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Debye-Waller factor of sodium: A comparison of theory and experiment

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We have compared the Debye-Waller factor of sodium calculated by three different theoretical methods with the recent measured values in the temperature range 80–295 K, using the Mössbauer γ-ray-scattering technique. The Mössbauer results are also compared with the two sets of earlier x-ray measurements, one of which extends to 365 K. The three theoretical methods are the following: the lowest-order anharmonic perturbation theory, a Green's-function method that includes anharmonic contributions of the lowest-order perturbation theory summed to infinity, and the molecular-dynamics method, which includes the anharmonic contributions to all orders. In all three methods the Ashcroft pseudopotential with the Vashishta-Singwi screening function is employed to generate the real-space two-body potential function whose range is cut off at the sixth-neighbor distance. Excellent agreement is found between the results of these three methods and the Mössbauer experimental results. The x-ray results are also in very good agreement with the Mössbauer data where the temperatures overlap in the measurements.

Over the past ten years, several calculations of the atomic mean-square displacement (MSD) have been reported in the literature[1–6] for the short- and long-range potential functions in monatomic fcc and bcc lattices, respectively. These calculations[4] have been carried out by the molecular-dynamics (MD) method, the Monte Carlo (MC) method, and the lowest-order (λ^2) perturbation theory. The results from the last method, when compared with the MD and MC methods provide an assessment of the adequacy of the lowest-order (cubic and quartic) perturbation theory because all anharmonic contributions are represented in the results of the MD and MC methods. Quite recently, the results of these three methods have also been compared with a Green's-function method for both the above types of potential function.[3,5] The latter calculation[5] represents the most successful comparison of the results obtained from an analytical method and a numerical procedure (i.e., the MC method) for a short-range potential (a 6-12 Lennard-Jones interaction potential for a nearest-neighbor model of a fcc lattice). On the other hand, the improvement in the results for the long-range potential (a sixth-neighbor interaction model for the bcc alkali metals) by the Green's-function method[3] was slight over the λ^2 theory. In other words, the λ^2 theory, Green's-function method, and MD method results compared with each other quite well.

The present work has been prompted by the recent measurements[7] of the Debye-Waller factor (DWF) in Na where no comparison was yet made between the above-mentioned theoretical calculations and the experimental values of the DWF. The isotropic part of the Debye-Waller factor is very simply related to the MSD.

In what follows we present a summary of the calculations from the above three methods and a comparison of the results with the experiments. Since it has been shown earlier by Shukla and Hübschle[5] that the λ^2 perturbation theory (λ^2 PT) results for the MSD can be obtained from the Green's-function method, we will summarize this method first, to avoid repetition of derivations of some equations of the MSD from the λ^2 PT.

The atomic displacement in a monatomic lattice at a site l and time t in direction α ($\alpha = x,y,z$) is given by

$$u_\alpha^l(t) = \left[\frac{\hbar}{2NM}\right]^{1/2} \sum_{\mathbf{q}} \sum_{j=1}^{3} \frac{e_\alpha(\mathbf{q},j)}{(\omega_{\mathbf{q}j})^{1/2}} e^{i\mathbf{q}\cdot\mathbf{r}_l} A_{\mathbf{q}j}(t) ,$$
$$A_{\mathbf{q}j} = a_{\mathbf{q}j} + a^\dagger_{-\mathbf{q}j} , \; A^\dagger_{\mathbf{q}j} = A_{-\mathbf{q}j} , \tag{1}$$

where $a^\dagger_{\mathbf{q}j}$ and $a_{\mathbf{q}j}$ are the usual creation and annihilation operators, $\omega_{\mathbf{q}j}$ is the phonon frequency, $e_\alpha(\mathbf{q},j)$ is the αth component of the eigenvectors for the wave vector q and branch index j, N is the number of unit cells in the crystal, M is the atom mass, $\hbar$ is the Planck constant divided by 2π, and $\mathbf{r}_l$ is the vector of the direct lattice. The summation over $\mathbf{q}$ is over the first Brillouin zone (BZ).

Squaring both sides of the above equation and summing over α, we find the following expression for $\langle u^2 \rangle$:

$$\langle u^2 \rangle = \frac{\hbar}{2NM} \sum_{\mathbf{q},\mathbf{q}'} \sum_{\alpha,j,j'} \frac{e_\alpha(\mathbf{q},j) e_\alpha(\mathbf{q}',j')}{(\omega_{\mathbf{q}j}\omega_{\mathbf{q}'j'})^{1/2}} \times e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{r}_l} \langle A_{\mathbf{q}j} A^\dagger_{\mathbf{q}'j'} \rangle , \tag{2}$$

where the angular brackets indicate the thermal average. This average is evaluated from the Green's function

$$G_{jj'}^{\mathbf{q}\mathbf{q}'}(\omega) = \frac{\omega_{\mathbf{q}j} \delta_{\mathbf{q}\mathbf{q}'} \delta_{jj'}}{\pi[\omega^2 - \omega_{\mathbf{q}j}^2 - 2\omega_{\mathbf{q}j}\Pi_{\mathbf{q}j}(\omega)]} , \tag{3}$$

employing the following two relations:

$$J_{jj'}^{\mathbf{q}\mathbf{q}'}(\omega) = -\lim_{\varepsilon \to 0} \left[\frac{2}{e^{\beta\hbar\omega} - 1} \operatorname{Im} G_{jj'}^{\mathbf{q}\mathbf{q}'}(\omega + i\varepsilon)\right] \tag{4}$$

and

$$\langle A_{\mathbf{q}j} A^{\dagger}_{\mathbf{q}'j'} \rangle = \int_{-\infty}^{\infty} J^{\mathbf{q}\mathbf{q}'}_{jj'}(\omega)\, d\omega \; . \tag{5}$$

In the above Green's function, $\Pi_{\mathbf{q}j}(\omega)$ is the so-called self-energy term which is related to the cubic and quartic terms of the anharmonic Hamiltonian. The contribution to $\Pi_{\mathbf{q}j}$ from the quartic term is independent of ω, but the cubic contribution is frequency dependent. However, in the high-temperature limit ($T > \Theta_D$, Θ_D is the Debye temperature), Shukla and Hübschle[5] have shown that correct expressions for $\langle u^2 \rangle$ are obtained by putting $\omega = 0$ in this contribution to Π. Referring the details of the calculation to Ref. 5, we find in the high-temperature limit the following expression for $\langle u^2 \rangle$:

$$\langle u^2 \rangle = \frac{k_B T}{NM} \sum_{\mathbf{q},j} \frac{1}{\Omega^2_{\mathbf{q}j}} \; , \tag{6}$$

$$\Omega^2_{\mathbf{q}j} = \omega^2_{\mathbf{q}j} - \frac{\lambda^2}{2\beta N} \sum_{\mathbf{q}_1,j_1} \sum_{\mathbf{q}_2,j_2} \Delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}) \frac{|\Phi(\mathbf{q}_1 j_1, \mathbf{q}_2, j_2, \mathbf{q}j)|^2}{\omega^2_{\mathbf{q}_1 j_1} \omega^2_{\mathbf{q}_2 j_2}} + \frac{\lambda^2}{2\beta N} \sum_{\mathbf{q}_1,j_1} \frac{\Phi(\mathbf{q}_1, j_1, -\mathbf{q}_1, j_1, \mathbf{q}, j, -\mathbf{q}, j)}{\omega^2_{\mathbf{q}_1 j_1}} \; ,$$

$$\Omega^2_{\mathbf{q}j} = \omega^2_{\mathbf{q}j} + \Delta_3(\mathbf{q}, j) + \Delta_4(\mathbf{q}, j) \; , \tag{7}$$

where the Φ function in general is defined by

$$\Phi(\lambda_1, \ldots, \lambda_n) = \frac{1}{2M^{n/2}} \sum_{l}{}' \sum_{\alpha,\ldots,\delta} \phi_{\alpha,\ldots,\delta}(|\mathbf{r}_l|) e_a(\lambda_1) \cdots e_\delta(\lambda_n)(1 - e^{-i\mathbf{q}_1 \cdot \mathbf{r}_l}) \times \cdots \times (1 - e^{i\mathbf{q}_n \cdot \mathbf{r}_l}) \; . \tag{8}$$

In the above equation, the prime over the l summation indicates the omission of the origin point, $\phi_{\alpha,\ldots,\delta}(|\mathbf{r}_l|)$ represents the tensor derivative of the pair potential $\phi(\mathbf{r})$, and λ_i collectively represents the wave vector $\mathbf{q}_i$ and branch indices j_i ($i = 1, 2, \ldots, n$). The Δ function in Eq. (7) is unity if the sum of arguments is zero or a vector of the reciprocal lattice and zero otherwise.

If after substituting for $\Omega^2_{\mathbf{q}j}$ from Eq. (7) into Eq. (6) and expansion is carried out in powers of λ^2, we find the following lowest-order (λ^2 PT) anharmonic contributions to $\langle u^2 \rangle$:

$$\langle u^2 \rangle_{\mathrm{qh}} = \frac{k_B T}{NM} \sum_{\mathbf{q},j} \frac{1}{\omega^2_{\mathbf{q}j}} \; , \tag{9}$$

$$\langle u^2 \rangle_Q = -\frac{(k_B T)^2 \lambda^2}{2N^2 M} \sum_{\substack{\mathbf{q}_1,j_1 \\ \mathbf{q}_2,j_2}} \frac{\Phi(\mathbf{q}_1, j_1; -\mathbf{q}_1, j_1; \mathbf{q}_2, j_2; -\mathbf{q}_2, j_2)}{\omega^2_{\mathbf{q}_1 j_1} \omega^4_{\mathbf{q}_2 j_2}} \; , \tag{10}$$

$$\langle u^2 \rangle_C = \frac{(k_B T)^2 \lambda^2}{2N^2 M} \sum_{\substack{\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3, \\ j_1,j_2,j_3}} \Delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3) \frac{|\Phi(\mathbf{q}_1, j_1; \mathbf{q}_2, j_2; \mathbf{q}_3, j_3)|^2}{\omega^2_{\mathbf{q}_1 j_1} \omega^2_{\mathbf{q}_2 j_2} \omega^4_{\mathbf{q}_3 j_4}} \; , \tag{11}$$

where the subscripts qh, Q, and C in Eqs. (9)–(11) stand for the quasiharmonic, quartic, and cubic contributions of the λ^2 PT.

The DWF expression $2M(Q)$, where Q is the scattering vector, is obtained by multiplying with $Q^2/3$ the above listed expressions for $\langle u^2 \rangle$. The corresponding contributions from the Green's-function method and the λ^2 PT are obtained from Eqs. (6) and (9)–(11), respectively. We denote the Green's-function result by a subscript "ren", because, the renormalized frequency $\Omega_{\mathbf{q}j}$, as given by Eq. (7), is used in this method. For the λ^2 PT, there are in total three contributions to the DWF and these are denoted by the subscripts qh, Q, and C, respectively.

Now we turn our attention to the numerical procedure used in obtaining the results from the Green's-function (GF) method, the λ^2 PT, and the MD method. In the GF method, for a given $\mathbf{q}$ and j, $\Omega^2_{\mathbf{q}j}$ is calculated from Eq. (6), which includes the contributions from the cubic and quartic shifts of the phonon frequencies. By substituting Eq. (8) into Eq. (7) and the plane-wave representation of the Δ function, the whole BZ sums needed in the calculation were expressed in terms of the $S_{\alpha\beta}$ tensors. These tensors can be calculated for the irreducible sector of the BZ and, from the expressions given in Shukla and Wilk,[8] can be obtained for the whole zone. The calculations were done for step lengths as low as $L = 6$ (432 wave vectors in the whole BZ) to as large as $L = 11$ (2662 wave vectors in the whole BZ), and the final results were obtained by graphical extrapolation which corresponds to the limit $L \to \infty$. A similar procedure was used in the calculation of the λ^2 PT contributions from Eqs. (9)–(11). For MD calculations described in much more detail in Shukla and Heiser,[2] a 250-particle sample size, initially located in a cube containing 5×5×5 bcc unit cells, was used as a starting point. Periodic-boundary conditions were used in the calculations to minimize the surface effects. As in our previous calculations,[1,2] the Beeman algorithm was used in the integration of the equations of motion of the 250 particles, and 3000 time steps were used in obtaining the final MSD results.

In all three methods, a real-space sixth-neighbor interaction potential was employed in the calculations. This potential was obtained from the Ashcroft pseudopotential with Vashishta-Singwi screening function.[9] The calculations were carried out for the temperatures in the range $93 \leq T \leq 365$ K, and appropriate volumes for the four temperatures in this range were chosen. The lattice constants are 4.234 Å (93 K), 4.251 Å (163 K), 4.288 Å (294 K), and 4.309 Å (365 K). The Debye-Waller slope $[2M(Q)/Q^2]$ calculated by the above three methods along with the experimental data of Crow *et al.*[7] is presented in Fig. 1. It is clear from these results that the agreement between the calculated and experimental values is very good for all temperatures.

There are two earlier x-ray measurements of the DWF in Na by Dawton[10] and Field and Medlin.[11] It might be of some interest to compare these with the most recent measurement of Crow *et al.* by a Mössbauer γ-ray-diffraction technique.

Since Crow *et al.* have not made this comparison, we present in Fig. 2 these experimental results along with the MD results. We note here that Field and Medlin[11] only did a room-temperature measurement. The results presented in Dawton's paper[10] are ratios of intensities at 180, 291, and 368 K, with a reference temperature of 117 K. We used an average of the intensities for the 310 and 400 reflections and the calculated intensity at 117 K. Once again, we find that the agreement is quite good between the MD and x-ray results except at the highest temperature. The x-ray results are also in very good agreement with the Mössbauer data where the temperatures overlap in the measurements.

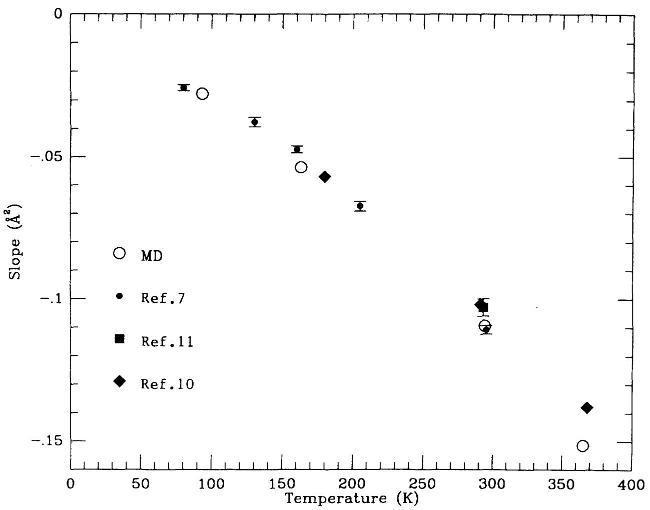

FIG. 2. Slope of the Debye-Waller factor in Na vs temperature. Open circles and dot represent the MD results and the experimental data of Crow *et al.*, respectively, and squares and diamonds are the x-ray results of Field and Medlin and Dawton, respectively.

Crow *et al.* have chosen to compare their results with two theoretical calculations of the DWF based on the quasiharmonic formula. In the first calculation, they used fixed-volume (5 K) phonon frequencies and calculated the slopes of the DWF for different temperatures, and in the other calculation they used temperature-dependent frequencies. Both calculations were done from the Na potential used previously in anharmonic calculations by Glyde and Taylor[12] and Shukla and Taylor.[13] How well the results of the DWF of Na for a fixed-volume (5 K) calculation from the Ashcroft pseudopotential and Vashishta-Singwi screening function compare with the Glyde and Taylor potential as used by Crow *et al.* can be seen from Fig. 3. In this figure the quasiharmonic,

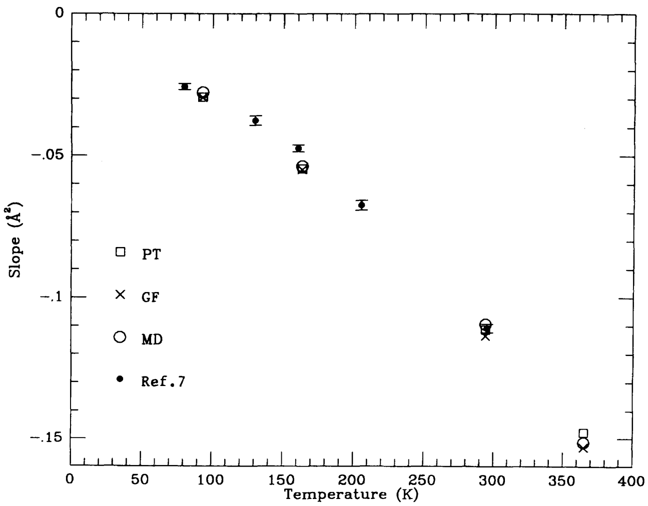

FIG. 1. Slope of the Debye-Waller factor in Na vs temperature. Squares are the λ^2 PT results, crosses are the Green's-function (GF) results, and open circles and dots represent the MD results and experimental points, respectively.

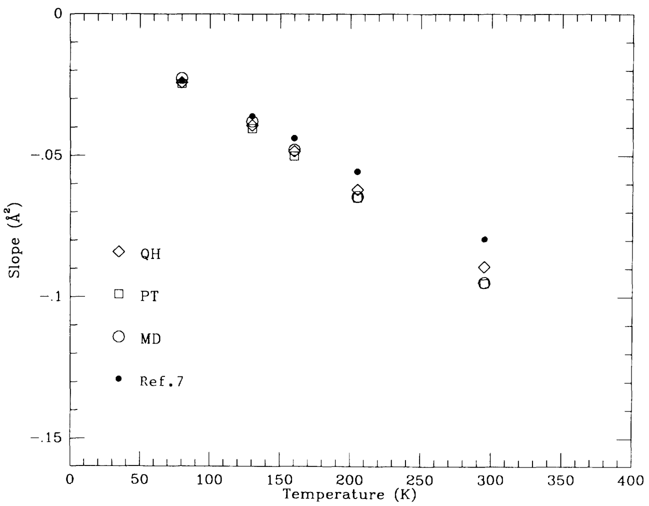

FIG. 3. Slope of the Debye-Waller factor in Na vs temperature for the fixed volume (5 K). Open diamonds, squares, and circles represent the quasiharmonic (qh), perturbation theory (PT), and molecular-dynamics (MD) results, respectively, and dots represent the 5-K qh calculation of Crow *et al.*

quasiharmonic plus the lowest-order (λ^2) anharmonic contributions, and the MD results, all for the 5-K volume, are compared with the quasiharmonic values as given in Table I of Crow *et al.* The MD values were interpolated from the results of Ref. 2 using a spline method, and the cubic anharmonic contribution was calculated from the best-converged sum given in Table II of Ref. 2. It can be seen that the quasiharmonic results by Crow *et al.* differ from our quasiharmonic result at high temperature. It is not clear how meaningful a comparison of theoretical values at 5 K with experiment is, because the experimental data is *not* reduced to the 5-K volume.

Finally, two points should be noted: (i) We have not allowed any polarization mixing j and j' in Eqs. (3) and (4). The Green's function is exactly diagonal in the harmonic approximation, and when the anharmonic terms of $O(\lambda^2)$ are included, the corrections arising from the mixing of j and j' terms to the MSD are insignificant. This is based on the unpublished results by one of the authors for the MSD calculated in the nondiagonal approximation for a Lennard-Jones potential.[14] (ii) We use the Ashcroft pseudopotential and the Vashishta-Singwi screening function to compare our various theoretically calculated values of the DWF with the experimental data of Crow *et al.* because this potential has been used extensively before in the harmonic and anharmonic calculations of alkali metals.[1-3]

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