ANHARMONIC CONTRIBUTIONS TO SPECIFIC HEAT AND THERMAL EXPANSION OF CRYSTALS

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A study is made of the anharmonic terms with a quadratic temperature dependence which appear in the specific heat and thermal expansion of crystals at high temperatures.

In studying thermophysical properties of solids such as the specific heat and the temperature coefficient of linear expansion (TCLE), it is necessary to take into account anharmonic terms in the free energy. This problem was first considered in [1, 2] and also in [3], where a similar calculation was made for the terms $\overline{\Phi_3^2}$ and $\overline{\Phi}_4$ leading to a linear temperature dependence of the specific heat. At temperatures comparable with the melting point ($T \geq {}^2/_3 T_{melt}$), it is necessary to take into account anharmonic terms of higher order.

The present work considers contributions to the specific heat and TCLE that depend quadratically on the temperature.

The Hamiltonian of a system of anharmonic oscillators is written in the form

$$H = H_0 + gW,\ W = \Phi_3 + \Phi_4 + \Phi_5 + \Phi_6. \tag{1}$$

The statistical sum for the crystal is

$$Z = \sum_\alpha [\Psi_\alpha, \exp(-\beta H_0 - \beta g W)\Psi_\alpha]. \tag{2}$$

The method used for the expansion of Z in terms of perturbations is that proposed in [4, 5]. Since W is proportional to the number of particles N, it is expedient to expand ln Z in powers of W, where

$$\ln Z(g) = \ln Z(0) + \sum_{k=1}^{\infty} \frac{1}{k!}\frac{\partial^k}{\partial g^k}(\ln Z)|_0 g^k. \tag{3}$$

The calculation is in accordance with perturbation theory. In the first order the terms $\overline{\Phi}_4$ and $\overline{\Phi}_6$ give a nonzero contribution to the free energy; in the second order, $\overline{\Phi_3^2}$ and $\overline{\Phi_4^2}$ are the significant terms; in the third order, $\overline{\Phi_3^2 \cdot \Phi_4}$; and in the fourth order, $(\overline{\Phi_3^2})^2$ and $\overline{\Phi_3^4}$. According to [6], the contribution due to $\overline{\Phi}_4$ is

$$F(\overline{\Phi}_4) = \overline{\Phi}_4 = \frac{1}{8NS}\sum_{\substack{kk' \\ \lambda\lambda'}} \frac{\Phi^{kk'}_{\lambda\lambda'}}{\omega^2\omega'^2}\varepsilon(\omega, T)\varepsilon(\omega', T), \tag{4}$$

where

$$\varepsilon(\omega, T) = h'\omega\left(\bar{n} + \frac{1}{2}\right);\ \bar{n} = \frac{1}{\exp(h'\omega/kT) - 1}.$$

The quasiharmonic mean $\overline{\Phi}_6$ is also easily calculated, although the computations are slightly more cumbersome. For Φ_6, by definition

$$\Phi_6 = \frac{1}{6!}\cdot\frac{1}{(SN)^2}\sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''\mathbf{k}^{IV}\mathbf{k}^{V} \\ \lambda\lambda'\lambda''\lambda'''\lambda^{IV}\lambda^{V}}} \Phi^{\mathbf{k}\ldots\mathbf{k}^V}_{\lambda\ldots\lambda^V} C_{\mathbf{k}}\ldots C_{\mathbf{k}^V}(b^{\mathbf{k}}_\lambda - b^{+-\mathbf{k}}_\lambda)\times\ldots\times(b^{\mathbf{k}^V}_{\lambda^V} - b^{+-\mathbf{k}^V}_{\lambda^V}),\ C_{\mathbf{k}} = \sqrt{h'/2\omega(\mathbf{k})}. \tag{5}$$

The creation and annihilation operators conform to the permutation rule

$$[b^{\mathbf{k}}_\lambda, b^{+-\mathbf{k}'}_{\lambda'}]_- = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\lambda\lambda'},\ [b^{\mathbf{k}}_\lambda, b^{\mathbf{k}'}_{\lambda'}]_- = [b^{+\mathbf{k}}_\lambda, b^{+\mathbf{k}'}_{\lambda'}]_- = 0. \tag{6}$$

Nonzero contributions to the mean $\overline{\Phi}_6$ are made by terms with an equal number of creation and annihilation operators. Hence it is necessary to consider the triad-equality conditions for the six indices **k**, **k'**, **k"**, **k'''**, $\mathbf{k}^{IV}$ and $\mathbf{k}^V$.

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If all the creation operators in Eq. (5) are written in front of the annihilation operators, the result, taking into account Eq. (6), is 15 triad-equality conditions for the indices ($\mathbf{k}=-\mathbf{k}'''$, $\mathbf{k}'=-\mathbf{k}^{IV}$, $\mathbf{k}''=-\mathbf{k}^{V}$, etc.)

The contributions are of the form

$$(\bar{n}+1)(\bar{n}'+1)(\bar{n}''+1);\ \bar{n}\bar{n}'\bar{n}'';\ (\bar{n}+1)\bar{n}'\bar{n}'';\ \bar{n}(\bar{n}'+1)(\bar{n}''+1);$$
$$\bar{n}(\bar{n}'+1)\bar{n}'';\ (n+1)\bar{n}'(\bar{n}''+1);\ \bar{n}\bar{n}'(\bar{n}''+1);\ (\bar{n}+1)(\bar{n}'+1)\bar{n}''.$$

Summing the contributions (taking into account the triad permutations of the indices) gives

$$15(2\bar{n}+1)(2\bar{n}'+1)(2\bar{n}''+1).$$

The final result is of the form

$$F(\bar{\Phi}_6)=\bar{\Phi}_6=-\frac{1}{48}\cdot\frac{1}{(SN)^2}\sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{k}''\\ \lambda\lambda'\lambda''}}\frac{\Phi^{6\mathbf{k}\mathbf{k}'\mathbf{k}''}_{\lambda\lambda'\lambda''}}{\omega^2\omega'^2\omega''^2}\varepsilon\varepsilon'\varepsilon''. \tag{7}$$

Now consider second-order perturbation theory. For $\overline{\Phi_3^2}$ [6]

$$F(\overline{\Phi_3^2})=-\frac{1}{48SN}\sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{k}''\\ \lambda\lambda'\lambda''}}\frac{|\Phi^{\mathbf{k}\mathbf{k}'\mathbf{k}''}_{\lambda\lambda'\lambda''}|^2}{(\omega\omega'\omega'')^2}\left[\frac{3\varepsilon_0\varepsilon'\varepsilon''+\varepsilon_0\varepsilon_0'\varepsilon_0''}{\varepsilon_0+\varepsilon_0'+\varepsilon_0''}+3\frac{2\varepsilon_0\varepsilon'\varepsilon''-\varepsilon\varepsilon'\varepsilon_0''-\varepsilon_0\varepsilon_0'\varepsilon_0''}{\varepsilon_0+\varepsilon_0'-\varepsilon_0''}\right], \tag{8}$$

where $\varepsilon=\varepsilon(\omega, T)$; $\varepsilon'=\varepsilon(\omega', T)$; $\varepsilon''=\varepsilon(\omega'', T)$; $\varepsilon_0=h'\omega/2$; $\varepsilon_0'=h'\omega'/2$; $\varepsilon_0''=h'\omega''/2$.

Using Eqs. (3) and (4) it is possible to obtain the result

$$F[(\bar{\Phi}_4)^2]=\frac{1}{2kT}\cdot\frac{1}{64(SN)^2}\left[\sum_{\substack{\mathbf{k}\mathbf{k}'\\ \lambda\lambda'}}\frac{\Phi^{4\mathbf{k}\mathbf{k}'}_{\lambda\lambda'}}{\omega^2\omega'^2}\varepsilon\varepsilon'\right]^2. \tag{9}$$

On the basis of Eqs. (2) and (3) the contribution due to $\overline{\Phi_4^2}$ may be written in the form

$$F(\overline{\Phi_4^2})=-\frac{1}{\beta Z(0)}\sum_{nm}|\Phi_{4nm}|^2\times \tag{10}$$
$$\times\frac{\exp[\beta(E_n-E_m)]-1-\beta(E_n-E_m)}{(E_n-E_m)^2}\exp(-\beta E_n),$$

where

$$\Phi_4=\sum_{\alpha\beta\gamma\delta}\varphi_{\alpha\beta\gamma\delta}\{B_{\alpha\beta\gamma\delta}+B^{+}_{-\alpha,-\beta,-\gamma,-\delta}+3\delta_{\alpha,-\beta}\delta_{\gamma,-\delta}\}; \tag{11}$$

$$\varphi_{\alpha\beta\gamma\delta}\equiv\frac{h'^2\Phi_{\alpha\beta\gamma\delta}}{96SN\sqrt{\omega_\alpha\omega_\beta\omega_\gamma\omega_\delta}};$$

$$B_{\alpha\beta\gamma\delta}\equiv b_\alpha b_\beta b_\gamma b_\delta-4b^{+}_{-\alpha}b_\beta b_\gamma b_\delta+3b^{+}_{-\alpha}b^{+}_{-\beta}b_\gamma b_\delta+$$
$$+6b^{+}_{-\alpha}b_\beta\delta_{\gamma,-\delta}-6b^{+}_{-\alpha}b^{+}_{-\beta}\delta_{\gamma,-\delta};$$

$$\alpha\equiv\begin{pmatrix}\mathbf{k}\\ \lambda\end{pmatrix};\quad \beta\equiv\begin{pmatrix}\mathbf{k}'\\ \lambda'\end{pmatrix};\quad \gamma\equiv\begin{pmatrix}\mathbf{k}''\\ \lambda''\end{pmatrix};\quad \delta\equiv\begin{pmatrix}\mathbf{k}'''\\ \lambda'''\end{pmatrix}.$$

Then, from Eqs. (10) and (11)

$$F(\overline{\Phi_4^2})=-\frac{1}{384}\cdot\frac{1}{(SN)^2}\sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''\\ \lambda\lambda'\lambda''\lambda'''}}\frac{|\Phi^{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}_{\lambda\lambda'\lambda''\lambda'''}|^2}{(\omega\omega'\omega''\omega''')^2}\times \tag{12}$$
$$\times\left[\frac{4\varepsilon_0\varepsilon'\varepsilon''\varepsilon'''+4\varepsilon\varepsilon_0'\varepsilon_0''\varepsilon_0'''}{\varepsilon_0+\varepsilon_0'+\varepsilon_0''+\varepsilon_0'''}+4\left(\frac{-3\varepsilon_0\varepsilon_0'\varepsilon_0''\varepsilon_0'''+3\varepsilon_0'''\varepsilon\varepsilon'\varepsilon''}{\varepsilon_0'+\varepsilon_0''+\varepsilon_0'''-\varepsilon_0}+\right.\right.$$
$$\left.+\frac{\varepsilon\varepsilon_0'\varepsilon_0''\varepsilon_0'''-\varepsilon_0\varepsilon'\varepsilon''\varepsilon'''}{\varepsilon_0'+\varepsilon_0''+\varepsilon_0'''-\varepsilon_0}\right)+3\left(\frac{2\varepsilon_0'''\varepsilon\varepsilon'\varepsilon''-2\varepsilon_0\varepsilon'\varepsilon''\varepsilon'''}{\varepsilon_0''+\varepsilon_0'''-\varepsilon_0-\varepsilon_0'}+\right.$$
$$\left.\left.+\frac{2\varepsilon_0\varepsilon_0'\varepsilon_0''\varepsilon'''-2\varepsilon\varepsilon_0'\varepsilon_0''\varepsilon_0'''}{\varepsilon_0''+\varepsilon_0'''-\varepsilon_0-\varepsilon_0'}\right)\right]-\frac{h'^2}{128(SN)^2}\sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{k}''\\ \lambda\lambda'\lambda''}}\frac{|\Phi^{\mathbf{k}\mathbf{k}'\mathbf{k}''-\mathbf{k}''}_{\lambda\lambda'\lambda''\lambda''}|^2}{(\omega\omega'\omega'')^2}\times$$
$$\times\left[\frac{2\varepsilon\varepsilon_0'}{\varepsilon_0+\varepsilon_0'}+\frac{\varepsilon'\varepsilon_0-\varepsilon\varepsilon_0'}{\varepsilon_0-\varepsilon_0'}\right].$$

In the third order, Eqs. (4) and (8) give

$$F(\overline{\Phi_3^2}\overline{\Phi_4}) = \frac{1}{kT}\cdot\frac{1}{384(SN)^2}\sum_{\substack{\mathbf{kk'}\\ \lambda\lambda'}}\frac{\Phi^{4\mathbf{kk'}}_{\lambda\lambda'}}{\omega^2\omega'^2}\varepsilon\varepsilon'\sum_{\substack{\mathbf{kk'k''}\\ \lambda\lambda'\lambda''}}\frac{|\Phi^{\mathbf{kk'k''}}_{\lambda\lambda'\lambda''}|^2}{\omega^2\omega'^2\omega''^2}\times$$

$$\times\left[\frac{3\varepsilon_0\varepsilon'\varepsilon''+\varepsilon_0\varepsilon_0'\varepsilon_0''}{\varepsilon_0+\varepsilon_0'+\varepsilon_0''}+3\,\frac{2\varepsilon_0\varepsilon'\varepsilon''-\varepsilon\varepsilon'\varepsilon_0''-\varepsilon_0\varepsilon_0'\varepsilon_0''}{\varepsilon_0+\varepsilon_0'-\varepsilon_0''}\right]. \tag{13}$$

The fourth-order contributions are

$$F[(\overline{\Phi_3^2})^2] = \frac{1}{2kT}[F(\overline{\Phi_3^2})]^2, \tag{14}$$

$$F(\overline{\Phi_3^4}) = -\frac{1}{48(SN)^2}\sum_{\substack{\mathbf{kk'k''}\\ \lambda\lambda'\lambda''}}\frac{|\Phi^{\mathbf{kk'k''}}_{\lambda\lambda'\lambda''}|^4}{\omega^4\omega'^4\omega''^4}\left\{\frac{1}{16(\varepsilon_0+\varepsilon_0'+\varepsilon_0'')^4}\times\right. \tag{15}$$

$$\times[(\varepsilon_0+\varepsilon_0'+\varepsilon_0''+kT)(\varepsilon+\varepsilon_0)^2(\varepsilon'+\varepsilon_0')^2(\varepsilon''+\varepsilon_0'')^2-$$

$$-(\varepsilon_0+\varepsilon_0'+\varepsilon_0''-kT)(\varepsilon-\varepsilon_0)^2(\varepsilon'-\varepsilon_0')^2(\varepsilon''-\varepsilon_0'')^2]+$$

$$+\frac{3}{16(\varepsilon_0-\varepsilon_0'-\varepsilon_0'')^4}[(\varepsilon_0-\varepsilon_0'-\varepsilon_0''+kT)(\varepsilon+\varepsilon_0)^2(\varepsilon'-\varepsilon_0')^2\times$$

$$\left.\times(\varepsilon''-\varepsilon_0'')^2-(\varepsilon_0-\varepsilon_0'-\varepsilon_0''-kT)(\varepsilon-\varepsilon_0)^2(\varepsilon'+\varepsilon_0')^2(\varepsilon''+\varepsilon_0'')^2]+\dots\right\}.$$

The free energy can be written in the form

$$F = -\frac{1}{\beta}\ln Z \equiv -kT\ln Z = F_{\text{harm}} + F(\overline{\Phi}_4) +$$

$$+F(\overline{\Phi_3^2}) + F(\overline{\Phi}_6) + F(\overline{\Phi_4^2}) + \dots + F(\overline{\Phi_3^4}). \tag{16}$$

The third and fourth terms in Eq. (16) are linear functions of temperature (at high temperature) and the subsequent terms give quadratic contributions to the specific heat and TCLE. The terms $F(\overline{\Phi}_6)$ and $F(\overline{\Phi_4^2})$ make the main contributions. In the limiting case of high temperatures ($\varepsilon = kT$), the quadratic contribution to the specific heat is

$$C_v^{(2)} = -T\frac{\partial^2 F}{\partial T^2} = \frac{k^3T^2}{(SN)^2}\left\{\frac{1}{8}\sum_{\substack{\mathbf{kk'k''}\\ \lambda\lambda'\lambda''}}\frac{\Phi^{6\mathbf{kk'k''}}_{\lambda\lambda'\lambda''}}{\omega^2\omega'^2\omega''^2}+\frac{1}{8}\sum_{\substack{\mathbf{kk'k''k'''}\\ \lambda\lambda'\lambda''\lambda'''}}\frac{|\Phi^{\mathbf{kk'k''k'''}}_{\lambda\lambda'\lambda''\lambda'''}|^2}{(\omega\omega'\omega''\omega''')^2}\right\}. \tag{17}$$

The relational parameters are [7]

$$\Phi^{\mathbf{kk'k''k'''}}_{\lambda\lambda'\lambda''\lambda'''} = \frac{1}{SN}\sum_{\substack{mnpr\\ \mu\nu\varkappa\sigma\\ ijkl}}\frac{\Phi^{\substack{mnpr\\ \mu\nu\varkappa\sigma}}_{ijkl}}{\sqrt{M_\mu M_\nu M_\varkappa M_\sigma}}\cdot e_i^\mu(\mathbf{k},\ \lambda)\cdot e_j^\nu(\mathbf{k}',\ \lambda')\times$$

$$\times e_k^\varkappa(\mathbf{k}'',\ \lambda'')\cdot e_l^\sigma(\mathbf{k}''',\ \lambda''')\cdot\exp\{i(\mathbf{k}\cdot R_\mu^m+\mathbf{k}'\cdot R_\nu^n+\mathbf{k}''\cdot R_\varkappa^p+\mathbf{k}'''\cdot R_\sigma^r)\};$$

$$\Phi^{6\mathbf{kk'k''}}_{\lambda\lambda'\lambda''} \equiv \Phi^{\mathbf{k-kk'-k'k''-k''}}_{\lambda\lambda\lambda'\lambda'\lambda''\lambda''}. \tag{18}$$

The sum over the wave vectors may be calculated approximately using a particular model of the forces acting in the crystal (central forces, for example, or nearest-neighbor interactions).

To estimate the order of magnitude of the results, consider a linear chain with nearest-neighbor interactions. The atomic-interaction function chosen is the Lennard-Jones potential

$$\varphi = -A/r^6 + B/r^{12}. \tag{19}$$

Then Eq. (17) takes the form

$$C_v^{(2)} = k^3T^2N\left\{\frac{q}{8f^3}+\frac{h^2}{8f^4}\right\}. \tag{20}$$

The relational parameters are calculated at the equilibrium position

$$f=\varphi_r^{\text{II}};\ g'=\varphi_r^{\text{III}};\ h=\varphi_r^{\text{IV}};\ p=\varphi_r^{\text{V}};\ q=\varphi_r^{\text{VI}};\ r'=\varphi_r^{\text{VII}}.$$

The sign of Eq. (20) depends on the properties of the forces acting in the crystal. Calculation gives

$$C_v^{(2)}/C_v^{\text{harm}} \cong \frac{5.5k^2T^2}{D^2}. \tag{21}$$

Similar calculations may be made for the TCLE. The corresponding contribution is proportional to $-l\partial^2F/\partial l\partial T$, which leads to the expression

$$\alpha^{(2)}/\alpha^{\text{harm}} = -3k^2T^2\left[\frac{-q}{8f^3} + \frac{r'}{24g'f^2} + \frac{hp}{12g'f^3} - \frac{h^2}{6f^4}\right]. \tag{22}$$

Substituting relational parameters calculated from Eq. (19) into Eq. (22) gives

$$\alpha^{(2)}/\alpha^{\text{harm}} \cong \frac{14k^2T^2}{D^2}. \tag{23}$$

The correction obtained evidently depends quadratically on temperature. Setting $D = (2\text{–}4)\cdot 10^5$ ∂J/mole, which corresponds to existing crystal-lattice energies, Eqs. (21) and (23) for T = 1000°K give the results

$$C_v^{(2)}/C_v^{\text{harm}} \approx (1-0.25)\,\%, \quad \alpha^{(2)}/\alpha^{\text{harm}} \approx (3-1)\,\%. \tag{24}$$

The calculations show that at sufficiently high temperatures these quadratic anharmonic contributions may be significant.

NOTATION

F, free energy of crystal; F_{harm}, harmonic part of free energy; H_0, Hamiltonian of system of harmonic oscillators; Ψ_α, eigenfunctions of operator H_0; g, dimensionless parameter; $\Phi^{mnp\ldots}_{\mu\nu\varkappa\ldots\, ijk\ldots}$ n-th derivative of potential energy with respect to displacement; Φ_3, Φ_4, etc., anharmonic parts of potential energy in expansion in powers of the displacement; ε, mean phonon energy; ω, phonon frequency; $\bar{n}$, mean number of phonons in the given state; $b^{\mathbf{k}}_\lambda$, $b^{+\mathbf{k}}$, annihilation and creation operators for phonon (**k**, λ); $\Phi_{4nm} \equiv \langle n|\Phi|m\rangle$, matrix elements of Φ_4 with functions Ψ_α; h', Planck's constant; T, absolute temperature; k, Boltzmann's constant; S, number of atoms in unit cell; N, number of cells in crystal; k, phonon wave vector; λ, index characterizing the number of vibrational branches (acoustic or optical) in the polarization direction; $e^\mu_i(\mathbf{k}, \lambda)$, i-th component of polarization vector e of μ-th branch; $\delta_{\mathbf{kk}'}$, $\delta_{\lambda\lambda'}$, etc., Kronecker deltas; R^m_μ, radius-vector characterizing the position of the μ-th atom in the m-th cell of the crystal; M_μ, M_ν, etc., atomic masses; φ^{I}_r, φ^{II}_r, etc., first, second, and subsequent derivatives of φ with respect to the distance r; φ, atomic-interaction function; A, B, coefficients characterizing attraction and repulsion; C_v, specific heat; C_v^{harm}, harmonic specific heat; α, TCLE; α^{harm}, quasiharmonic approximation to TCLE; l, interatomic distance in linear chain; D, sublimation energy per atom.

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