theta_D (\phi'/\phi)^{1/2}. \quad (18)$$

The values of the room temperature impurity frequency moments are listed with the mass modified Debye temperatures for various hosts in table 2.

The frequency moments are plotted against the mass modified Debye temperatures in figure 3. It is interesting to note from tables 1 and 2 that the major contributions to the second-order Doppler shift and hence the frequency moments of the ^{57}Fe impurity vibrating in different metallic solids, come from the mass disordering term whereas the contributions due to force constant change term to SOD shifts are very small, only about 1–23% of the force constant term. The mass disordering contribution varies from about 2% for Ni to as large as 50% for Au which indicates that the second-order Doppler shift increases with increase in host masses characterising the localized impurity vibrations. Figure 3 indicates the variation of impurity frequency moments

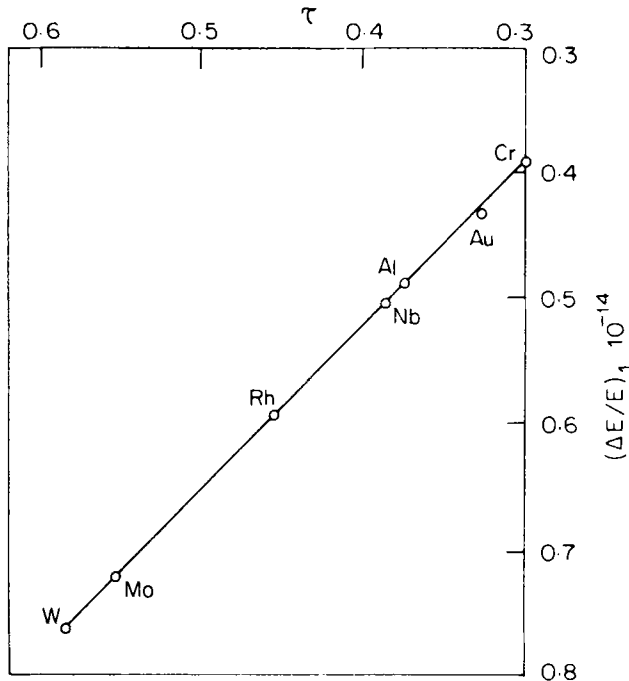


Figure 1. Variation of $(\Delta E/E)_1$ for ^{57}Fe impurity with τ values in different metallic solids.

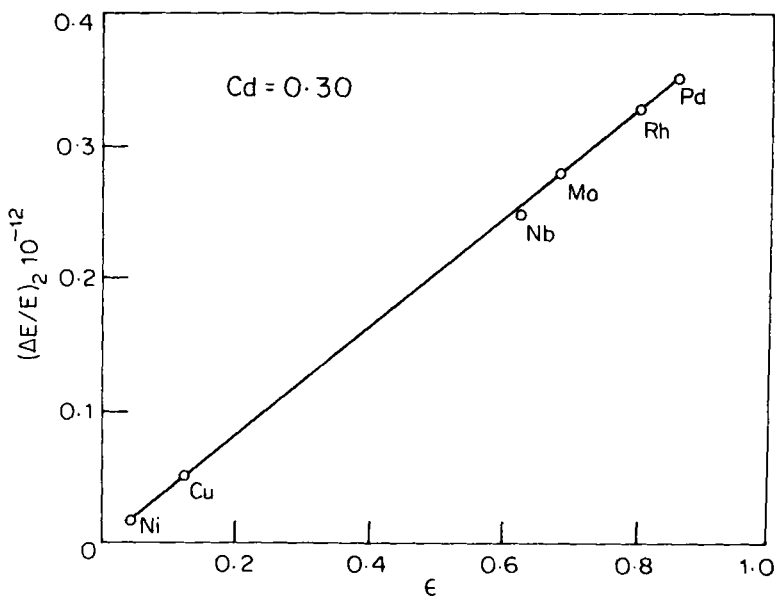


Figure 2. Variation of $(\Delta E/E)_2$ for ^{57}Fe impurity with ϵ values in different hosts ($C_d = 0.3$).

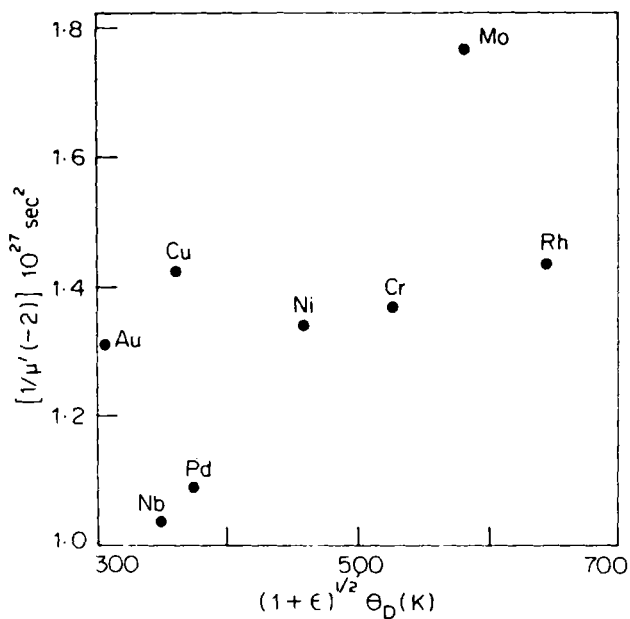


Figure 3. Inverse frequency moments of ^{57}Fe impurity vs mass modified Debye-temperature of the hosts.

Table 2. Mass modified Debye temperatures of the hosts and frequency moments for ^{57}Fe impurity in different solids.

Host	$\langle V^2 \rangle_{300(\text{K})} \times 10^8$ (cm^2/sec^2)	$\langle X^2 \rangle_{300(\text{K})}$ $\times 10^{-19}$ (cm^2)	$1/\mu'(-2) \times 10^{27}$ (sec^2)	$(1 + \epsilon)^{1/2} \theta_D(k)$
Ni	22.115	5.504	1.339	459
Cu	22.772	5.164	1.470	363
Cr	21.067	5.151	1.363	527
Au	40.191	10.180	1.316	307
Pd	28.227	8.670	1.085	375
Nb	25.520	8.187	1.039	351
Mo	26.847	5.104	1.753	585
Rh	27.774	6.251	1.481	647

with host Debye-temperatures thus characterizing the impurity vibrations in various hosts. However better results are expected when we consider anharmonic lattice vibrations and change in the symmetry behaviours of crystals due to the presence of impurities.

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