International Journal of Theoretical Physics, Vol. 32, No. 5, 1993

Thermodynamics of Impure Anharmonic Crystals

Ram Singh,[1] B. D. Indu,[2] R. P. Gairola,[2] and M. N. Sharma[3]

Received March 30, 1992

The vibrational thermodynamic properties of doped anharmonic solids are investigated using thermodynamic Green's functions. The study uses cubic and quartic anharmonic interactions, and different masses and force constants for the impurity and host lattice atoms. The explicit expressions so derived for the partition function, free energy, entropy, and lattice heat capacity for these solids in the low-impurity-concentration limit are discussed for various situations. Our results are modified due to the presence of interaction terms between the anharmonic and localized fields and reduce to those obtained by earlier workers as limiting cases.

1. INTRODUCTION

The thermodynamic properties of anharmonic crystals have been discussed by various workers (Maradudin *et al.*, 1961; Born and Huang, 1954; Shukla and Müller, 1970, 1971; Pathak, 1965; Shukla, 1966, 1980; Shukla and Wilk, 1974; Cowley and Shukla, 1974; Shukla and Taylor, 1974; Klein and Koehler, 1977; Barron, 1963; Pathak and Varshni, 1969; Leibfried and Ludwig, 1961). These authors have studied the free energy, partition function, and specific heat of anharmonic crystals using different approaches. Maradudin *et al.* (1961; Maradudin and Fein, 1962) have discussed the anharmonic contributions to the thermodynamic properties of solids, starting with the expansion of the partition function, in terms of an anharmonic Hamiltonian. However, frequent use has been made of harmonically approximated expressions in discussing anharmonic solids. Shukla and Müller (1970, 1971; Shukla and Wilk, 1974; Shukla and Taylor, 1974) obtained the Helmholtz free energy by thermal averaging of the interaction

---

[1] Department of Physics, Government P.G. College, Rishikesh, U.P., India.
[2] Crystal Impurity Division, Department of Physics, H.N.B. Garhwal University, Post Box No. 21, Srinagar 246174, Garhwal, U.P., India.
[3] Department of Physics, Lucknow University, Lucknow, U.P., India.

Hamiltonian instead of evaluating it through the partition function. Moreover, the anharmonic terms (F_3 and F_4) in the expansion of the free energy have been replaced by the corresponding thermally averaged terms in the internal energy of system (Shukla and Müller, 1970, 1971). The free energy and the lattice heat capacity (LHC) calculations have been carried out using various forms of the potentials, viz. Morse, Rydberg, and Born–Mayer potentials (Shukla, 1966, 1980). The energy and LHC of anharmonic crystals have also been discussed by Pathak (1965) quantum mechanically, making use of the thermal average of the crystal Hamiltonian. However, the cubic contribution to the energy has been approximated in terms of the quartic contribution, which has been thoroughly dealt with in an approximate way. Leibfried and Ludwig (1961; Maradudin *et al.*, 1961; Maradudin and Fein, 1962; Barron, 1963) have used perturbation techniques to estimate various vibronic thermodynamic properties. Formal expressions for these properties have been obtained by them in a semiclassical approach, using various models.

In all the work cited above, no attempt has been made to account for the vibrational thermodynamic properties of doped anharmonic crystals. It is well known that the introduction of defects in the crystals changes their vibrational spectrum drastically (Elliott, 1966; Maradudin, 1966). Bahadur and Sharma (1974) have, however, studied the LHC of impure harmonic crystals with the aid of double-time thermal Green's functions. So far we have not come across any published work investigating the various thermodynamic properties of doped anharmonic crystals.

In the present work, we investigate the partition function, free energy, and LHC of an isotopically disordered anharmonic crystal using thermodynamic Green's functions. The effects of mass and force constant change terms between the impurity and host lattice atoms are taken into account, and the cubic and quartic anharmonic terms are also retained in the crystal Hamiltonian. The present approach gives us an opportunity to study the effect of interaction terms, if any, between the crystal anharmonic and localized fields in discussing the above vibrational properties of the solids. Since the anharmonic and localized fields are simultaneously present in the same crystal, it is most likely that the phonons of one field may interact with the phonons of the other field, giving rise to the impurity–anharmonicity interaction in the interacting mode (Gairola, 1983, 1984, 1991; Indu, 1990). Our approach is based neither on the Bloch expansion formula (Maradudin *et al.*, 1961; Pathak, 1965) nor on the semiclassical treatment (Barron, 1963; Pathak and Varshni, 1969; Leibfried and Ludwig, 1961), but is fully based on the quantum dynamics of phonons (Indu, 1990). Any change in the physical properties of a crystal due to the introduction of defects will lead to a change in the phonon spectrum, through changes in the density of states

(DOS). Therefore, we explore the vibrational thermodynamic properties by considering the changes in the DOS. The lattice energy is evaluated with the help of the DOS, which depends on the frequency and temperature (Indu, 1990). So the present formulation is a sensitive, accurate, and systematic way to discuss the thermodynamic properties of doped anharmonic solids.

This paper is divided into eight sections. Section 2 deals with the general thermodynamic features arranged sequentially, which are discussed in detail in the forthcoming sections. The Hamiltonian and Green's functions are discussed in Section 3. The anharmonic contributions to the partition function (PF), free energy (FE), entropy, and LHC are evaluated in Sections 4–7. Section 8 is devoted to discussion and conclusions.

2. THERMODYNAMICS OF CRYSTALS

To discuss the physical properties of a solid, which are often the thermal average values, the partition function provides us a convenient starting point. For our system, the partition function is defined as

$$Z = \sum_{n_{kj}} e^{-\beta E} \tag{1}$$

where $\beta = (k_B T)^{-1}$ and E is the average lattice energy, which depends on n_{kj}, the occupation number of the vibrating mode. The energy E of the system has been widely discussed as the thermal average $\langle H \rangle$ of the crystal Hamiltonian by various workers (Shukla and Müller, 1970, 1971; Pathak, 1965). Some authors (Born and Huang, 1954) have constructed E by summing the individual energies of the independent oscillators in a semiclassical approach. Maradudin *et al.* (1961; Maradudin and Fein, 1962) replaced E by H in equation (1) and considered the trace of the rhs in equation (1), using a Bloch expansion. We follow the approach of Indu (1990) to express E by its equivalent density of states (DOS) expression

$$E = \int d\omega \, N(\omega)(n_{kj} + \tfrac{1}{2})\hbar\omega \tag{2}$$

with $N(\omega)$, the DOS, being expressed in the Lehmann representation (Launay, 1956),

$$N(\omega) = -\sum_{k} \operatorname{Im} G_{kk'}(\omega + i\varepsilon) \tag{3}$$

Here $G_{kk'}(\omega)$ is the Fourier-transformed Green's function for the system, to be discussed in Section 3.

The free energy is the usual expression

$$F=-\beta^{-1}\ln Z \tag{4}$$

The entropy S of the system is given by

$$S=-(\partial F/\partial T)=k_B\beta^2\nabla_\beta F \tag{5}$$

where $\nabla_\beta=\partial/\partial\beta$ has been introduced for convenience. The LHC C_v is related to the entropy of the system by the following relation:

$$C_v=T(\partial S/\partial T)_v=-\beta\nabla_\beta S \tag{6}$$

3. FORMULATION

It is evident from equation (3) that the calculation of the DOS is reduced to evaluating the Green's function for the system. The necessary Green's functions can be evaluated via the equation of motion method, as propounded by Zubarev (1960), by considering the specific Hamiltonian.

3.1. Hamiltonian for a Doped Anharmonic Crystal

The Hamiltonian can be conveniently expressed in the second quantized form as

$$H=H_0+H_D+H_A \tag{7}$$

with

$$H_0=(\hbar/4)\sum_k\omega_k(A_k^*A_k+B_k^*B_k) \tag{8}$$

$$H_D=-\hbar\sum_{k_1k_2}[C(k_1,k_2)B_{k_1}B_{k_2}-D(k_1,k_2)A_{k_1}A_{k_2}] \tag{9}$$

$$H_A=\hbar\sum_{s>3}\sum_{k_1k_2\ldots k_s}V^{(s)}(k_1,k_2,\ldots,k_s)A_{k_1}A_{k_2}\ldots A_{k_s} \tag{10}$$

Here $V^{(s)}(k_1,k_2,\ldots,k_s)$ represent the various anharmonic coupling coefficients (Pathak, 1965) and $C(k_1,k_2)$ and $D(k_1,k_2)$ are the mass and the force constant change parameters, respectively (Bahadur and Sharma, 1974). In the above equations the index k_s has been introduced to represent k_sj_s for brevity, with k_s being the wave vector and j_s, the polarization index.

3.2. Green's Functions and Phonon Spectrum

Consider the following retarded double-time thermal Green's function (Zubarev, 1960):

$$G_{kk'}(t,t')=-i\theta(t-t')\langle[A_k(t),A_{k'}(t')]\rangle=\langle\langle A_k(t);A_{k'}(t')\rangle\rangle \tag{11}$$

Writing the equation of motion of $G_{kk'}(t, t')$ with the aid of Hamiltonian (7) and Fourier transforming, one finally gets the solution in the form (Gairola, 1983, 1984; Indu, 1990)

$$G_{kk'}(\omega) = \pi^{-1}\omega_k \eta_{kk'}[\omega^2 - \tilde{\omega}_k^2 - 2\omega_k P(kk', \omega)]^{-1} \tag{12}$$

where

$$\eta_{kk'} = \delta_{kk'} + 4C(-k, k')\omega_k^{-1} \tag{13}$$

$$\tilde{\omega}_k^2 = \omega_k^2 + (\omega_k/2\pi)\left\{\langle[L_k(t), B_{k'}^*(t')]\rangle + (4/\omega_k)\sum_{k_1} C(-k, k_1)\langle[L_k(t), B_{k'}^*(t')]\rangle\right\}_{t=t'} \tag{14}$$

$$L_k(t) = F_k(t) + \sum_{k_1}[4C(-k, k_1)/\omega_k]F_{k_1}(t) + 4\pi\sum_{k_1} R(-k, k_1)A_{k_1}(t) \tag{15}$$

$$F_k(t) = 2\pi \sum_{s>3}\ \sum_{k_1k_2\ldots k_{s-1}} sV^{(s)}(k_1, k_2, \ldots, k_{s-1}, -k) \times A_{k_1}(t)\ldots A_{k_{s-1}}(t) \tag{16}$$

and

$$R(-k, k_1) = (\omega_{k_1}/\omega_k)C(-k, k_1) + D(-k, k_1) + (4/\omega_k)\sum_{k_2}{}' C(-k, k_2)D(-k_2, k_1) \tag{17}$$

The self-energy operator or response function $P(kk', \omega)$ appearing in equation (12) is given by

$$P(kk', \omega) = (2\pi)^{-1}\langle\langle L_k(t); L_{k'}^*(t')\rangle\rangle_\omega \tag{18}$$

and can be evaluated via the equivalent zeroth-order renormalized Hamiltonian

$$H_{\text{ren}} = (\hbar/4)\sum_k [(\tilde{\omega}_k^2/\omega_k)A_k^*A_k + \omega_k B_k^* B_k] \tag{19}$$

as discussed elsewhere (Gairola, 1983, 1984, 1991; Indu, 1990; Indu and Gairola, 1985) by separating the response function into real and imaginary parts

$$P(kk', \omega + i\varepsilon) = \Delta_k(\omega) - i\Gamma_k(\omega); \qquad \varepsilon \to 0^+ \tag{20}$$

where $\Delta_k(\omega)$ and $\Gamma_k(\omega)$ denote the shift and width in the phonon spectrum, respectively, for which one obtains the following expressions:

$$\Delta_k(\omega) = \Delta_k^A(\omega) + \Delta_k^D(\omega) + \Delta_k^{AD}(\omega) \tag{21}$$

$$\Gamma_k(\omega) = \Gamma_k^A(\omega) + \Gamma_k^D(\omega) + \Gamma_k^{AD}(\omega) \tag{22}$$

where the superscripts *A*, *D*, and *AD* denote the contributions arising due to anharmonic, defect, and combined interactions, respectively. These contributions are given by

$$\Delta_k^A(\omega) = \Delta_k^{(3)}(\omega) + \Delta_k^{(4)}(\omega) \tag{23}$$

$$\Delta_k^{(3)}(\omega) = 18 \sum_{k_1 k_2} |V^{(3)}(k_1, k_2, -k)|^2 \eta_1 \times [S_1^{(+)} \omega_{+\alpha}(\omega^2 - \omega_{+\alpha}^2)^{-1} + S^{(-)} \omega_{-\alpha}(\omega^2 - \omega_{-\alpha}^2)^{-1}] \tag{24}$$

$$\Delta_k^{(4)}(\omega) = 48 \sum_{k_1 k_2 k_3} |V^{(4)}(k_1, k_2, k_3, -k)|^2 \eta_2 \times [S_2^{(+)} \omega_{+\beta}(\omega^2 - \omega_{+\beta}^2)^{-1} + 3S_2^{(-)} \omega_{-\beta}(\omega^2 - \omega_{-\beta}^2)^{-1}] \tag{25}$$

$$\Delta_k^D(\omega) = 16P \sum_{k_1} R(-k, k_1) R^*(-k, k_1) \omega_k (\omega^2 - \tilde{\omega}_{k_1}^2)^{-1} \tag{26}$$

$$\Delta_k^{AD}(\omega) = 16 \sum_{k_1} |C(-k, k_1)|^2 \omega_k^{-2} \Delta_{k_1}^A(\omega) \tag{27}$$

$$\Gamma_k^A(\omega) = \Gamma_k^{(3)}(\omega) + \Gamma_k^{(4)}(\omega) \tag{28}$$

$$\Gamma_k^{(3)}(\omega) = 18\pi \varepsilon(\omega) \sum_{k_1 k_2} |V^{(3)}(k_1, k_2, -k)|^2 \eta_1 \times [S_1^{(+)} \omega_{+\alpha} \delta(\omega^2 - \omega_{+\alpha}^2) + S_1^{(-)} \omega_{-\alpha} \delta(\omega^2 - \omega_{-\alpha}^2)] \tag{29}$$

$$\Gamma_k^{(4)}(\omega) = 48\pi \varepsilon(\omega) \sum_{k_1 k_2 k_3} |V^{(4)}(k_1, k_2, k_3, -k)|^2 \eta_2 \times [S_2^{(+)} \omega_{+\beta} \delta(\omega^2 - \omega_{+\beta}^2) + 3S_2^{(-)} \omega_{-\beta} \delta(\omega^2 - \omega_{-\beta}^2)] \tag{30}$$

$$\Gamma_k^D(\omega) = 16\pi \varepsilon(\omega) \sum_{k_1} R(-k, k_1) R^*(-k, k_1) \omega_k \delta(\omega^2 - \tilde{\omega}_{k_1}^2) \tag{31}$$

$$\Gamma_k^{AD}(\omega) = 16 \sum_{k_1} |C(-k, k_1)|^2 \omega_k^2 \Gamma_{k_1}^A(\omega) \tag{32}$$

Here *P* denotes the principal value and $\varepsilon(\omega)$ has the following property:

$$\varepsilon(\omega) = \begin{cases} 1 & \text{for} \quad \omega > 0 \\ -1 & \text{for} \quad \omega \ll 0 \end{cases} \tag{33}$$

In the above equations we introduced the following symbols for convenience:

$$S_1^{(\pm)} = n_{k_2} \pm n_{k_1}; \qquad S_2^{(\pm)} = 1 \pm n_{k_1}n_{k_2} + n_{k_2}n_{k_3} \pm n_{k_3}n_{k_1} \tag{34}$$

$$\eta_i = (\omega_{k_1}\omega_{k_2} \ldots \omega_{k_{i+1}})/(\tilde{\omega}_{k_1}\tilde{\omega}_{k_2} \ldots \tilde{\omega}_{k_{i+1}}) \tag{35}$$

$$\omega_{\pm\alpha} = \tilde{\omega}_{k_1} \pm \tilde{\omega}_{k_2}; \qquad \omega_{\pm\beta} = \tilde{\omega}_{k_1} \pm \tilde{\omega}_{k_2} \pm \tilde{\omega}_{k_3} \tag{36}$$

with

$$n_k = \coth(\beta\hbar\omega_k/2) \tag{37}$$

The required Green's function (12) now assumes the form

$$G_{kk'}(\omega + i\varepsilon) = \pi^{-1}\omega_k\eta_{kk'}[\omega^2 - \bar{\omega}_k^2 + 2i\omega_k\Gamma_k(\omega)]^{-1} \tag{38}$$

with

$$\bar{\omega}_k^2 = \tilde{\omega}_k^2 + 2\omega_k\Delta_k(\omega) \tag{39}$$

4. PARTITION FUNCTION

The partition function for the crystal system can be obtained after substituting the value of E from equation (2) into equation (1). The density of phonon states is, in the Lehman representation (Dederichs, 1977),

$$N(\omega) = -\sum_k \operatorname{Im} G_{kk'}(\omega + i\varepsilon) \tag{40}$$

whence the average lattice energy using equation (2) and equation (38) is

$$E = 2\pi^{-1}\hbar \int d\omega\ \omega_k^2\omega\,\eta_{kk'}(n_k(\omega) + \tfrac{1}{2})$$

$$\times\,\Gamma_k(\omega)[(\omega^2 - \bar{\omega}_k^2)^2 + 4\omega_k^2\Gamma_k^2(\omega)]^{-1} \tag{41a}$$

$$= E_d + E_{nd} \tag{41b}$$

where subscripts d and nd represent the diagonal ($k = k'$) and nondiagonal ($k \neq k'$) contributions, respectively, and are given by

$$E_d = E_d^D + E_d^A + E_d^{AD} \tag{42a}$$

and

$$E_{nd} = (2\hbar/\pi) \sum_{k \neq k'} \omega_k\bar{\omega}_k[n(\omega) + \tfrac{1}{2}]\Gamma_k(\omega)(\omega^2 - \bar{\omega}_k^2)^{-2} \tag{42b}$$

The various contributions to the diagonal part E_d can be expressed in the following forms:

$$E_d^D = 16\hbar\varepsilon(\tilde{\omega}_{k_1}) \sum_{k_1} R(-k, k_1)R^*(-k, k_1)\bar{\omega}_k\omega_k^2\omega_{k_1}$$
$$\times [n(\tilde{\omega}_{k_1}) + \tfrac{1}{2}](\tilde{\omega}_{k_1}^2 - \bar{\omega}_k^2)^{-2} \tag{43}$$

$$E_d^{AD} = 16 \sum_{k_1} |C(-k, k_1)|^2 \omega_k^{-2} E_d^A(k_1) \tag{44}$$

$$E_d^A = E_d^{(3)} + E_d^{(4)} \tag{45}$$

$$E_d^{(3)} = 36\hbar \sum_{k_1k_2} |V^{(3)}(k_1, k_2, -k)|^2 \omega_k^2\bar{\omega}_k\eta_1\{\varepsilon(\omega_{+\alpha})S_1^{(+)}[n(\omega_{+\alpha}) + \tfrac{1}{2}]\omega_{+\alpha}$$
$$\times (\omega_{+\alpha}^2 - \bar{\omega}_k^2)^{-2} + \varepsilon(\omega_{-\alpha})S_1^{(-)}\omega_{-\alpha}[n(\omega_{-\alpha}) + \tfrac{1}{2}](\omega_{-\alpha}^2 - \bar{\omega}_k^2)^{-2}\} \tag{46}$$

$$E_d^{(4)} = 96\hbar \sum_{k_1k_2k_3} |V^{(4)}(k_1, k_2, k_3, -k)|^2$$
$$\times \omega_k^2\bar{\omega}_k\eta_2\{\varepsilon(\omega_{+\beta})S_2^{(+)}\omega_{+\beta}[n(\omega_{+\beta}) + \tfrac{1}{2}]$$
$$\times (\omega_{+\beta}^2 - \bar{\omega}_k^2)^{-2} + 3\varepsilon(\omega_{-\beta})S_2^{(-)}\omega_{-\beta}[n(\omega_{-\beta}) + \tfrac{1}{2}](\omega_{-\beta}^2 - \bar{\omega}_k^2)^{-2}\} \tag{47}$$

Here, $E_d^A(k_1)$ in equation (44) can be obtained from E_d^A in equation (45) by replacing k with k_1. The above equations for the average lattice energy are used in equation (1) to obtain the partition function in the form

$$Z = \sum_{n_k} \exp[-\beta(E_d^D + E_d^{(3)} + E_d^{(4)} + E_d^{AD})] \tag{48a}$$

$$= Z^D Z^{(3)} Z^{(4)} Z^{3D} Z^{4D} \tag{48b}$$

with

$$Z^D = \tfrac{1}{2} \prod_{k_1} \operatorname{cosech} x^D(\beta) \tag{49a}$$

$$Z^{(3)} = \tfrac{1}{4} \prod_{k_1k_2} \operatorname{cosech} x^{(+3)}(\beta) \operatorname{cosech} x^{(-3)}(\beta) \tag{49b}$$

$$Z^{(4)} = \tfrac{1}{4} \prod_{k_1k_2k_3} \operatorname{cosech} x^{(+4)}(\beta) \operatorname{cosech} x^{(-4)}(\beta) \tag{49c}$$

$$Z^{3D} = \tfrac{1}{4} \prod_{k_1k_2} \operatorname{cosech} x^{(+3D)}(\beta) \operatorname{cosech} x^{(-3D)}(\beta) \tag{49d}$$

$$Z^{4D} = \tfrac{1}{4} \prod_{k_1k_2k_3} \operatorname{cosech} x^{(+4D)}(\beta) \operatorname{cosech} x^{(-4D)}(\beta) \tag{49e}$$

In the above equations, we have introduced for convenience the following notations:

$$\begin{aligned}
x^{D}(\beta) &= 8\hbar\beta\,\varepsilon(\tilde{\omega}_k)R(-k, k_1)R^*(-k, k_1)\omega_k^2\bar{\omega}_k\omega_1(\omega_{k_1}^2-\bar{\omega}_k^2)^{-2} \\
&= \beta x^{D} \qquad (50a)
\end{aligned}$$

$$\begin{aligned}
x^{(\pm 3)}(\beta) &= 18\hbar\beta|V^{(3)}(k_1, k_2, -k)|^2\eta_1\omega_k^2\bar{\omega}_k\varepsilon(\omega_{\pm\alpha}) \\
&\quad\times S_1^{(\pm)}\omega_{\pm\alpha}(\omega_{\pm\alpha}^2-\bar{\omega}_k^2)^{-2} \\
&= \beta S_1^{(\pm)}x^{(\pm 3)} \qquad (50b)
\end{aligned}$$

$$\begin{aligned}
x^{(\pm 4)}(\beta) &= 288\hbar\beta|V^{(4)}(k_1, k_2, k_3, -k)|^2\eta_2\omega_k^2\bar{\omega}_k\varepsilon(\omega_{\pm\beta}) \\
&\quad\times S_2^{(\pm)}\omega_{\pm\beta}(\omega_{\pm\beta}^2-\bar{\omega}_k^2)^{-2} \\
&= \beta S_2^{(\pm)}x^{(\pm 4)} \qquad (50c)
\end{aligned}$$

$$\begin{aligned}
x^{(\pm 3D)}(\beta) &= 288\hbar\beta(\omega_1/\omega_k)^2\bar{\omega}_k|C(-k, k_1)V(k_1, k_2, -k)|^2 \\
&\quad\times \eta_1\varepsilon(\omega_{\pm\alpha})S_1^{(\pm)}\omega_{\pm\alpha}(\omega_{\pm\alpha}^2-\bar{\omega}_k^2)^{-2} \\
&= \beta S_1^{(\pm)}x^{(\pm 3D)} \qquad (50d)
\end{aligned}$$

$$\begin{aligned}
x^{(\pm 4D)}(\beta) &= 768\hbar\beta(\omega_1/\omega_k)^2\bar{\omega}_k|C(-k, k_1)V(k_1, k_2, k_3, -k)|^2 \\
&\quad\times \eta_2\varepsilon(\omega_{\pm\beta})S_1^{(\pm)}\omega_{\pm\beta}(\omega_{\pm\beta}^2-\bar{\omega}_k^2)^{-2} \\
&= \beta S_2^{(\pm)}x^{(\pm 4D)} \qquad (50e)
\end{aligned}$$

where $\omega_{k_s}=\omega_s$ has been written for brevity.

5. FREE ENERGY

Having obtained the appropriate partition function for the anharmonic crystal containing substitutional impurities, we can calculate the Helmholtz free energy in the following form:

$$F=-\beta^{-1}\ln Z=F^{D}+F^{(3)}+F^{(4)}+F^{3D}+F^{4D} \qquad (51)$$

where

$$F^{D}=\beta^{-1}\sum_{k_1}\ln[2\sinh x^{D}(\beta)] \qquad (52a)$$

$$F^{(3)}=\beta^{-1}\sum_{k_1k_2}\ln[4\sinh x^{(+3)}(\beta)\sinh x^{(-3)}(\beta)] \qquad (52b)$$

$$F^{(4)}=\beta^{-1}\sum_{k_1k_2k_3}\ln[4\sinh x^{(+4)}(\beta)\sinh x^{(-4)}(\beta)] \qquad (52c)$$

$$F^{3D}=\beta^{-1}\sum_{k_1k_2}\ln[4\sinh x^{(+3D)}(\beta)\sinh x^{(-3D)}(\beta)] \qquad (52d)$$

and

$$F^{4D} = \beta^{-1} \sum_{k_1 k_2 k_3} \ln[4 \sinh x^{(+4D)}(\beta) \sinh x^{(-4D)}(\beta)] \tag{52e}$$

The defect contribution to the free energy is given by equation (52a). In the classical high-temperature limit (indicated by subscript h) the contribution becomes

$$F_h^D \cong \sum_{k_1} [\beta^{-1} \ln(2\beta x^D) + (\beta/3!)(x^D)^2 + (\beta^3/5!)(x^D)^4 + \cdots] \tag{53}$$

The temperature dependence as given by equation (53) resembles the results of Maradudin *et al.* (1961) derived in the harmonic approximation. This is because the presence of defects is encountered in the problem through a quasiharmonic Hamiltonian [equation (9)]. However, the effects of the defect contribution and the frequency dependence are contained in equation (53) through the parameter x^D, which can be read from equation (50a).

The low-temperature limit (represented by l) of F^D is as follows:

$$F_l^D \cong \sum_{k_1} \{x^D - \beta^{-1}[\exp(-2\beta x^D) + \tfrac{1}{2} \exp(-4\beta x^D) + \cdots]\} \tag{54}$$

The temperature dependence in equation (54) again resembles closely the low-temperature results of Maradudin *et al.* (1961) obtained in the harmonic approximation. The defect contribution to the free energy of a doped crystal has hardly been discussed in the literature.

We now discuss the anharmonic contribution to the free energy, which has widely been discussed by several authors (Maradudin *et al.*, 1961; Born and Huang, 1954; Shukla and Müller, 1970, 1971; Shukla, 1966, 1980; Shukla and Wilk, 1974; Cowley and Shukla, 1974; Shukla and Taylor, 1974; Barron, 1963) using different approaches. The cubic anharmonic contribution given by equation (52b) reduces in the high-temperature limit to

$$\begin{aligned} F_h^{(3)} \cong \beta^{-1} \sum_{k_1 k_2} \Big\{ & \ln[4(\beta S_1^{(+)}) x^{(+3)} (\beta S_1^{(-)}) x^{(-3)}] \\ & + \frac{1}{3!} [(\beta S_1^{(+)} x^{(+3)})^2 + (\beta S_1^{(-)} x^{(-3)})^2] \\ & + \frac{1}{5!} [(\beta S_1^{(+)} x^{(+3)})^4 + (\beta S_1^{(-)} x^{(-3)})^4] + \cdots \Big\} \end{aligned} \tag{55}$$

In the low-temperature limit, this becomes

$$F_l^{(3)} \cong \sum_{k_1 k_2} \beta^{-1}\{(\beta S_1^{(+)} x^{(+3)} + \beta S_1^{(-)} x^{(-3)}) \\ - [\exp(-2\beta S_1^{(+)} x^{(+3)}) + \exp(-2\beta S_1^{(+)} x^{(-3)})]\} \tag{56}$$

At high temperatures,

$$\beta S_1^{(\pm)} \cong 2\hbar(\tilde{\omega}_{k_2}^{-1} \pm \tilde{\omega}_{k_1}^{-1})$$

whereas at low temperatures

$$\beta S_1^{(\pm)} = \beta\left[1 + 2\sum_{n=1}^{\infty} \exp(-n\beta\hbar\tilde{\omega}_k)\right]$$

It should be recalled that the renormalized phonon frequencies $\tilde{\omega}_k$ are temperature dependent, given by

$$\tilde{\omega}_k^2 = \omega_k^2 + \omega_k \Omega_k(f, T) \tag{57a}$$

with

$$\Omega_k(f, T) = \Omega_k^D + \Omega_k^A + \Omega_k^{AD} \tag{57b}$$

$$\Omega_k^D = 4[C(-k, k_1) + D(-k, k_1) + D(-k, -k') + (\omega_{k'}/\omega_k)C(-k, -k')] \\ +(16/\omega_k)\sum_{k'}(\omega_{k'}/\omega_k)[C(-k, k_1) + D(-k, -k')] \\ +D(-k, k')[1 + C(-k, k_1)] + C(-k, k_1)D(-k, k_1) \tag{57c}$$

$$\Omega_k^A = -12\pi \sum_{k_1 k_2} [4V_3(-k_1, -k', -k)V_3(k_1, k_2, -k) \\ -V_4(k_1, k_2, -k', -k)\omega_k^{-1}]J_k(\omega) \tag{57d}$$

$$\Omega_k^{AD} = -48\pi \sum_{k_1 k_2} C(-k, k_1)[4V_3(k_1, k', -k_1)V_3(k_1, k_2, -k) \\ -V_4(k_1, k_2, -k', -k)\omega_k^{-1}\omega_{k_1}^{-1}]J_k(\omega) \tag{57e}$$

where $J_k(\omega)$ is the spectral density function and f is the fractional impurity concentration (n/N).

The quartic anharmonic contribution to the free energy in the high-temperature limit is given by

$$F_h^{(4)} \cong \beta^{-1} \sum_{k_1k_2k_3} \Bigg\{ \ln[4(\beta S_2^{(+)})x^{(+4)}(\beta S_2^{(-)})x^{(-4)}] + \frac{1}{3!}[(\beta S_2^{(+)}x^{(+4)})^2 + (\beta S_2^{(-)}x^{(-4)})^2 + (\beta S_2^{(-)}x^{(-4)})^2] + \frac{1}{5!}[(\beta S_2^{(+)}x^{(+4)})^4 + (\beta S_2^{(-)}x^{(-4)})^4] + \cdots \Bigg\} \tag{58}$$

The low-temperature limit of $F^{(4)}$ is given as

$$F_l^{(4)} \cong \sum_{k_1k_2k_3} \{[(S_2^{(+)}x^{(+4)} + S_2^{(-)}x^{(-4)})] - \beta^{-1}[\exp(-2\beta S_2^{(+)}x^{(+4)}) + \exp(-2\beta S_2^{(-)}x^{(-4)})]\} \tag{59}$$

The factors $\beta S_2^{(\pm)}$ in the above expressions tend to $(k_{\mathrm{B}}T)$ and $(k_{\mathrm{B}}T)^{-1}$ in the high- and low-temperature limits, respectively.

The free energy contributions by the interacting terms between cubic anharmonic and defects (F^{3D}) and quartic anharmonic and defects (F^{4D}) at high and low temperatures are given by

$$F_h^{3D} \cong \beta^{-1} \sum_{k_1k_2} \{\ln(4\beta S_1^{(+)}x^{(+3D)}\beta S_1^{(-)}x^{(-3D)}) + (1/3!)[(\beta S_1^{(+)}x^{(+3D)})^2 + (\beta S_1^{(-)}x^{(-3D)})^2] + (1/5!)[(\beta S_1^{(+)}x^{(+3D)})^4 + (\beta S_1^{(-)}x^{(-3D)})^4] + \cdots\} \tag{60}$$

$$F_h^{4D} \cong \beta^{-1} \sum_{k_1k_2k_3} \{\ln(4\beta S_2^{(+)}x^{(+4D)}\beta S_2^{(-)}x^{(-4D)}) + (1/3!)[(\beta S_2^{(+)}x^{(+4D)})^2 + (\beta S_2^{(-)}x^{(-4D)})^2] + (1/5!)[(\beta S_2^{(+)}x^{(+4D)})^4 + (\beta S_2^{(-)}x^{(-4D)})^4] + \cdots\} \tag{61}$$

$$F_1^{3D} \cong \sum_{k_1k_2} \{(S_1^{(+)}x^{(+3D)} + S_1^{(-)}x^{(-3D)}) - \beta^{-1}[\exp(-2\beta S_1^{(+)}x^{(+3D)}) + \exp(-2\beta S_1^{(-)}x^{(-3D)})]\} \tag{62}$$

$$F_1^{4D} \cong \sum_{k_1k_2k_3} \{(S_2^{(+)}x^{(+4D)} + S_2^{(-)}x^{(-4D)}) - \beta^{-1}[\exp(-2\beta S_2^{(+)}x^{(+4D)}) + \exp(-2\beta S_2^{(-)}x^{(-4D)})]\} \tag{63}$$

6. ENTROPY

The anharmonic contribution to the entropy of a doped crystal has not been much discussed in the literature. Usually, the anharmonic contribution is obtained by replacing the harmonic phonon frequencies by mean anharmonic frequencies in the harmonic expression (Barron, 1965; Hui and Allen, 1975) (quasiharmonic approximation), which obviously is a crude approximation. In the present work, the various contributions to the crystal entropy are obtained through equation (5), using a nonperturbative technique, in the following form:

$$S = S^{D} + S^{A} + S^{AD} \tag{64}$$

where

$$S^{D} = -Nk_{\mathrm{B}} \ln 2 - k_{\mathrm{B}} \sum_{k_1} [\ln \sinh(\beta x^{D}) - n_D \beta x^{D}] \tag{65a}$$

$$\begin{aligned} S^{(3)} = -2N^2 k_{\mathrm{B}} \ln 2 - k_{\mathrm{B}} \sum_{k_1 k_2} \{ &\ln[\sinh(\beta x^{(+3)}) \sinh(\beta x^{(-3)})] \\ &-\beta[x^{(+3)} n_{+3} \sigma_1^{+} + x^{(-3)} n_{-3} \sigma_1^{-}]\} \end{aligned} \tag{65b}$$

$$\begin{aligned} S^{(4)} = -2N^3 k_{\mathrm{B}} \ln 2 - k_{\mathrm{B}} \sum_{k_1 k_2 k_3} \{ &\ln[\sinh(\beta x^{(+4)}) \sinh(\beta x^{(-4)})] \\ &-\beta[x^{(+4)} n_{+4} \sigma_2^{+} + 3x^{(-4)} n_{-4} \sigma_2^{-}]\} \end{aligned} \tag{65c}$$

$$\begin{aligned} S^{(3D)} = -2N^2 k_{\mathrm{B}} \ln 2 - k_{\mathrm{B}} \sum_{k_1 k_2} \{ &\ln[\sinh(\beta x^{(+3D)}) \sinh(\beta x^{(-3D)})] \\ &-\beta[x^{(+3D)} n_{+3D} \sigma_1^{+} + x^{(-3D)} n_{-3D} \sigma_1^{-}]\} \end{aligned} \tag{65d}$$

$$\begin{aligned} S^{(4D)} = -2N^3 k_{\mathrm{B}} \ln 2 - k_{\mathrm{B}} \sum_{k_1 k_2 k_3} \{ &\ln[\sinh(\beta x^{(+4D)}) \sinh(\beta x^{(-4D)})] \\ &-\beta[x^{(+4D)} n_{+4D} \sigma_2^{+} + 3x^{(-4D)} n_{-4D} \sigma_2^{-}]\} \end{aligned} \tag{65e}$$

with

$$n_i = \coth(\beta x^{i}); \qquad i = D, (\pm 3), (\pm 4), (\pm 3D), (\pm 4D) \tag{66a}$$

$$\sigma_1^{\pm} = S_1^{(\pm)} - (\beta \hbar)[\omega_2(n_2^2 - 1) \pm \omega_1(n_1^2 - 1)] \tag{66b}$$

$$\sigma_2^{\pm} = S_2^{(\pm)} \mp (\beta \hbar/2)[\tilde{n}_1^2(n_2 + n_3) \pm \tilde{n}_2^2(n_3 \pm n_1) \pm \tilde{n}_3^2(n_1 \pm n_2)] \tag{66c}$$

$$n_j = \coth(\beta \hbar \omega_j/2), \qquad j = 1, 2, 3, \ldots \tag{66d}$$

$$\tilde{n}_j^2 = \omega_j(n_j^2 - 1) \tag{66e}$$

The above expressions (65) for the entropy describe the effect of cubic and quartic anharmonicity besides the defect parameters. However, the temperature dependence of the entropy is manifested in two ways: the direct dependence can be found by inspection through β terms, whereas the implicit dependence is revealed through renormalized phonon frequencies [equation (57)].

7. LATTICE HEAT CAPACITY

The temperature derivative of the entropy function leads to the LHC equation (6) as follows:

$$C_v = C^D + C^{(3)} + C^{(4)} + C^{(3D)} + C^{(4D)} \tag{67}$$

with

$$C^D = k_B \sum_{k_1} [x^D(\beta)]^2 \operatorname{cosech}^2 x^D(\beta) \tag{68a}$$

$$\begin{aligned} C^{(3)} = k_B\beta \sum_{k_1k_2} \{&(\beta\hbar)[x^{(+3)}n_{+3}(\tilde{n}_2^2+\tilde{n}_1^2) + x^{(-3)}n_{-3}(\tilde{n}_2^2-\tilde{n}_1^2) - \beta\hbar\omega_2 n_2\tilde{n}_2^2] \\ &+ 2x^{(+3)}(\sigma_1^+)^2\tilde{n}_{+3}^2 - 2x^{(-3)}(\sigma_1^-)^2\tilde{n}_{-3}^2\} \end{aligned} \tag{68b}$$

$$\begin{aligned} C^{(4)} = k_B\beta^2 \sum_{k_1k_2k_3} \{&x^{(+4)}n_{+4}[x^{(+4)}(n_{+4})^{-1}(n_{+4}-1)(\sigma_2^+)^2 - \nabla_\beta\sigma_2^+] \\ &+ x^{(-4)}n_{-4}[3x^{(-4)}(n_{-4})^{-1}(n_{-4}-1)(\sigma_2^-)^2 - 3\nabla_\beta\sigma_2^- - (2\beta)^{-1}\sigma_2^-]\} \end{aligned} \tag{68c}$$

$$\begin{aligned} C^{(3D)} = k_B\beta \sum_{k_1k_2} \{&x^{(+3D)}n_{+3D}\sigma_1^+ + x^{(-3D)}n_{-3D}\sigma_1^- \\ &- \beta x^{(+3D)}[n_{+3D}\nabla_\beta\sigma_1^+ - \tilde{n}_{+3D}^2(\sigma_1^+)^2] \\ &- \beta x^{(-3D)}[n_{-3D}\nabla_\beta\sigma_1^- - \tilde{n}_{-3D}^2(\sigma_1^-)^2]\} \end{aligned} \tag{68d}$$

$$\begin{aligned} C^{(4D)} = k_B\beta^2 \sum_{k_1k_2k_3} \{&x^{(+4D)}n_{+4D}\sigma_2^+ + x^{(-4D)}n_{-4D}\sigma_2^- \\ &- \beta x^{(+4D)}[n_{+4D}\nabla_\beta\sigma_2^+ - \tilde{n}_{+4D}^2(\sigma_2^+)^2] \\ &- 3\beta x^{(-4D)}[n_{-4D}\nabla_\beta\sigma_2^- - \tilde{n}_{-4D}^2(\sigma_2^-)^2]\} \end{aligned} \tag{68e}$$

with

$$\nabla_\beta\sigma_1^\pm = (\hbar/2)[\beta\hbar(\tilde{n}_2^2\omega_2 n_2 \pm \tilde{n}_1^2\omega_1 n_1) - (\tilde{n}_2^2 \pm \tilde{n}_1^2)] \tag{69a}$$

$$\nabla_\beta\sigma_2^\pm = 2\nabla_\beta S_2^{(\pm)} - \beta\nabla_\beta^2 S_2^{(\pm)} \tag{69b}$$

$$\nabla_\beta S_2^{(\pm)} = \mp(\hbar/2)[\tilde{n}_1^2(n_2+n_3) \pm \tilde{n}_2^2(n_3 \pm n_1) \pm \tilde{n}_3^2(n_1 \pm n_2)] \tag{69c}$$

$$\begin{aligned} \nabla_\beta^2 S_2^{(\pm)} = (\hbar/2)[&\pm n_1 n_2(\omega_1\tilde{n}_1^2 + \omega_2\tilde{n}_2^2) \\ &+ n_2 n_3(\omega_2\tilde{n}_2^2 + \omega_3\tilde{n}_3^2) \pm n_3 n_1(\omega_3\tilde{n}_3^2 + \omega_1\tilde{n}_1^2) \\ &\pm \tilde{n}_1^2\tilde{n}_2^2 \pm \tilde{n}_2^2\tilde{n}_3^2 \pm \tilde{n}_3^2\tilde{n}_1^2] \end{aligned} \tag{69d}$$

8. DISCUSSION AND CONCLUSIONS

In the present paper, we have started with the various contributions (Z^D, Z^A, Z^{AD}) to the partition function of the impurity-induced anharmonic crystal and subsequently developed this approach to evaluate these contributions to various other thermodynamic properties of the crystal. These include the free energy, entropy, and the lattice heat capacity.

The expression for the free energy is given by equation (51), whose high- and low-temperature limits F_h and F_l, for various contributions, have been mentioned in Section 5. These expressions frequently involve terms like $\beta S_1^{(\pm)}$ and $\beta S_2^{(\pm)}$. It should be noted that at high and low temperatures these terms vary as

$$\begin{aligned} \beta S_1^{(\pm)} &\cong 2\hbar(\tilde{\omega}_2^{-1} \pm \tilde{\omega}_1^{-1}) && \text{high-temperature limit} && (70a)\\ &\cong \beta \exp(-\beta\hbar\omega_k) && \text{low-temperature limit} && (70b) \end{aligned}$$

and

$$\begin{aligned} \beta S_2^{(\pm)} &\cong \beta^{-1} \sim k_\mathrm{B}T && \text{high-temperature limit} && (71a)\\ &\cong \beta \sim (k_\mathrm{B}T)^{-1} && \text{low-temperature limit} && (71b) \end{aligned}$$

Equation (70a) represents the implicit temperature dependence of the term $\beta S_1^{(\pm)}$ through the renormalized temperature-dependent frequencies $\tilde{\omega}_1$ and $\tilde{\omega}_2$.

The entropy of the doped anharmonic crystal is given by equation (64), with the various contributions mentioned in equation (65). The high- and low-temperature limits of these contributions can be summarized as follows:

$$S_h^D = -k_\mathrm{B} \sum_{k_1} [\ln \beta x^D + (\beta x^D)^2/3! + \cdots] \tag{72a}$$

$$S_l^D = -k_\mathrm{B} \sum_{k_1} [\beta x^D + \ln(1 - e^{-2\beta x^D})] \tag{72b}$$

$$\begin{aligned} S_h^{(3)} = -k_\mathrm{B} \sum_{k_1 k_2} \{&\ln(\beta^2 x^{(+3)} x^{(-3)}) + (\beta^2/3!)[(x^{(+3)})^2 + (x^{(-3)})^2] + \cdots \\ &-\beta S_1^{(+)} - \beta S_1^{(-)} + (2/\beta^2\hbar)[(\omega_2/\tilde{\omega}_2^2)^2 - (\omega_1/\tilde{\omega}_1^2)^2]\} \qquad (73a)\\ \cong -k_\mathrm{B} \sum_{k_1 k_2} \{&\ln(\beta^2 x^{(+3)} x^{(-3)}) + (\beta^2/3!)[(x^{(+3)})^2 + (x^{(-3)})^2] + \cdots \\ &-2\hbar^{-1}[2\tilde{\omega}_2^{-1} - (1/\beta^2)(\tilde{\omega}_2^{-2} - \tilde{\omega}_1^{-2})]\} \qquad (73b) \end{aligned}$$

$$\begin{aligned} S_l^{(3)} = -k_\mathrm{B} \sum_{k_1 k_2} \{&\beta(x^{(+3)} + x^{(-3)}) + \ln[(1 - e^{-\beta x^{(+3)}})(1 - e^{-\beta x^{(-3)}})] \\ &-\beta(x^{(+3)} n_{+3} \sigma_1^{+} + x^{(-3)} n_{-3} \sigma_1^{-})_l\} \end{aligned} \tag{74}$$

where $(\ldots)_l$ denotes the low-temperature limit of the quantity, with the aid of the functional reduction

$$\coth(\beta\hbar\omega_j/2) = n_j \Rightarrow \left(1 + 2\sum_{n=1}^{\infty} e^{-n\beta\hbar\omega_j}\right) \tag{75}$$

In the similar way, the high- and the low-temperature limits of the other contributions $S^{(4)}$, $S^{(3D)}$, and $S^{(4D)}$ can be obtained.

The LHC of the anharmonic disordered crystal is given by equation (67), with various contributions mentioned in equation (68). Experiments (Launay, 1956; Kagan and Ioselevskii, 1963; Karlsson, 1970; Hartmann *et al.*, 1970) show that the LHC is highly sensitive at low temperatures. It is well known that defects play an important role in the low-temperature region in describing the dynamical properties of solids. Several authors (Manheim, 1968; Agrawal, 1980; Tiwari and Agrawal, 1973) have described the change in the LHC due to substitutional impurities by considering the effect of force constant change only, but the present theory (Indu, 1990) suggests that this change depends not only on the mass change parameters and the force constant changes, but also on the cross terms of third- and fourth-order anharmonic parameters with the defect terms (such as $C^{(3D)}$ and $C^{(4D)}$). The change in the LHC due to the introduction of impurities is given by

$$\Delta C_v = C^D + C^{(3D)} + C^{(4D)} \tag{76}$$

where C^D gives the leading contribution. At low temperature this varies as $\exp(-2\beta x^D)$, and it becomes independent of temperature in the classical high-temperature limit.

In the present work, we have discussed the thermodynamic properties of an impure anharmonic crystal by considering the average lattice energy based on the DOS, which, in turn, depends on the imaginary part of the Green's function, here evaluated without using any quasiharmonic approximation. The shortcoming of the quasiharmonic approximation in the evaluation of thermodynamic properties has already been remarked by Barron (1963). One important feature of this work is that the DOS is also temperature dependent besides its dependence on impurity concentration (Indu, 1990). A knowledge of the average lattice energy E leads to the evaluation of the partition function and consequently to the other related thermodynamic properties. The various expressions for these properties involve the entire phonon spectrum, through the present Green's functions. The evaluation of these Green's functions includes the contributions of all possible impurity modes, anharmonic modes, and interference (*AD*) modes.

ACKNOWLEDGMENT

This work represents partial fulfillment of the Ph.D. thesis of one of the authors (R.S.) at the H.N.B. Garhwal University.

REFERENCES

Agrawal, Bal K. (1980). *Physical Review B*, **22**, 6294.

Bahadur, R., and Sharma, P. K. (1974). *Solid State Communications*, **15**, 621.

Barron, T. H. K. (1963). In *Proceedings of International Conference on Lattice Dynamics*, Copenhagen, p. 301.

Barron, T. H. K. (1965). *Discussions of Faraday Society*, **40**, 69.

Born, M., and Huang, K. (1954). *Dynamical Theory of Crystal Lattices*, Oxford University Press, Oxford, p. 278.

Cowley, E. R., and Shukla, R. C. (1974). *Physical Review B*, **9**, 1261.

Dederichs, P. H. (1977). *New Concepts in the Physics of Phonons.*

Elliott, R. J. (1966). In *Phonons in Perfect Lattices and in Lattices With Point Imperfections*, R. W. H. Stevenson, ed., Oliver and Boyd, Edinburgh, p. 377.

Gairola, R. P. (1983). *Acta Physica Polonica A*, **63**, 121.

Gairola, R. P. (1984). *Physica Status Solidi* (*b*), **125**, 65.

Gairola, R. P. (1991). *International Journal of Modern Physics B*, **5**, 815.

Hartmann, W. M., Culbert, H. V., and Huebener, R. P. (1970). *Physical Review B*, **1**, 1486.

Hui, J. C. K., and Allen, P. B. (1975). *Journal of Physics C: Solid State Physics*, **8**, 2923.

Indu, B. D. (1990). *International Journal of Modern Physics B*, **4**, 1379.

Indu, B. D., and Gairola, R. P. (1985). *Indian Journal of Theoretical Physics*, **33**, 115.

Kagan, Yu. M., and Ioselevskii, Ya. A. (1963). *Zhurnal Eksperimentalnoi i Teoreticheskoi Fiziki*, **45**, 819 [*Soviet Physics-JETP*, **18**, 562 (1964)].

Karlsson, A. V. (1970). *Physical Review B*, **2**, 3332.

Klein, M. L., and Koehler, T. R. (1977). *Rare Gas Solids*, Vol. 1, Academic Press, New York.

Launay, J. D. (1956). In *Solid State Physics*, Vol. 2, F. Seitz and D. Turnbull, eds., Academic Press, New York, p. 220.

Leibfried, G., and Ludwig, W. (1961). In *Solid State Physics*, Vol. 12, F. Seitz and D. Turnbull, eds., Academic Press, New York, p. 331.

Manheim, P. D. (1968). *Physical Review*, **165**, 1011.

Maradudin, A. A. (1966). In *Solid State Physics*, Vol. 18, F. Seitz and D. Turnbull, eds., Academic Press, New York, p. 273.

Maradudin, A. A., and Fein, A. E. (1962). *Physical Review*, **128**, 2589.

Maradudin, A. A., Flinn, P. A., and Coldwell Horsfall, R. A. (1961). *Annals of Physics*, **15**, 337, 360.

Pathak, K. N. (1965). *Physical Review A*, **139**, 1569.

Pathak, K. N., and Varshni, Y. P. (1969). *Physical Review Letters*, **28A**, 539.

Shukla, R. C. (1966). *Journal of Chemical Physics*, **45**, 4178.

Shukla, R. C. (1980). *International Journal of Thermophysics*, **1**, 73.

Shukla, R. C., and Müller, E. R. (1970). *Physica Status Solidi* (*b*), **39**, 561.

Shukla, R. C., and Müller, E. R. (1971). *Physica Status Solidi* (*b*), **43**, 413.

Shukla, R. C., and Taylor, B. R. (1974). *Physical Review B*, **9**, 4116.

Shukla, R. C., and Wilk, L. (1974). *Physical Review B*, **10**, 3660.

Tiwari, M. D., and Agrawal, Bal K. (1973). *Physica Status Solidi* (*b*), **58**, 209.

Zubarev, D. N. (1960). *Uspekhi Fizicheskikh Nauk*, **71**, 71 [*Soviet Physics-Uspekhi*, **3**, 320 (1960)].