Calculation of Debye-Waller temperature factors for GaAs

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1 Motivation and Introduction

- Accurate simulations required for quantitative HR(S)TEM
- Simulations based on Fourier-components of Coulomb potential

$$V^{hkl} \propto \sum_{\mu} D_{\mu}^{hkl}(T) f_{\mu}^{hkl} \exp[2\pi i \vec{k}^{hkl} \vec{r}_{\mu}]$$

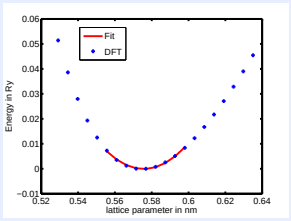
- f_{μ}^{hkl}: atomic scattering amplitudes (ASAs) of atom μ
- $D_{\mu}^{hkl}(T) = \exp(-k_i B_{\mu;ij} k_j)$: temperature dependent factor containing the Debye-Waller-factor $B_{\mu;ij}$

- f_{μ}^{hkl} influenced by redistribution of charge due to bonds
  ⇒ Accounting for redistribution using modified ASAs [1]
- $B_{\mu;ij}(T) = 2\pi^2 u_{\mu;ij}(T)$
  with $u_{\mu;ij}$: static correlation function of the displacement (SCFD)
- $u_{\mu;ij}(T)$ not accurately known for many materials and not for all temperatures

2 Computation of phonon frequencies

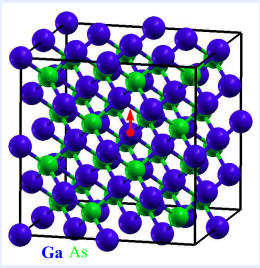
- Using method of Parlinski et al. [2]

1. Computation of lattice parameter within density functional theory DFT
   - DFT computations carried out using the WIEN2k code [3]
   - Computation of total energy as function of lattice parameter



   - Fitting the total energy in vicinity of the minimum energy by a parabola
     ⇒ Equilibrium lattice parameter
     ⇒ Structure without residual forces

2. Calculation of Hellmann-Feynman forces using DFT
   - Generation of Supercells (e.g. 2x2x2)
   - Displacement $\vec{U}$ of one non-equivalent atoms for each cell



   - Computation of Hellmann-Feynman forces acting on each atom due to the displacement

3. Deriving force-constant matrices
   - Forces $F_i(n,\mu)$ and force-constant matrices $\Phi(n,\mu,m,\nu)$ connected by Hooke's law

     $F_i(n,\mu) = -\sum_{m,\nu,j} \Phi(n,\mu,m,\nu) U_j(m,\nu)$
     μ,ν atom indices
     m,n primitive cell indices
   - Inversion of Hook's law
     ⇒ Force-constant matrices

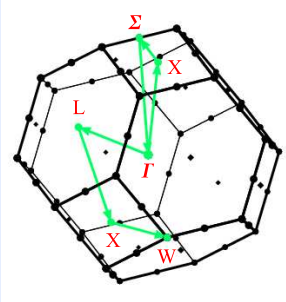
4. Deriving dynamical matrices and phonon frequencies
   - Fourier transform of force-constant matrices
     ⇒ Dynamical matrix $D(\vec{k};\mu,\nu)$

     $D(\vec{k},\mu,\nu) = \frac{1}{M_\mu M_\nu} \sum_l \Phi(0,\mu,l,\nu) \exp\left(-2\pi i \vec{k}\left[\vec{R}(0,\mu) - \vec{R}(m,\nu)\right]\right)$
     $\vec{R}(m,\nu)$: position of atom ν
     M_ν: position of atom ν
     $\vec{k}$: wave vector of the phonon
   - Diagonalization

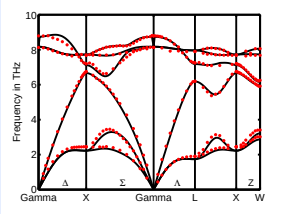
     $\omega^2(\vec{k},j)\vec{e}(\vec{k},j) = D(k)\vec{e}(\vec{k},j)$
     $\omega(\vec{k},j)$: phonon frequency for $\vec{k}$ and phonon branch j

3 Derivation of T-dependence of the SCFD

1. Phonon dispersion relation
   - Here e.g. for GaAs: Forces from a 2x2x2 supercell using local density approximation (LDA) as exchange and correlation potential
   - Calculation of phonon frequencies according to section 2 along directions in Brillouin zone

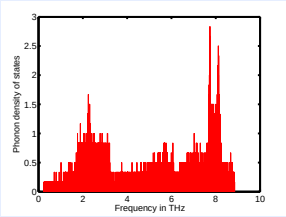


   - Resulting phonon dispersion curve (black lines)



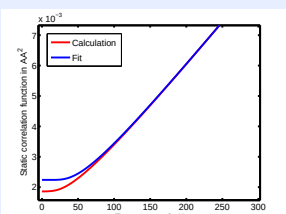
   - Compared with experimental phonon frequencies (red points) from Ref. [4]

2. Phonon density of states
   - Calculation of phonon frequencies belonging to about 10^6 wave-vectors
   - Histogram of number of phonons within a certain frequency interval
     ⇒ Phonon density of states



3. Calculation of the SCFD
   - SCFD in harmonic approximation given by

     $u_{\mu;ij} = \frac{\hbar r}{2M_\mu} \int_0^\infty d\omega g(\omega) \frac{1}{\omega} \coth(\frac{\hbar\omega}{2k_B T})$
     $g(\omega)$ phonon density of states
     r number of degrees of freedom
   - $u_{\mu;ij}$=u_μ becoming a scalar for sphalerite type materials
   - u_{Ga} as function of temperature (red line)



   - (Blue line): fit with the Einstein model
     → Good fit at high T
     → Slight deviations at low T

4 Fitting procedure

1. The mean value theorem
   - For two functions $f(t)$ and $g(t)$ continuous on $[a;b]$ and $g(t) \geq 0$:

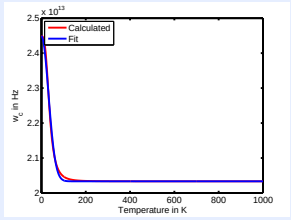
     $\int_a^b f(t)g(t)dt = f(c)\int_a^b g(t)dt$
   - c being an intermediate value in $[a;b]$

2. Application of the mean value theorem

$$u_{\mu;ij} = \frac{\hbar r}{2M_\mu} \int_0^\infty d\omega \underbrace{g(\omega)}_{g(t)} \underbrace{\frac{1}{\omega}\coth(\frac{\hbar\omega}{2k_B T})}_{f(t)}$$

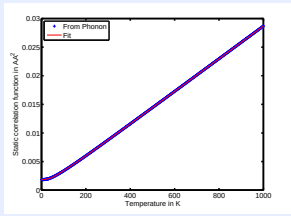
$$u_{\mu;ij} = \frac{\hbar}{2M_\mu \omega_{c;\mu}(T)} \coth(\frac{\hbar\omega_{c;\mu}(T)}{2k_B T}) \quad (*)$$

   - Weakly T-dependent characteristic frequency
   - $\omega_{c;\mathrm{Ga}}(T)$ (red curve)



   - Fit of $\omega_{c;\mu}(T)$ by a gaussian (blue curve)
     $A\exp(-T^2/\sigma^2) + \omega_0$ ⇒ only σ as fit parameter
     A and ω_0 known from the analytic expressions of $\omega_{c;\mu}(0)$ and $\omega_{c;\mu}(\infty)$

   - Inserted into Eq. (*)
     ⇒ Fitted T-dependence of the SCFD



   - Maximum deviation between fit and calculated data lower than 1%
   - Fit parameters given in the paper

6 Discussion and Conclusion

- Phonon dispersion relation computed on basis of DFT
- Good agreement of experimental and computed phonon frequencies
- Experimental SCFD at T=287K [5] in 10^{-2}Å^2:

	Experiment [5]	here	Theory[6]
u_{Ga}	0.844	0.8447 ± 0.0018	0.7840
u_{As}	0.716	0.7257 ± 0.0020	0.8440

- Values of this work in better agreement with experiment than values of Ref. [6]

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