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VIBRATIONS OF SUBSTITUTIONAL IMPURITIES IN SEMICONDUCTORS

O.H. Nielsen

Institute of Physics, University of Aarhus, DK-8000 Århus C, Denmark

Abstract - The Green's function technique has been studied in detail, permitting numerical calculations of mean-square amplitudes in perfect and impure lattices. The $^{119}$Sn substitutional atom is distinguished by being an isovalent impurity in Si, Ge and $\alpha$-Sn, and by being an amphoteric dopant in the III-V semiconductors. Several impurity models are employed for quantitative interpretation of Mössbauer Debye-Waller factors from a systematic study by Weyer et al.

1. Green's functions. - The well known Green's function technique for vibrational correlation functions (mean-square amplitudes) can be amended with a few expressions facilitating actual calculations. The Green's function eqs. (2.4.44), (8.5.5) of Ref. 1 can be written for real $\omega$ as

$$G_{\alpha\beta}(l_k, l'_{k'}; \omega \pm i\delta) = \frac{1}{M_{l_k} M_{l'_{k'}}} \left[ \int \frac{g_{\alpha\beta}(l_k, l'_{k'}; \omega)}{\omega^2 - \omega^2} \, d\omega + \frac{i\pi}{2\omega} g_{\alpha\beta}(l_k, l'_{k'}; \omega) \right]$$

where $g_{\alpha\beta}(l_k, l'_{k'}; \omega)$ is a generalized density of states (DOS) function which for the perfect lattice is calculated as a Brillouin-zone sum. $P\int$ denotes a principal value integral which may be evaluated numerically as in Ref. 2. The impurity Green's function $U$ is found by solving eq. (8.5.2) of Ref. 1

$$\left[ \Gamma - U \cdot (\Delta_p + 2M \cdot \omega^2) \right] U = \tilde{U},$$

which for practical purposes may be separated into two coupled equations for the real and imaginary parts using eq. (1), see eq. (9) of Ref. 2. Correlation functions are easy to obtain when the DOS functions have been calculated, since the fluctuation-dissipation theorem yields with eq. (1)

$$\langle u_\alpha(l_k)u_\beta(l'_{k'}) \rangle = \frac{\hbar}{2M_{l_k} M_{l'_{k'}}} \int_0^{\infty} \frac{1}{\omega} g_{\alpha\beta}(l_k, l'_{k'}; \omega) \cdot \coth(\frac{1}{2}k_B T) \, d\omega$$

In particular, the mean-square vibrational amplitude of a lattice atom or an impurity is given by eq. (3) using the $g_{\alpha\beta}(l_k, l_k; \omega)$ matrix element of the DOS function. For comparison with experimental data it is often convenient to expand the coth-factor to obtain an expression for $\langle u_\alpha^2(l_k) \rangle$ at high temperatures ($k_B T > \hbar \omega_{\text{max}} / 2\pi$) in terms of weighted moments of the DOS. The moments can be recast in terms of Debye temperatures rigorously defined by

$$\Theta_D(n) = \frac{\hbar}{k_B} \left[ \frac{N+3}{3} \int_0^{\infty} \omega^N g_{\alpha\beta}(l_k, l_k; \omega) \, d\omega \right]^{\frac{1}{N}}; \quad N \geq 3.$$
The indices \((\alpha, \kappa)\) are understood for \(\Theta_D(N)\) (which can vary significantly with \(N\)). The expansion of eq. (3) becomes

\[
\langle u_{\alpha}(\kappa) \rangle^2 = \frac{3k_B T}{M_{\alpha\kappa}} \left[ \frac{M_{\alpha\kappa}}{k_B \Theta_D(-2)} \right]^2 \left[ 1 + \left( \frac{\Theta_D(-2)}{6T} \right)^2 - \left( \frac{\Theta_D(-2)}{60T^2} \right)^2 + \ldots \right]
\]

(5)

The terms indicated usually give accurate values when \(T \approx \frac{1}{6} \Theta_D(-2)\). Fitting high-temperature \(\langle u_{\alpha}(\kappa) \rangle^2\) data will thus determine a \(\Theta_D(-2)\) value. An interesting observation is that by eq. (1) the \(N = -2\) moment of the DOS is simply given by \(-M_{\alpha\kappa} \Phi_{\alpha\kappa}(\kappa, \kappa; \omega = 0)\). Applying this to a substitutional impurity yields by eq. (2) the relation

\[
\Theta_D'(-2) = \Theta_D(-2) \cdot \sqrt{\frac{M_{\alpha\kappa}}{M_{\alpha \kappa}^{\prime}}} \cdot F(G; \Delta \Phi),
\]

(6)

where a prime refers to the impurity. The function \(F\) is found by solving eq. (2) at \(\omega = 0\). A mass defect with \(\Delta \Phi = 0\) has \(F = 1\). A model for impurity mean-square amplitudes at high temperatures would aim at calculating \(F\) for various \(\Delta \Phi\).

2. Interpretation of Mössbauer data.- The \(^{119}\)Sn substitutional impurity in both group \(V\) and group \(III-V\) semiconductors has been investigated by Mössbauer spectroscopy, determining the temperature variation of the Debye-Waller factor. For Si, Ge and \(\alpha\)-Sn, Weber's adiabatic bond-charge model was applied for the perfect lattice phonons to yield the \(\Theta_D(N)\). A hierarchy of impurity vibration models have been considered: (1) The mass defect model (see above) proved insufficient for Si, Ge, but of course good in \(\alpha\)-Sn. (2) The simple and analytical Mannheim model quantified the \(\Theta_D(-2)\) in terms of force constant weakenings. However, this model assumes n.n. central forces making the diamond structure unstable. Furthermore, the force constant changes, necessary within this model, were rather large, and better models seem warranted for the semiconductors. (3) A model using the bond charge model concepts was constructed, neglecting any changes in the long-range Coulomb forces. Changing simultaneously all impurity potentials to fit \(\Theta_D'(-2)\), resulted in force constant changes of -26% (Si) and -27% (Ge). For GaP, GaAs, GaSb, InP, InAs, and InSb a number of phonon models were compared with neutron diffraction determinations of \(\langle u_{\alpha}(\kappa) \rangle^2\), rendering the rigid ion and deformation dipole models insufficient. Some of the shell models gave reasonable results. Site-selective implantation of \(^{119}\)Sn yielded a complete set of \(\Theta_D'(-2)\) values which were analyzed using eq. (6) to determine the values of \(F\). The III- and V-impurity sites were clearly distinguishable in terms of \(F\), and showed an unexpected qualitative difference between \(^{119}\)Sn being in a Ga- or an In-compound.

References.