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Anomalies of phonon spectra and anharmonic effects in metals and alloys due to proximity of the Fermi level to singular points of band structure

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Abstract. We investigate singularities of phonon spectra and anharmonic effects in metals due to the proximity of the Fermi level ε_F to singular points ε_c in the electron density of states $N(\varepsilon)$. As an example, we consider the case of the Van Hove singularity, when at small $\eta = \varepsilon_F - \varepsilon_c$ the singular part of $N(\varepsilon_F)$ varies as $\eta_{\pm}^{1/2}$, where $\eta_{\pm} = \pm \eta \theta(\pm \eta)$ and $\theta(x)$ is zero at $x < 0$ and unity at $x > 0$. We show that contributions to phonon frequencies ω_k that are non-analytic in η are proportional to $\eta_{\pm}^{3/2}$ at $k > k_s$ and to $\eta_{\pm}^{1/2}$ at $k < k_s$, where $k_s \sim \eta_{\pm}^{1/2}$ is some characteristic value of the wavenumber k . Within the model with a weak pseudopotential, v , an explicit expression is given for the singular part of the dynamic matrix for all not small $k > k_s \sim (v\eta_{\pm})^{1/2}$. In thermodynamics, low-frequency phonon dispersion at $k \sim k_s$ results in anomalous temperature dependences at low $T \sim T_s = T_D(v\eta_{\pm})^{1/2}$, where T_D is the Debye temperature. At $T > T_s$ non-analytic contributions to the thermal expansion coefficients are proportional to $\eta_{\pm}^{1/2}$, while in the temperature derivatives of the elastic constants and of the optic phonon frequencies with $k = 0$ they grow as $\eta_{\pm}^{-1/2}$. The results are compared with the available experimental data.

1. Introduction

Anomalies of kinetic and thermodynamic properties of metals connected with the proximity of the Fermi level ε_F to singular points ε_c in the electron density of states $N(\varepsilon)$ (to be called for brevity state-density singularity (SDS) effects) have been widely discussed in the literature; see e.g. [1, 2]. The point ε_c may be the Van Hove singularity point in $N(\varepsilon)$, connected with the electronic topological transition (ETT) [3], and may not formally be a non-analyticity point of $N(\varepsilon)$ but correspond to the region of its sharp variation, e.g. a narrow peak of $N(\varepsilon)$, which is characteristic of many transition-metal alloys [4, 5]. Recent theoretical and experimental studies show that, in a number of significant characteristics, such as the thermopower [6–9], shear constants [1, 2, 10], thermal expansion [1, 11], microhardness [12], structural stability [10, 13], etc, the SDS effects may be pronounced and strong. As an example, in figure 1 we show the concentration anomaly in the value of dc_{44}/dT in Nb–Mo alloys observed by de Camargo *et al* [1], which they attributed to the SDS effects.

Anomalies in phonon spectra ω_k in the vicinity of the ETT were discussed by Dagens [14]. He showed that, if the singular contribution to $N(\varepsilon_F)$ at small $\eta = (\varepsilon_F - \varepsilon_c)/\varepsilon_c$ had a 'one-sided' form $N_s(\varepsilon_F) = A\eta_{\pm}^{1/2}$ characteristic of the ETT (where $\eta_{\pm} = \pm \eta \theta_{\pm}$, $\theta_{\pm} =$

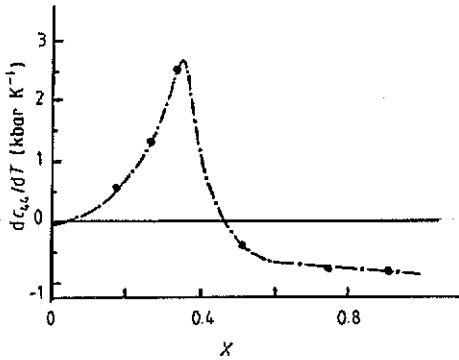


Figure 1. The concentration dependence of the temperature derivative $\pi_{44}(x) = dc_{44}/dT$ in the $Nb_{1-x}Mo_x$ alloys at $T = 300$ K [1].

$\theta(\pm\eta)$ and $\theta(x)$ is unity at $x > 0$ and zero at $x < 0$), then at $\eta \rightarrow 0$ all the frequencies ω_k displayed 'one-sided' singularities of the form $\omega_k^s = A\eta^{3/2}$. He also discussed singularities of Kohn anomalies in ω_k near the ETT and concluded that they result in unusual terms f_{sK} in averages over the phonon spectrum $f = \langle \omega_k^n \rangle$ having the form $f_{sK} = A|\eta|^{3/2}(1 - \theta_{\pm})$ and being non-zero on the side of the ETT where $N(\eta)$ is regular.

The consideration of Dagens [14] was phenomenological, without attempting to estimate microscopically the scale and form of the anomalies. Therefore, it is desirable to verify and specify it using some microscopic model, e.g. that with a weak pseudopotential. Moreover, Dagens [14] treated mainly phonons with not small wavevectors k , while at small k the singularities with respect to η in $\omega_k(\eta)$ get stronger (which was mentioned in his paper, too). This must result in some peculiarities in the low-temperature dependences of thermodynamic characteristics near the ETT. Finally, the SDS anomalies in characteristics of the anharmonic effects, such as the thermal expansion coefficients $\beta_i(T)$ and the temperature derivatives of elastic constants dc_{ij}/dT , of phonon frequencies $d\omega_k/dT$, etc. can be of considerable interest. There are a number of experimental indications of the importance of the SDS effects in these characteristics (see e.g. [1, 11]), but theoretically, they have apparently not yet been discussed.

The present paper deals with the above-mentioned problems. For definiteness, in the same way as in [2], we discuss mainly the ETT case, though all the qualitative results are applicable to the general case of a sharp change of $N(\varepsilon)$ in the vicinity of a certain ε_c . In section 2 we consider singularities of phonon spectra ω_k for different values of the wavenumber k . In section 3 we explicitly calculate the non-analytic part of the dynamic matrix in the model of interaction of electrons with only one face of the Brillouin zone (BZ) [15], which is known to describe exactly all the singularities connected with the ETT. We show, in particular, that the mentioned unusual f_{sK} term suggested by Dagens [14] is absent in this model as well as in other cases when the ETT occurs in the vicinity of the BZ symmetry point. In section 4 we consider manifestations of the discussed SDS effects in thermodynamic and anharmonic characteristics, in particular in the thermal expansion coefficient β , and the temperature derivatives of the elastic constant $\pi_{ij} = dc_{ij}/dT$ and of the optical phonon frequency $\pi_{\mu} = d\omega_{\mu}/dT$. In section 5 we illustrate the scale and character of the discussed SDS effects with the model calculations of the concentration dependences of $\beta(x)$, $\pi_{\eta}(x)$ and $\pi_{\mu}(x)$ for the disordered alloys $Li_{1-x}Mg_x$ and $Cd_{1-x}Mg_x$ having the ETT at certain values $x = x_c$. The experimental results for microhardness and hardness in these alloys are also discussed. The main conclusions are

summarized in section 6. Some of the results of this work were reported earlier in a short communication [16].

2. Singularities in the dynamic matrix near the electronic topological transition

As in [14], we proceed from the general expression for the dynamic matrix $\mathbf{D}(\mathbf{k})$ [17] in terms of the dielectric matrix $\epsilon = 1 + \nu_c \mathbf{\Pi}$, where $\mathbf{\Pi} = \mathbf{\Pi}_{q_1, q_2}$ is an irreducible polarization operator [18], while $\nu_c = \nu_c(q) = 4\pi e^2/q^2$ is the Coulomb interaction of electrons:

$$D^{\alpha\beta, nn'}(\mathbf{k}) = \frac{1}{M} \left(\Phi^{\alpha\beta, nn'}(\mathbf{k}) - \delta_{nn'} \sum_m \Phi^{\alpha\beta, nm}(0) \right) \tag{1a}$$

$$\Phi^{\alpha\beta, nn'}(\mathbf{k}) = \sum_{g_1, g} (k_\alpha + g_{1\alpha})(k_\beta + g_{1\beta}) \varphi^{nn'}(\mathbf{k} + \mathbf{g}_1, \mathbf{k} + \mathbf{g}) \tag{1b}$$

$$\varphi^{nn'}(q_1, q) = \delta_{q_1 q} 4\pi e^2 z_n z_{n'} / q^2 \Omega - w_n^*(q_1) (\mathbf{\Pi} \epsilon^{-1})_{q_1, q} w_{n'}(q) e^{i(q_1 \cdot \rho_n - q \cdot \rho_{n'})}. \tag{1c}$$

Here \mathbf{g}_1 and \mathbf{g} are reciprocal lattice vectors; the n and n' indices label different ions with masses M_n , charges z_n and basis vectors ρ_n in the unit cell; Ω is the unit-cell volume and $w_n(q)$ is the form factor of the ion pseudopotential. If the pseudopotential is non-local, then in considering the singularities discussed below connected with electronic states having quasi-momentum \mathbf{p} close to some 'critical' value \mathbf{p}_c , $w(q)$ should be understood as the matrix element $\langle \mathbf{p}_c | \hat{w} | \mathbf{p}_c + \mathbf{q} \rangle$ with $|\mathbf{p}_c + \mathbf{q}| \approx p_c \approx p_F$, where p_F is the Fermi momentum [2].

The anomalies under consideration are related to singularities in the polarization operator $\mathbf{\Pi}_{q_1, q}$, which obeys the Dyson equation

$$\mathbf{\Pi}_{\mathbf{k}+\mathbf{g}_1, \mathbf{k}+\mathbf{g}} = \sum_p \sum_{g_2, g_3} G_{p-g_2, p} G_{p-k-g_3, p-k-g_1-g_2} \Gamma(p-k-g_3, p, k+g). \tag{2}$$

Here we use the same four-dimensional notation as in [2]: $p = (\mathbf{p}, \omega_n)$, $\mathbf{k} + \mathbf{g}_i = (\mathbf{k} + \mathbf{g}_i, 0)$; $\omega_n = (2n + 1)\pi T$ are discrete frequencies of the temperature diagram technique [18]; the sum over p means summation over \mathbf{p} and ω_n and projections of the electron spin σ ; while G and Γ are the electronic Green function and the vertex part [18].

As noted by Dagens [14] and illustrated in section 3, the singular contribution $\mathbf{\Pi}_s$ to the matrix $\mathbf{\Pi}$ can be approximately represented as

$$\mathbf{\Pi}_{\mathbf{k}+\mathbf{g}_1, \mathbf{k}+\mathbf{g}}^s = \sum_{i, j} M_i(\mathbf{k}, \mathbf{g}_1) M_j^*(\mathbf{k}, \mathbf{g}) \xi_{ij}(\mathbf{k}) \tag{3a}$$

$$\xi_{ij}(\mathbf{k}) = 2 \sum_p \frac{n_i(\mathbf{p}) - n_j^*(\mathbf{p} + \mathbf{k})}{\epsilon_j(\mathbf{p} + \mathbf{k}) - \epsilon_i(\mathbf{p})}. \tag{3b}$$

Here M_i and M_j are some non-singular functions of η , $\epsilon_i(\mathbf{p})$ is the electron energy with quasi-momentum \mathbf{p} in the i th band and $n_i(\mathbf{p}) = \theta[\epsilon_F - \epsilon_i(\mathbf{p})]$ is the electron occupation number. For simplicity, we neglect the temperature smearing of the Fermi distribution and consider only the most interesting case of not too high $T < \epsilon_F \eta$, while at higher T all the singularities connected with the ETT are smoothly smeared [3, 6].

Let the ETT be connected with the electronic states in the band with $i = n$, so that ε_c is $\varepsilon_n(\mathbf{p}_c)$, the singularity in $N(\varepsilon)$ near ε_c be determined by the partial contribution $N_n(\varepsilon)$,

$$N_n(\varepsilon) = 2 \sum_p \delta[\varepsilon - \varepsilon_n(\mathbf{p})] \quad (4)$$

and the singular part $N_n^s(\varepsilon)$ have the form $A(\pm \xi)^{1/2} \theta(\pm \xi)$, where $\xi = (\varepsilon - \varepsilon_c)/\varepsilon_c$. Then the non-analytical contribution ξ_{nj}^s to equation (3b) at $k \neq 0$ up to the non-singular factor $[\varepsilon_j(\mathbf{p} + \mathbf{k}) - \varepsilon_i(\mathbf{p})]^{-1}$ corresponds to replacement of the factor $\delta[\varepsilon - \varepsilon_n(\mathbf{p})]$ in equation (4) by $\theta[(\varepsilon_F - \varepsilon_n(\mathbf{p}))]$. After integration over p this yields Dagens' [14] result: $\xi_{nj}^s \sim \eta_{\pm}^{3/2}$. At the same time, if $k \rightarrow 0$, in the diagonal terms of equation (4b), the singularity increases up to the square root one: $\xi_{nn}^s = N_n^s(\varepsilon_F) \sim \eta_{\pm}^{1/2}$. Since the second term $\Phi(0)$ in the dynamic matrix (1a) (at all k) contains expressions $\Pi_{k+\mathbf{g}_1, k+\mathbf{g}}$ with $k = 0$, it could be inferred from the above that at all k there exists a singular term $\sim \eta_{\pm}^{1/2}$ in the frequencies $\omega_k(\eta)$.

In fact, however, after summation over \mathbf{g}_1 and \mathbf{g} in equation (1b), the most singular contributions will be shown below to cancel, and at not small k Dagens' result $\omega_k^s \sim \eta_{\pm}^{3/2}$ remains true. However, at k smaller than a certain k_s , in equation (1a) no such cancellation occurs, the expansion over k comprises the $\eta_{\pm}^{1/2}$ terms, and in the elastic constants c_{ij} and in the optic phonon frequencies at the BZ centre, ω_μ , the singularities over η are square root ones [2].

The boundary values of the wavenumber, k_s , at which the transition from the dependence $\omega^s \sim \eta_{\pm}^{3/2}$ to $\omega^s \sim \eta_{\pm}^{1/2}$ takes place, can be most easily estimated from continuity considerations. At small k , the expansion of the dynamic matrix $\mathbf{D}(k) \sim \omega_k^2$ begins from the terms $\sim k^2$; thus, for the acoustic phonons $\omega_k^2 \sim c_{ij} k^2 \sim (a + b\eta_{\pm}^{1/2})k^2$ [2]. By joining the singular part of this expression with $\omega^s \sim \eta_{\pm}^{3/2}$ at $k \geq k_s$, we find $k_s \sim k_{\max} \eta_{\pm}^{1/2}$. Actually, k_s is determined from the condition that the $\mathbf{p} - \mathbf{p}_c$ values significant for the appearance of the singularity in equation (3b), namely $|\mathbf{p} - \mathbf{p}_c| \leq \rho_c \eta_{\pm}^{1/2}$, should be smaller than k_s . This results in precisely the above estimate of k_s .

Let us now discuss the dependence of the ω^s and k_s values on the reduced pseudopotential $v \sim w(\mathbf{g})/\varepsilon_F$ at small v . Note that for actual metals the part of the v parameter in the discussed effects is usually played by the ratio of pseudogaps at the BZ boundary, Δ , to $2\varepsilon_F$, which is often small even in transition metals. Therefore, the estimates given below may be applicable not only to nearly free-electron (NFE) metals, though the formulae of the NFE model from [2] will be used for their derivation.

Within this model, the ETT corresponds to 'touching' or 'overflow' of the Fermi surface (FS) over the BZ face, i.e. formation of a 'neck' or a new cavity of the FS with centre at the point $\mathbf{p}_c = \frac{1}{2}\mathbf{g}_c$, where \mathbf{g}_c is the corresponding value of the reciprocal lattice vector. The effects related to the ETT are characterized by the ratio of the reduced pseudopotential v to the parameter α of the proximity of ε_F to the 'unperturbed' energy ε_c^0 :

$$v = \bar{V}(\mathbf{g}_c)/\varepsilon_c^0 \quad \alpha = (\varepsilon_F - \varepsilon_c^0)/\varepsilon_c^0 \quad \varepsilon_c^0 = p_c^2/2m_*. \quad (5)$$

Here m_* is an effective mass at $\mathbf{p} = \mathbf{p}_F$ in the absence of interaction with the lattice, while $\bar{V}(\mathbf{g})$ is an effective pseudopotential renormalized by the electron-electron interaction and given by formula (12b) in [2]. The value $\alpha = -v$ corresponds to the point of the ETT related to touching, and $\alpha = v$ to the overflow of the FS over the BZ face.

To estimate the non-analytical contributions ξ_{nj}^s in (3b), it is convenient to write down the electron energies $\varepsilon_i(\mathbf{p})$ with \mathbf{p} close to \mathbf{p}_c in the form

$$\varepsilon_{1,2}(\mathbf{p}) - \varepsilon_c^0 = \varepsilon_c^0[\rho^2 + z^2 \mp (v^2 + 4z^2)^{1/2}] \tag{6}$$

where $z = (\mathbf{p} - \mathbf{p}_c)\mathbf{p}_c/p_c^2$ is the longitudinal component, while $\boldsymbol{\rho} = (\mathbf{p} - \mathbf{p}_c - z\mathbf{p}_c)/p_c$, is the transverse component of the reduced quasi-momentum $(\mathbf{p} - \mathbf{p}_c)/p_c$, and indices 1 and 2 correspond to the lower and upper bands. The expansion of $\varepsilon_i(\mathbf{p})$ near $\varepsilon_c = \varepsilon_i(\mathbf{p}_c) = \varepsilon_c^0(1 \mp v)$ has the form $\varepsilon_c^0[\rho^2 \mp z^2(2/v \mp 1)]$, while the singularities ξ^s in $\xi_{nj}^s(\mathbf{k})$ in equation (3b) are determined by the $\mathbf{p} - \mathbf{p}_c$ region corresponding to the values $|\varepsilon_n - \varepsilon_c| \leq \varepsilon_c \eta_{\pm}$. Therefore, at not small k , when the energy denominators $\Delta_{jn}(\mathbf{p}, \mathbf{k}) = \varepsilon_j(\mathbf{p} + \mathbf{k}) - \varepsilon_n(\mathbf{p})$ in equation (3b) are not small, we have: $\xi_{nj}^s(\mathbf{k}) \sim (v\eta_{\pm}^2)^{1/2}$. However, at $k \rightarrow 0$ the NFE splitting of bands 1 and 2 near \mathbf{p}_c is low, $\Delta_{jn}(\mathbf{p}_c, 0) \sim v$, and $\xi_{12}^s(0) \sim (\eta_{\pm}^3/v)^{1/2}$. Thus, at $k \rightarrow 0$ the singular contributions ξ^s and Π^s increase and turn out to be larger by $1/v$ than those at not small k . Therefore, at small v and not small $k \geq k_s \sim k_{\max}(v\eta_{\pm})^{1/2}$, the singularities in $\mathbf{D}(\mathbf{k})$ in equation (1a) are determined mainly by the second term $\Phi(0)$, i.e. are k -independent and have the order $\mathbf{D}_s \sim (v^3\eta_{\pm}^2)^{1/2}$.

Using the expressions for the $\Pi_{g,1,g}^s$ values obtained in [2], these \mathbf{D}_s contributions can be written explicitly. As discussed in [2], in the lowest order in v , the singular contributions Π^s are proportional to v and are present only in the $\Pi_{g,g}^s$ and $\Pi_{-g,g}^s$ components where $\mathbf{g} = \mathbf{g}_c = 2\mathbf{p}_c$. By expanding expressions (1) to first order in Π^s , we obtain for the singular contribution \mathbf{D}_s at $k > k_s$:

$$D_s^{\alpha\beta,nn'} = \frac{1}{M_n} \delta_{nn'} \sum_g g_{\alpha} g_{\beta} w_n(\mathbf{g}) \varepsilon_0^{-2} \exp(-i\mathbf{g} \cdot \boldsymbol{\rho}_n) [\Pi_{g,g}^s V^*(\mathbf{g}) - \Pi_{-g,g}^s V(\mathbf{g})] \tag{7}$$

where ε_0 is the value of the dielectric function $\varepsilon(q)$ in the homogeneous Fermi liquid at $q = 2p_F$. Using expressions (15) and (16) from [2] for the values $\Pi_{\pm g,g}^s$ and integrating over \mathbf{p} , i.e. over $\boldsymbol{\rho}$ and z , we have (for the considered case of not high $T < \varepsilon_F \eta_{\pm}$)

$$D_s^{\alpha\beta,nn'} = \frac{1}{M_n} \delta_{nn'} \sum_g g_{\alpha} g_{\beta} \bar{w}_n(\mathbf{g}) \exp(-i\mathbf{g} \cdot \boldsymbol{\rho}_n) \bar{V}^*(\mathbf{g}) 2bF(\alpha/v, v) / \varepsilon_c^0. \tag{8}$$

Here $b = 3z/16$, where z is the number of valence electrons per atom [2], and $F(\alpha/v, v)$ has the form

$$F(\alpha/v, v) = \alpha\theta(\alpha^2 - v^2)\{(1 - v^2/\alpha^2)^{1/2} - \ln[\alpha + (\alpha^2 - v^2)^{1/2}/v]\} - \alpha \ln v. \tag{9}$$

Near the ETT points $\alpha = \pm v$, expression (9) has a singularity of the form $(\eta_{\pm}^3/v)^{1/2}$. Figure 2 presents the dependence of the function F/v on $x = \alpha/v$ at the value $v = 0.055$ (corresponding to the model of $\text{Li}_{1-x}\text{Mg}_x$ alloys, discussed in section 5, at $x_{\text{Mg}} \approx 0.4$) as well as the function $f(x) = (F + \alpha \ln v)/v$ and its derivatives.

In accordance with equation (8), the dependence shown in figure 2 (curve A) illustrates the character of variation of the phonon frequencies ω_k near the ETT. Its form agrees with the general considerations on the 'band' tendencies of the structural stability. It is known that, as ε_F approaches the minimum (maximum) point in $N(\varepsilon)$, it results, generally speaking, in a gain (loss) in the band energy E_b , in comparing E_b for different structures. Correspondingly, one could expect here a certain increase (decrease) of the lattice stability, hardening (softening) of the ω_k . For a qualitative consideration, we apply equation (8) to the case of monatomic cubic crystals. Then the coefficient before F in equation (8) is reduced to a positive value proportional to $\delta_{\alpha\beta} g^2 |w(\mathbf{g})|^2$ and the sign

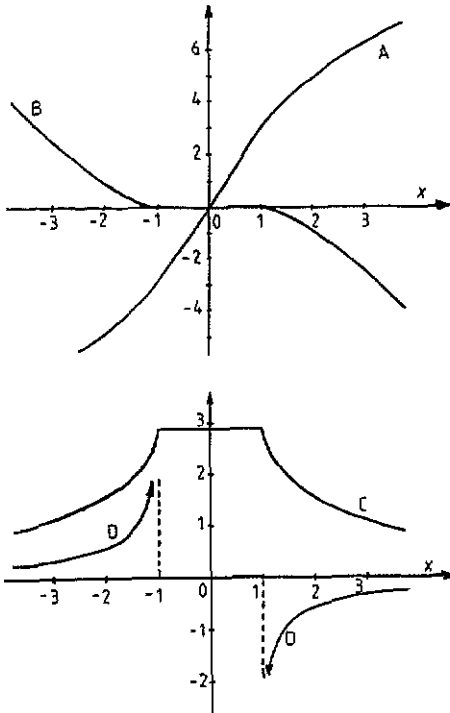


Figure 2. (A) The function $F(x, \nu)/\nu$ from equation (9) at the value of $\nu = 0.055$, (B) $f(x) = (F + \alpha \ln \nu)/\nu$, (C) df/dx and (D) d^2f/dx^2 .

of $D_s \sim (\omega_k^2)_s$ coincides with that of F . In the model considered, the point $\alpha = \nu$ corresponds to the minimum, while the point $\alpha = -\nu$ corresponds to the maximum in $N(\epsilon)$ [2]. It is clear from figure 2 that near $\alpha = \nu$ there indeed occurs a certain hardening of $\omega_k(x)$ with respect to the mean, linear variation, while close to $\alpha = -\nu$ an analogous softening of $\omega_k(x)$ takes place. Note that at small $k < k_s$ these band tendencies of the structural stability manifest themselves still more sharply [2].

Let us now discuss the general character of the $\omega_{k\lambda}$ dependence on k , ν and η for different branches λ of the phonon spectrum at the considered $|\eta| \leq \nu \ll 1$. Since $\omega_{k\lambda}^2$ is the eigenvalue of the $\mathbf{D}(k)$ matrix in equation (1), it follows from the above that $\omega_{k\lambda}^2$ has the following form:

$$\omega_{k\lambda}^2 = \omega_{k\lambda, \text{reg}}^2 + (\nu\eta_{\pm})^{3/2} f_{\lambda}(k/k_s, \eta/\nu). \tag{10}$$

Here $\omega_{k\lambda, \text{reg}}^2$ denotes contributions to $\omega_{k\lambda}^2$ regular at the ETT, while $k_s = k_{\text{max}}(\nu\eta_{\pm})^{1/2}$. So, if λ in equation (10) corresponds to the acoustic branch, the expansion of the function $f_{\lambda}(x, y)$ at small x has the form $\sum x_{\alpha} x_{\beta} c_{\alpha\beta}^{\lambda}$ with $c_{\alpha\beta}^{\lambda}$ being regular at small $y = \eta/\nu$. Thus the anomalous contributions c_{ij}^s to the elastic constants have the order $(\nu\eta_{\pm})^{1/2}$ relative to the regular terms $c_{ij, \text{reg}}$ (except for the bulk modulus B , in which there is the singular contribution $B^s \sim (\nu^5 \eta_{\pm})^{1/2}$; see [2]). For the optical branches λ , $f_{\lambda}(x, y)$ in equation (10) at $x \rightarrow 0$ behaves as $f_{\lambda}(0, y) \sim 1/y$ (due to the presence of the mentioned terms $\xi_{5n\pi}^s \sim (\nu\eta_{\pm})^{1/2}$ in equation (3)), so that the singular terms have the order $\omega_{\mu}^s \sim (\nu^5 \eta_{\pm})^{1/2}$ at $k < k_s$. At the same time, at not small $k > k_s$ all the f_{λ} in equation (10) tend to k -independent expressions analytical over η and determined by formulae (7)–(9).

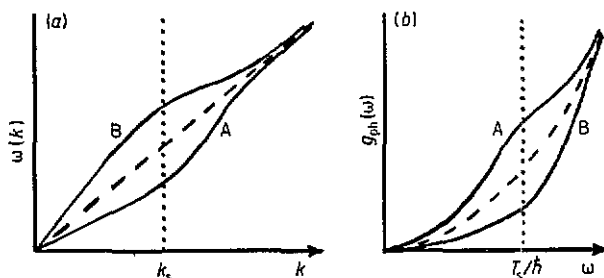


Figure 3. The character of the low-frequency dispersion of acoustic phonons (a) and of their spectral density $g_{ph}(\omega)$ (b) in the case when ε_F is close to the singular point ε_c in the electronic density of states $N(\varepsilon)$. Curves A correspond to the case when the singular part $N_s(\varepsilon)$ rises at ε_c ; curves B to that when $N_s(\varepsilon)$ drops near ε_c .

Figure 3 shows schematically the dependence (following from equation (10)) of the acoustic phonon frequencies ω on k at $k \sim k_s$ and the corresponding spectral density of phonons, $g_{ph}(\omega)$ (at the increased scale of anomalies). The broken curves in figure 3 correspond to $\omega(k)$ or $g_{ph}(\omega)$ for $k > k_s$. It is clear that the dispersion of $\omega(k)$ near k_s brings about a specific behaviour of the low-frequency $g_{ph}(\omega)$, which resembles that in the presence of quasi-local vibrations. However, the sharp sensitivity of the considered effects to the sign and magnitude of the parameter $\varepsilon_F - \varepsilon_c$ (e.g. to the composition of an alloy) should be a peculiar characteristic of these effects.

3. Calculations of the polarization operator and singular contributions to the dynamic matrix for the Williams and Weaire model

To illustrate the above general results, as well as to study the Kohn anomalies in the ETT region, in this section we present explicit expressions of the quantities $\Pi_{k+g_1, k+g}$ and the singular contributions to $\mathbf{D}(k)$ for the Williams and Weaire model [15] corresponding to the interaction of electrons with only one BZ face. At small v this model exactly describes all the phenomena connected with the ETT, since in this case the contributions of different BZ faces are separated and enter into the results additively [2].

As was discussed in [2], for the most interesting case of small $k \approx k_{max}v$ the singular contributions Π^s are present only in the $\Pi_{k+g, k+g}$ and $\Pi_{k-g, k+g}$ components in equation (2). Using the two-wave approximation for the Green function G and other methods and approximations described in [2], after summing over ω_n in equation (2) and redenoting the integration variable, $p \rightarrow p + k/2$, we obtain

$$\Pi_{k+g, k+g} = \sum_{p, \sigma} (g_- h_+ R_{11} + g_+ g_- R_{12} + h_+ h_- R_{21} + g_+ h_- R_{22}) \quad (11)$$

$$\Pi_{k-g, k+g} = \sum_{p, \sigma} v_0 (R_{11} - R_{12} - R_{21} + R_{22}) / 4f_+ f_-.$$

Here $v_0 = V(g)/\varepsilon_c^0$, the functions f , g , h and R_{ij} are

$$f = f(z) = (v^2 + 4z^2)^{1/2} \quad g(z) = (f - 2z)/2f \quad h(z) = (f + 2z)/2f \quad (12a)$$

$$R_{ij} = [n(\varepsilon_i^-) - n(\varepsilon_j^+)] / (\varepsilon_j^+ - \varepsilon_i^-) \quad (12b)$$

z is the same as in equation (6) and the '+' or '-' index of the functions stand for the replacement of the p argument with $p + k/2$ or $p - k/2$; thus, $f_+ = f(z + q/2)$, where $q = k \cdot p_c / p_c^2$, etc. The singularities in expressions (11) are, evidently, connected only with the non-analyticity of the R_{ij} functions (12b), which substantiates using the estimate (3) for the singular contributions Π^s .

If we go over in equations (11) from p to the variables ρ and z used in equation (6) and integrate over ρ , the $\Pi_{k\pm g, k+g}$ values take the form

$$\Pi_{k\pm g, k+g} = \sum_{i,j=1}^2 \Pi_{k\pm g, k+g}^{ij} = \sum_{i,j=1}^2 (m_* p_c / 2\pi^2) \int dz F_{\pm g, g}^{ij}(z) J_{ij}(z) \tag{13}$$

$$J_{ij} = \theta(-\varphi_{ij}) + \theta(\varphi_{ij})\theta(\Delta_i^\dagger) \{ 2\theta(\chi_{ij}^-) + q_\perp^{-2}(\chi_{ij}^+ - \varphi_{ij}^{1/2}) [1 - \theta(\chi_{ij}^-)\theta(\Delta_j^-)] \}.$$

Here $F_{\pm g, g}^{ij}$ stands for the coefficients of R_{ij} in equations (11), $q_\perp = k_\perp / p_c = (k^2 - q^2 p_c^2)^{1/2} / p_c$ is the transverse component of k in p_c units, while the functions $\Delta_i^\dagger(z)$, $\chi_{ij}^\pm(z)$ and $\varphi_{ij}(z)$ are

$$\Delta_i^\dagger = \alpha - z_\pm^2 + f_i^\dagger \quad f_i^\dagger = (-1)^{i+1} f_\pm \quad \chi_{ij}^\pm = \chi_{ij} \pm q_\perp^2 \tag{14a}$$

$$\chi_{ij} = f_i^+ - f_j^- - 2qz \quad \varphi_{ij} = q_\perp^4 + q_\perp^2(q^2 + 4z^2 - 2f_i^+ - 2f_j^- - 4\alpha) + \chi_{ij}^2. \tag{14b}$$

In the $v = 0$ case, in equations (13) we can put $f^\dagger = 2z_\pm$, and integration over z yields the known Lindhard expression for Π .

In studying the dependence of the Π_{ij} singularities on ϵ_F or $\alpha = \epsilon_F / \epsilon_c^0 - 1$, it is more convenient to consider the derivatives $d\Pi^j/d\alpha$ instead of the Π^j values in equations (13):

$$\frac{d}{d\alpha} \Pi_{k\pm g, k+g}^j = (m_* p_c / 2\pi^2) \int dz \varphi_{\pm g, g}^{-1/2}(z) F_{\pm g, g}^j(z) \theta(\varphi_{ij}) \theta(\Delta_i^\dagger) [1 - \theta(\chi_{ij}^-)\theta(\Delta_{ij})]. \tag{15}$$

The expressions (13)–(15) allow one to study the singularities of Π and $\mathbf{D}(k)$ in equation (1) in an explicit form.

Let us consider, for example, the intraband term Π^{11} in equation (15). In this term the ETT corresponds to the FS touching the BZ at $\alpha = -v$, and $N(\epsilon_F)$ is singular at $\delta = -(\alpha + v) > 0$: $N_s(\delta) = -(2v\delta)^{1/2} \theta(\delta)$. Let us first discuss the Kohn anomalies in ω_k near the ETT. For the considered term Π^{11} these anomalies are located on the surface in k -space determined by the relation

$$\epsilon_1[(k + g)/2] = \epsilon_1(p_c + k/2) = \epsilon_F \tag{16}$$

while the singular contribution to equation (15) arises from the region of small z values. It is clear from geometric considerations that the Kohn anomalies in Π_{11} at $\delta > 0$ occur only for not too small $q > q_0 = (\alpha^2 - v^2)^{1/2} \approx (2v\delta)^{1/2}$. Therefore, we assume q to be not too small: $v|\delta| \leq q^2 < v$. For these q values the relation (15) for Π_{11} can be written as

$$\frac{d}{d\alpha} \Pi_{k\pm g, k+g}^{11} = (m_* p_c / 2\pi^2) F_{\pm g, g}^{11} J \tag{17}$$

where $F_{g, g}^{11} = 1/4$, $F_{-g, g}^{11} = V(g)/4|V(g)|$, $J = (J_s - J_t)/2q_\perp$, the J_t term has no Kohn

singularities at small $\gamma = [\epsilon_1(\mathbf{p}_c + \mathbf{k}/2) - \epsilon_F]/\epsilon_c^0$, and J_s is expressed in terms of the first-order elliptic integral $F(\kappa)$ [19]:

$$\gamma > 0 \quad J_s = 2(A^2 + 4B\gamma)^{-1/4} F(y^{1/2}) \tag{18a}$$

$$\gamma < 0, A > 0 \quad J_s = 2^{3/2}[A + (A^2 + 4B\gamma)^{1/2}]^{-1/2} F(y^{-1/2}) \tag{18b}$$

$$F(\kappa) = \int_0^{\pi/2} (1 - \kappa^2 \sin^2 \varphi)^{-1/2} d\varphi. \tag{18c}$$

Here $y = \frac{1}{2}[1 + A(A^2 + 4B\gamma)^{-1/2}]$ while $A = A(q, q_\perp)$ and $B = B(q, q_\perp)$ are
 $A = 8(\delta - \gamma + 3q^4/8v^3)/q_\perp^2 v \quad B = 8(\delta - \gamma + 3q^2/2v)/q_\perp^2 v^3. \tag{19}$

In equations (1) and (15)–(19), the Kohn anomaly of conventional form, $\omega_k^{sK} \sim \gamma \ln |\gamma|$, corresponds to small values of $|4B\gamma| \ll A^2$, when

$$J_s \rightarrow |A|^{-1/2} [\ln(A^2/B|\gamma|) + 4 \ln 2]. \tag{20}$$

However, if the A value in equation (19) is small, the singularity enhances. Thus, for $A^2 \ll 4B\gamma$, from equation (18a) we have

$$J_s \rightarrow (4/B\gamma)^{1/4} F(1/2) = 2.6(B\gamma)^{-1/4}. \tag{21}$$

which, according to equations (1) and (17) means: $\omega_k^{sK} \sim \gamma^{3/4}$. Physically, this enhancement of the Kohn singularity up to the power 3/4 is connected with the flattening of the FS in the anomaly region: one can see that the value $A = 0$ corresponds to the point of vanishing of one of the reciprocal radii of curvature of the surface (16).

It is also seen from equations (19) and (20) that at small δ and q the amplitude of a conventional logarithmic Kohn anomaly may increase sharply, changing with δ and q as $A^{-1/2} \sim (v\delta + 3q^4/8)^{-1/2}$. This may correspond qualitatively to the effects of the ‘giant Kohn anomaly in sound’, observed in a number of metals, Cd, Zn, γ -Sn [20], for which the proximity of ϵ_F to the ETT point is characteristic [11].

Let us use the same example to discuss the singularities over δ (or η) in Π and $\mathbf{D}(k)$ at small $q \ll q_0 = (2v\delta)^{1/2}$ (i.e. $k \ll k_s$ in the notation of section 2). If we consider, for definiteness, only not too large $q_\perp, qq_0 > q^2 + vq_\perp^2/2$, then in relation (17) the expansion of J in powers of q/q_0 and q_\perp/q_0 has the form

$$J = (v/2q_0)[1 + (q^2 - vq_\perp^2/2)/3q_0^2 + \dots] \tag{22}$$

which, according to equation (17), means

$$\Pi_s^{11}(q) = C_1(v\delta)^{1/2} + C_2q^2(v\delta)^{-1/2} + \dots \tag{23}$$

where C_1 and C_2 are constants. If, upon substitution of Π into equation (1), the contribution \mathbf{D}_s to $\mathbf{D}(k)$ that is singular in δ had the same order as that in Π_s , the singularities in the elastic constants c_{ij} would have the form $c_{ij}^s \sim (v\delta)^{-1/2}$ instead of the true one $c_{ij}^s \sim (v\delta)^{1/2}$ found in [2].

However, actually, at small k values the singularities in $\mathbf{D}(k)$ are weaker than those in Π because of cancellation of the main terms in the summation over g_1 and g in equation (1b). Thus, in the case of small v under discussion, for the singular contribution Φ_s in equation (1b) we have

$$\begin{aligned} \Phi_s^{\alpha\beta}(k) = \sum_g [g_\alpha(V_{k+g}\Pi_{k+g,k+g}^s - V_{k-g}\Pi_{k-g,k+g}^s) \\ + k_\alpha(V_{k+g}\Pi_{k+g,k+g}^s + V_{k-g}\Pi_{k-g,k+g}^s)](k_\beta + g_\beta)V_{k+g}^* \end{aligned} \tag{24}$$

(for simplicity, the crystal is assumed to be monatomic). If, for the discussed small k values, in equation (24) we put $V_{k+g} \approx V_g$, $V_{k-g} \approx V_{-g} = V_g^*$ and use the main approximation in the $v\delta$ parameter in Π , then the coefficient of g_α , i.e. the main term of equation (24), vanishes. Since the expansion in k of the expression (24) begins, evidently, at terms of order k^2 , this results in the above-noted weakening of singularities near the ETT in $\mathbf{D}(k)$ at small k , as compared with $\Pi(k)$.

Let us now consider in the same model the problem of singularities near the ETT in powers of frequency averaged over the BZ, $f = \langle \omega_k^n \rangle$, e.g. in the zero-point phonon energy $E_{zp} \sim \langle \omega_k \rangle$. Let us denote f_s^+ the non-analytic part of f at $\delta > 0$, and f_s^- at $\delta < 0$. At $\delta > 0$ all the ω_k have a non-analytic part $\omega^s \sim (v\delta)^{3/2}$ at $k > k_s = k_{\max}(v\delta)^{1/2}$, while at $k < k_s$, $\omega^s \sim c_{ij}^s k \sim k(v\delta)^{1/2}$. In integration over the BZ, the contribution of the region $k < k_s$ is small, and $f_s^+ \approx \text{const}(v\delta)^{3/2}$, which agrees with the result given by Dagens [14]. However, for $\delta < 0$ our conclusion disagrees with that of Dagens. He assumed that the singular contributions to $\langle \omega_k^n \rangle$ and to the polarization operator $\langle \Pi \rangle$ are proportional to each other:

$$\langle \omega_k^n \rangle_s = f_s = \text{const} \langle \Pi_s \rangle. \tag{25}$$

Calculating the contribution to $\langle \Pi_s \rangle$ corresponding to the Kohn anomalies, he obtained (in our notation) $\langle \Pi_s \rangle = \text{const}(-\delta)^{3/2} \theta(-\delta)$, whence he concluded that $f_s^- = \text{const}(-\delta)^{3/2}$, i.e. $f_s^- \sim |\delta|^{3/2}$, too.

The direct calculation of the $\langle \Pi_s^{(1)} \rangle$ value according to equation (15) agrees with Dagens' above result for $\langle \Pi_s \rangle$. However, the main assumption (25) in the case under consideration, $p_c = g/2$, is not fulfilled. The calculations show that the discussed singular contribution of the Kohn anomalies to $\langle \Pi_s \rangle$ arises from the region of small $(k/k_{\max}, q, q_\perp) \approx v\delta^{1/2}$ in which the contribution of Π_s to $\mathbf{D}(k)$ was mentioned to be multiplied by k^2 , which corresponds to the contribution $\omega^s \sim k\Pi_s$ in the frequency. Thus, in calculating $f_s = \langle \omega_k^n \rangle_s$, the quantity $k\Pi_s$, rather than Π_s , should be integrated over the BZ, which results in the appearance of additional factors $|\delta|^{1/2}$ or $|v\delta|^{1/2}$ in the result. Therefore, the singular term f_s^- turns out to be proportional to $\delta^2 v^{7/2}$ or to $\delta^2 v^4$, being much less than $f_s^+ \sim (v\delta)^{3/2}$ in both powers δ and v .

Thus, if the ETT corresponds to the BZ symmetry point $p_c = g/2$, the singularities at the ETT in $f = \langle \omega_k^n \rangle$ are apparently 'one-sided', as in all the other physical characteristics of a crystal [2, 3, 6]: $f_s = f_s^+ = \text{const}(v\eta_\pm)^{3/2}$. If $p_c \neq g/2$, the estimate of the f_s^- contribution generally speaking needs separate consideration. However, our results allow one to assume that, even if the term $f_s^- \sim |\eta|^{3/2}$ is present in this case, it will be much less than the 'normal' f_s^+ one in the v parameter.

4. Singularities near the ETT in thermodynamic properties and anharmonic effects

The peculiarities of the phonon spectra discussed in sections 2 and 3 must give rise to anomalies in the temperature and concentration dependences of different characteristics of the crystal. Let us first consider the specific heat $C(T)$. The early dispersion of phonons at $k \sim k_s = k_{\max}(v\eta_\pm)^{1/2}$ mentioned in section 2 causes the conventional low-temperature expression $C = \gamma T + \alpha T^3$ to hold true only at very low $T \ll T_s = T_D(v\eta_\pm)^{1/2} \ll T_D$ (where T_D is the Debye temperature), while at $T \sim T_s$ anomalies in the $C(T)$ dependence similar to those observed in the case of quasi-local impurity levels will arise. So, the following

limiting dependences hold for the phonon contribution $C_{\text{ph}}(T)$ to the specific heat (per atom):

$$T \ll T_s \quad C_{\text{ph}} = A_{1r}T^3 + A_0(v\eta_{\pm})^{1/2}T^3 \quad (26a)$$

$$T_s \ll T \ll T_D \quad C_{\text{ph}} = A_{1r}T^3 + A_1(v\eta_{\pm})^{3/2}T \quad (26b)$$

$$T_D \ll T \quad C_{\text{ph}} = 3 - [A_{2r} - A_2(v\eta_{\pm})^{3/2}]T^{-2}. \quad (26c)$$

Here the coefficients $A_{1r}, A_{2r} > 0$ correspond to the regular contribution $\omega_{k\lambda, \text{reg}}^2$ to equation (10), while the constants A_i are positive (negative) if the singular part $N_s(\epsilon)$ rises (drops) when ϵ approaches ϵ_c , as occurs in the NFE model of sections 2 and 3 at $\alpha < -v$ ($\alpha > v$).

Let us discuss the anomalies in the thermal expansion coefficients β_i and the temperature derivatives of the elastic constants $\pi_{ij} = dc_{ij}/dT$. The quantities $\beta_i = du_i/dT$ (where u_i is a uniform spontaneous strain) are related to the generalized pressures p_i (the derivatives over u_i of the free energy density F) as

$$\beta_i = \sum_j (c^{-1})_{ij} dp_j/dT = \beta_i^e + \beta_i^{\text{ph}} \quad (27)$$

$$p_i = -\partial F/\partial u_i = -\partial(F_e^* + F_{\text{ph}})/\partial u_i.$$

Here c^{-1} is the ‘compliance’ matrix (the inverse of the elastic constant matrix) while F_e^* and F_{ph} are the contributions of electronic excitations and phonons to F (see e.g. [11]). The electronic contributions β_i^e were discussed earlier [2, 3, 11]. Near the ET they increase as $\eta_{\pm}^{-1/2}$, but their absolute values are usually small and they are noticeable only at lowest $T \ll (T_D^3/\epsilon_F)^{1/2}$. Below we shall consider only the phonon contribution β_i^{ph} , omitting the ‘ph’ superscript for brevity: $\beta_i = \beta_i^{\text{ph}}$.

The elastic constant c_{ij} can be written as a sum of the c_{ij}^0 term corresponding to the regular crystal at $T = 0$ without allowing for phonons, the phonon contribution c_{ij}^{ph} and the ‘quasi-harmonic’ term c_{ij}^{qh} describing the variation of c_{ij}^0 due to thermal expansion of the crystal [21]:

$$c_{ij}(\Omega, T) = c_{ij}^0(\Omega_0) + c_{ij}^{\text{ph}}(\Omega_0, T) + c_{ij}^{\text{qh}}(\Omega_0, T) \quad (28a)$$

$$c_{ij}^{\text{ph}} = \partial^2 F_{\text{ph}}/\partial u_i \partial u_j \quad c_{ij}^{\text{qh}} = -\sum_k p_k \partial c_{ij}^0/\partial p_k = -\sum_k p_k (c^{-1})_{kl} \partial c_{ij}^0/\partial u_l. \quad (28b)$$

Here Ω is the atomic volume, Ω_0 is its value at $T = 0$, and we neglect the contribution of electronic excitations, $c_{ij}^{e*} \sim c_{ij}^0(T/\epsilon_F)^2$, as well as higher-order anharmonic contributions.

Following [21], we can express the derivatives of F_{ph} over u_i in terms of those of the dynamic matrix, $\mathbf{D}_i = \partial \mathbf{D}/\partial u_i$ and $\mathbf{D}_{ij} = \partial^2 \mathbf{D}/\partial u_i \partial u_j$:

$$p_i^{\text{ph}} = -\frac{\partial F_{\text{ph}}}{\partial u_i} = -\frac{\hbar}{4N\Omega_0} \sum_{k\lambda} \frac{1}{\omega_{k\lambda}} (2n_{k\lambda} + 1) D_i^{\lambda\lambda} \quad (29a)$$

$$c_{ij}^{\text{ph}} = \frac{\partial^2 F_{\text{ph}}}{\partial u_i \partial u_j} = \frac{\hbar}{4N\Omega_0} \sum_{k\lambda} \left[\frac{2n_{k\lambda} + 1}{\omega_{k\lambda}} D_{ij}^{\lambda\lambda} - \left(\frac{2n_{k\lambda} + 1}{\omega_{k\lambda}^3} + \frac{n_{k\lambda}(n_{k\lambda} + 1)}{T\omega_{k\lambda}^2} \right) D_i^{\lambda\lambda} D_j^{\lambda\lambda} \right. \\ \left. + \sum_{\mu \neq \lambda} \frac{1}{(\omega_{k\lambda}^2 - \omega_{k\mu}^2)} \left(\frac{2n_{k\lambda} + 1}{\omega_{k\lambda}} - \frac{2n_{k\mu} + 1}{\omega_{k\mu}} \right) D_i^{\lambda\mu} D_j^{\mu\lambda} \right]. \quad (29b)$$

Here $n_{k\lambda} = [\exp(\hbar\omega_{k\lambda}/T) - 1]^{-1}$ is the Bose function and $D_i^{\lambda\mu}$ denotes the matrix element

between phonon states with polarization vectors $e_{k\lambda}$ and $e_{k\mu}$; thus $D_i^{\lambda\mu} = (e_{k\lambda}, \mathbf{D}_i e_{k\mu})$.

In estimating singular terms in equations (27)–(29), consider that differentiation of the small value $\eta = \varepsilon_T/\varepsilon_c - 1$ over u_i converts it generally speaking into a not small one $\partial\eta/\partial u_i$. It transforms the $\eta^{n+1/2}$ factor into $\eta^{n-1/2}\partial\eta/\partial u_i$, i.e. enhances the singularity. Thus, in estimating the most singular contributions in equations (29), the frequencies $\omega_{k\lambda}$ may be replaced with the regular terms $\omega_{k\lambda, \text{reg}}$ from equation (10), \mathbf{D}_i and \mathbf{D}_{ij} may be understood as derivatives only of the non-analytical term \mathbf{D}_s in equations (8) and (10), and in equation (29b) one can retain only the most singular first term with $D_{ij}^{\lambda\lambda}$. As in equations (26), the form of the singular contributions β_i^s and π_{ij}^s will be different for different T :

$$T \ll T_s \quad \beta_i^s = A_0^i \eta_{\pm}^{-1/2} T^3 \quad \pi_{ij}^s = B_0^{ij} \eta_{\pm}^{-3/2} T^3 \quad (30a)$$

$$T_s \ll T \ll T_D \quad \beta_i^s = A_1^i \eta_{\pm}^{1/2} T \quad \pi_{ij}^s = B_1^{ij} \eta_{\pm}^{-1/2} T \quad (30b)$$

$$T_D \ll T \quad \beta_i^s = A_2^i \eta_{\pm}^{1/2} \quad \pi_{ij}^s = B_2^{ij} \eta_{\pm}^{-1/2}. \quad (30c)$$

To find the total β_i or π_{ij} , one should add the regular contributions β_i^r or π_{ij}^r (of the form $T^3 A_{1r}^i$ or $T^3 B_{1r}^{ij}$ at $T \ll T_D$ and A_{2r}^i or B_{2r}^{ij} at $T_D \gg T$) to expressions (30).

If the reduced pseudopotential v is small (as in the cases treated in sections 2 and 3), in estimating derivatives \mathbf{D}_i and \mathbf{D}_{ij} in equations (29) one should distinguish between the cases of bulk strain $u_1 = \Delta\Omega/\Omega$ and shear strain $u_s \neq u_1$ [2]. In the zero approximation over v the parameter $\eta^{(0)} = p_T^2/p_c^2 - 1$ does not change under uniform compression. Therefore, the non-zero contribution to $\partial\eta/\partial u_1$ arises only from the terms with $\partial v/\partial u_1$, so that $\partial\eta/\partial u_1$ is first order in v . At the same time, the derivatives of η with respect to the shear strain u_s are not small: $\partial\eta^{(0)}/\partial u_s = -\partial \ln \varepsilon_c^0/\partial u_s \sim 1$. Therefore, for cubic or weakly anisotropic metals, in which thermal expansion corresponds to bulk strain only, the coefficients A_0, A_1, A_2 in equations (29) have orders $v^{3/2}, v^{5/2}, v^{5/2}$, respectively. In anisotropic metals the anomalies in the spontaneous shear strain may be $1/v$ times as strong as those in the bulk strain, so that β_i can even change sign near the ETT [11]. By analogous reasoning, the anomalies in the temperature derivatives of shear constants, $\pi_{ss'}$, are generally $1/v^2$ times as strong as those for the bulk modulus. Thus the values $B_0^{ss'}, B_1^{ss'}, B_2^{ss'}$ in equations (30) are of order $v^{1/2}, v^{3/2}, v^{3/2}$, respectively, while for $\pi_{11} = dB_{11}/dT$, we have $(B_0^{11}, B_1^{11}, B_2^{11}) \sim (v^{5/2}, v^{7/2}, v^{7/2})$.

Let us present explicit expressions for the singular contributions β_i^s and π_{ij}^s in equations (29) for the NFE model considered in sections 2 and 3. At not too low temperatures $T > T_s$, in the integrals over the BZ (29) only the values $k > k_s$ are significant, for which the singular part \mathbf{D}_s of the dynamic matrix is given by equation (8). For the case of monotomic cubic crystals, e.g. BCC or FCC, this expression takes the form

$$D_s^{\alpha\beta} = \delta_{\alpha\beta} (2b/3M) n_c \varepsilon_c^0 v^2 F(\alpha/v, v) \quad (31)$$

where n_c is the multiplicity of the critical vector $g = g_c$ in the reciprocal lattice. As has been noted above, in finding the singular terms p_i^s and c_{ij}^s in equations (29), one can understand by \mathbf{D}_i and \mathbf{D}_{ij} the derivatives of only the non-analytical term \mathbf{D}_s (31), while in equation (29b) only the first term with $D_{ij}^{\lambda\lambda}$ may be retained. Then the values p_i^s and c_{ij}^s in equations (29) turn out to be proportional to the mean square of the atomic thermal displacements along each of the axes, $\langle x^2 \rangle$, and for the β_i^s and π_{ij}^s values we have

$$\beta_i^s = - \left(\frac{d}{dT} \langle x^2 \rangle \right) \frac{1}{B\Omega_0} b n_c \varepsilon_c^0 g^2 v^2 \frac{\partial}{\partial u_i} F(\alpha/v, v) \quad (32a)$$

$$\pi_{ij}^s = \left(\frac{d}{dT} \langle x^2 \rangle \right) \frac{1}{\Omega_0} b n_c \varepsilon_c^0 g^2 v^2 \frac{\partial^2}{\partial u_i \partial u_j} F(\alpha/v, v). \quad (32b)$$

In the case of non-cubic metals, the product $\langle x^2 \rangle g^2$ in equations (32) is replaced by an analogous expression corresponding to the lattice symmetry. Thus, for uniaxial, e.g. HCP, crystals this expression has the form $\langle x_{\parallel}^2 \rangle g_{\parallel}^2 + \langle x_{\perp}^2 \rangle g_{\perp}^2$, where the subscripts \parallel and \perp correspond to directions parallel and transverse to the main axis. The $\langle x^2 \rangle$ values vary smoothly with alloy composition and can be estimated, for example, using the Debye model.

In estimating π_{ij}^s , we considered above only the phonon contribution (29b) in equation (28a). One can easily see that allowing for the quasi-harmonic term $\pi_{ij, \text{qh}}^s$ does not change this estimate. At $T < T_s$ the term $\pi_{ij, \text{qh}}^s$ is $\eta^{\pm 1/2}$ times smaller than $\pi_{ij, \text{ph}}^s$, while at $T > T_s$ both terms have the same η dependence. So, at small ν in cubic or weakly anisotropic crystals the derivatives of shear constants, $\pi_{ss', \text{qh}}^s$, are ν times smaller than $\pi_{ss', \text{ph}}^s$.

Let us discuss the relations (30). First, we see that $\beta_i(T)$ and $\pi_{ij}(T)$, as well as the specific heat $C(T)$, display a characteristic change in their temperature dependence at $T \sim T_s \sim T_D(\nu\eta_{\pm})^{1/2}$. In β_i and, in particular, in π_{ij} the singularities near the ETT are much stronger than those in $C(T)$. We also see that, unlike the majority of anomalies at the ETT discussed earlier, the singularities in π_{ij} (in particular, for the derivatives of the shear moduli, $\pi_{ss'}$) should also be large at not small T , changing with η in the same way as, for example, the low-temperature thermopower coefficient $\alpha(\eta) \sim \eta^{\pm 1/2}$ [6].

In discussing the temperature derivatives of the phonon frequencies, $d\omega/dT$, we shall consider for simplicity only those for optical phonons with $k = 0$ (in non-monatomic, e.g. HCP, crystal cells). The atomic displacements in these phonon modes correspond to the uniform 'internal' strain u_{μ} , analogous to the acoustic strain u_i , and within the harmonic approximation their frequencies ω_{μ} (similarly to the elastic constants c_{ij}) can be found by differentiating the energy E (per atom) over u_{μ} . Thus, for the HCP crystal with identical atoms, the frequencies ω_c and ω_a of homogeneous vibration of sublattices along and transverse to the hexagonal axis can be found from [22]:

$$M\omega_c^2 = (\partial^2 E / \partial u_c^2)_{\Omega} \quad M\omega_a^2 = (\partial^2 E / \partial u_a^2)_{\Omega}. \tag{33}$$

The analogy between the $M\omega_{\mu}^2$ and c_{ij} values is also retained in considering the anharmonic contributions. Thus it is clear from the expression for the anharmonic shifts of the phonon frequencies $\Delta\omega_{\mu}$ and for the free energy $F(u_{\mu}, T)$ (given, e.g. by equations (35.2), (35.4) and (34.1) in [23]) that the four-phonon contribution to $\Delta\omega_{\mu}$ (being, as mentioned, the most singular one over the parameter η) is given just by the first term on the RHS of equation (29b) with replacement of the matrix elements $D_{ij}^{\lambda\lambda} = (\partial^2 \mathbf{D} / \partial u_i \partial u_j)_{\lambda\lambda}$ by $D_{\mu\mu}^{\lambda\lambda} = (\partial^2 \mathbf{D} / \partial u_{\mu}^2)_{\lambda\lambda}$. Therefore, for the singular contributions π_{μ}^s to $\pi_{\mu} = d\omega_{\mu}/dT$ within the temperature intervals in equations (26a), (26b) and (26c), we obtain expressions analogous to those in equations (30):

$$\pi_{\mu}^s = B_0^{\mu} \eta_{\pm}^{-3/2} T^3 \quad \pi_{\mu}^s = B_1^{\mu} \eta_{\pm}^{-1/2} T \quad \pi_{\mu}^s = B_2^{\mu} \eta_{\pm}^{-1/2}. \tag{34}$$

If the pseudopotential ν is small, the B_i^{μ} dependence on ν is generally speaking the same as that for the B_i^1 values in equations (30) corresponding to the bulk modulus ($B_0^{\mu}, B_1^{\mu}, B_2^{\mu}$) $\sim (\nu^{5/2}, \nu^{7/2}, \nu^{7/2})$. This is because the derivatives of the parameter η over the internal strain u_{μ} , as well as its volume derivatives $\partial\eta/\partial u_1$, are generally proportional to ν [2].

Using expression (8), it is possible to obtain explicit relations (analogous to equation (32b)) for π_{μ}^s within the NFE model described in sections 2 and 3. Thus, for

the HCP crystal with identical atoms, at $T > T_s$, by analogy with equations (32b) and (33), we obtain

$$\frac{d}{dT}\{\omega_a^2, \omega_c^2\} = \frac{d}{dT}(\langle x_{\parallel}^2 \rangle g_{\parallel}^2 + \langle x_{\perp}^2 \rangle g_{\perp}^2) \frac{4b}{M\Omega} n_c \varepsilon_c^0 v^2 \left\{ \frac{\partial^2}{\partial u_a^2}, \gamma^{-2} \frac{\partial^2}{\partial u_c^2} \right\} F\left(\frac{\alpha}{v}, v\right) \quad (35)$$

where $\gamma = c/a$ is the tetragonality parameter. Equations (34) and (35) show that near the ETT the high-temperature derivatives $\pi_{\mu} = d\omega_{\mu}/dT$ rise as $\eta_{\pm}^{-1/2}$, as also do $\pi_{ij} = dc_{ij}/dT$. However, at small v the anomalies in π_{μ} are v^2 times smaller than those in the shear constant derivatives.

The relations (34) hold for the phonons with small $k < k_s$. For phonons with large $k > k_s$, by analogy with the results of sections 2 and 3, one could expect weakening of anomalies over η . Thus, for $T > T_s$ and $k > k_s$, the estimate of the quasi-harmonic non-analytical contribution $\pi_{kl, \text{qh}}^s$ to $\pi_{kl} = d\omega_{kl}/dT$ yields $\pi_{kl, \text{qh}}^s \sim \eta_{\pm}^{1/2}$. Therefore, one should expect the strongest anomalies in the anharmonic characteristics for the phonons with small k values.

5. Model calculations for Li-Mg and Cd-Mg alloys

In this section we illustrate the scale and character of the discussed anomalies in the anharmonic effects by model calculations for disordered Li-Mg and Cd-Mg alloys. With changing concentration x in these alloys, ETT apparently takes place: the anomalies assigned to the ETT were observed in the BCC $\text{Li}_{1-x}\text{Mg}_x$ alloys at $x_c = 0.19$ [7, 12] and in the HCP $\text{Cd}_{1-x}\text{Mg}_x$ alloys at $x_{c1} = 0.06$ and $x_{c2} = 0.12$ [9]. Since both alloys consist of metals with a relatively weak electron-ion interaction, they can be treated as model systems for studying the SDS effects in NFE alloys. Earlier, model calculations for the Li-Mg alloys were used in estimating the SDS anomalies in kinetic [6] and elastic [2] characteristics. Here we apply the same model to estimate the SDS effects in the high-temperature values of $\beta_i(T)$, $\pi_{ij}(T)$ and $\pi_{\mu}(T)$. In addition, we shall discuss some experimental data on microhardness and hardness in the Li-Mg and Cd-Mg alloys, which apparently point to noticeable manifestations of the SDS effects in these quantities, too.

We shall estimate β_i^s , π_{ij}^s and π_{μ}^s by relations (32) and (35) using the NFE alloy model and approximations described in [2]. Within this model all the basic parameters of the $A_{1-x}B_x$ alloy, i.e. the valence $z(x)$, the atomic volume $\Omega(x)$, the effective pseudopotential $w(x)$, the Debye temperature $T_D(x)$, the non-singular contributions to the elastic constants $c_{ij}(x)$, etc. are described in the simplest mean crystal approximation (MCA): $z(x) = z_A(1-x) + z_Bx$, etc. The pseudopotentials $w(\mathbf{q})$ of pure metals are taken in the Animalu-Heine form (equation (46) in [2]). The parameters $w(\mathbf{q})$ and $\tilde{V}(\mathbf{g})$ for Li and Mg are given in [2]; for Cd they were estimated similarly and are $r_0 = 1.575$ au, $U = 3.48$, $q_0 = 2p_F = 1.481$ au, while the value $\lambda = \Gamma_0 Z_0 / \varepsilon_0$ in equation (12b) of [2] for Cd was put equal to $\lambda_{\text{Cd}} = 1.25$ to bring into coincidence the position of the ETT in the $\text{Cd}_{1-x}\text{Mg}_x$ alloy, corresponding to FS overflow over the BZ face at point L, with the observed $x_{c2} = 0.12$ [9, 11]. To illustrate the sensitivity of the results to the type and anisotropy of the crystalline structure, the calculations were carried out for the BCC, FCC and HCP Li-Mg and HCP Cd-Mg alloys. For the $c/a = \gamma$ parameter in the pure HCP metals we use the experimental values ($\gamma_{\text{Li}} = 1.633$, $\gamma_{\text{Mg}} = 1.623$, $\gamma_{\text{Cd}} = 1.886$) while for the alloys $\gamma(x)$ was found in the MCA. The $\langle x_i^2 \rangle$ values in equations

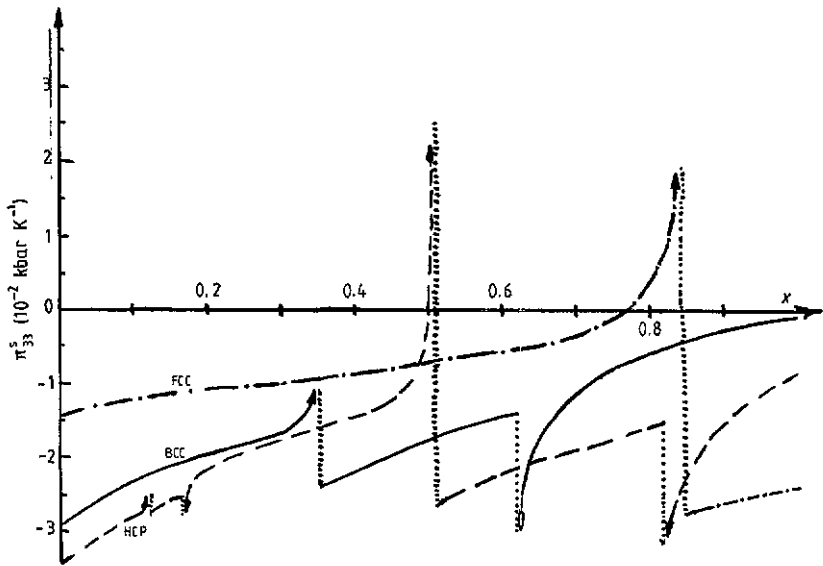


Figure 4. High-temperature values of the non-analytical contributions $\pi_{33}^i = (dB_{33}/dT)_s$ for the $\text{Li}_{1-x}\text{Mg}_x$ alloy model described in section 5. The curves correspond to the BCC (—), FCC (---) or HCP (-·-·-) structures.

(32) and (35) were calculated in the Debye model (neglecting their anisotropy for the HCP crystals). For definiteness, we present the results only for the high temperatures $T > T_D$, when $\langle x^2 \rangle$ is proportional to T , and in the Debye model $\langle x^2 \rangle = 3\hbar^2 T/MT_D^2$. For T_D , the experimental values 336, 387 and 212 K were used in pure Li, Mg and Cd, respectively.

The calculation results are presented in figures 4–7. In figures 4 and 5, the ETT points for the Li–Mg alloys correspond to successive touchings and overflows of the FS at the following points of the BZ (and structures): N (BCC); L and X (FCC); M, A' and L (HCP). In these figures we present the temperature derivatives $\pi_{ij} = dB_{ij}/dT$ of only the shear constants, $B_{44} = c_{44}$ and $B_{33} = (c_{11} - c_{12})/2$. In the derivative of the bulk modulus, dB/dT , the anomalies at the ETT, as noted, are v^2 times weaker and are almost imperceptible in the figures (as well as for the $\partial B/\partial\Omega$ values in figure 6 in [2]).

Let us discuss the results for $\pi_{ij}(x)$. In accordance with equations (30) and (32b), the singular part π_{ij}^s close to the x_c points increases as $x_{\pm}^{-1/2}$, where $x_{\pm} = \pm(x - x_c)\theta[\pm(x - x_c)]$, in the model under consideration (which neglects the concentration and temperature smearing of the ETT), and can be either negative or positive. The latter case may be of particular interest in connection with the known problem of the development of elinvar alloys, i.e. those with small $\pi_{ij} = dB_{ij}/dT$ values. As known, in the absence of special reasons, the π_{ij} values are negative, in compliance with the lattice 'softening' with rising T ; see, e.g. [21]. Therefore, if near the ETT the singular contribution $\pi_{ij}^s(x) > 0$, by changing the concentration x near x_c one can generally speaking achieve its compensation with the regular contribution $\pi_{ij}^{reg} < 0$, obtaining for the total $\pi_{ij} = \pi_{ij}^s + \pi_{ij}^{reg}$ any values, e.g. $\pi_{ij} \approx 0$. Note also that then this must hold within the whole high-temperature range of $T > T_D$ and not only in the narrow temperature interval as often happens in conventional magnetic elinvar alloys. Therefore, investigations of the described 'band' mechanism of elinvar behaviour may be quite interesting.

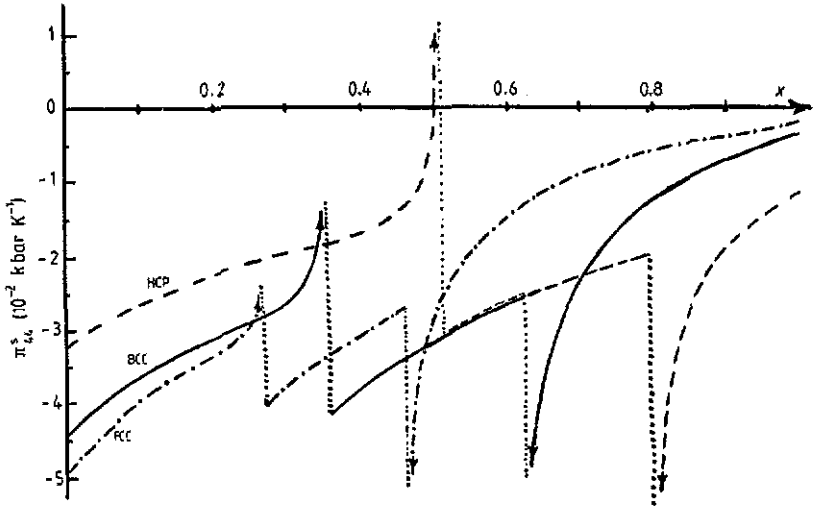


Figure 5. The same as figure 4 but for $\pi_{44}^s = (d\bar{B}_{44}/dT)_s$.

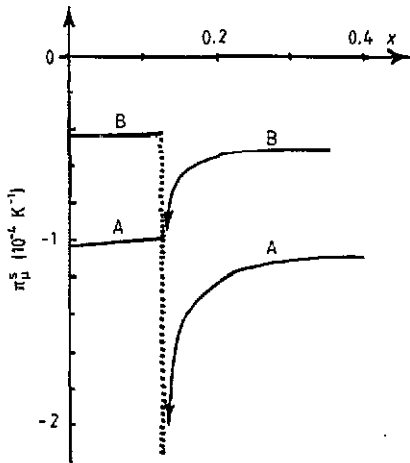


Figure 6. High-temperature values of the non-analytical contributions π_{μ}^s for the $\text{Cd}_{1-x}\text{Mg}_x$ alloy model: (A) $\pi_a = (d\bar{\omega}_a/dT)_s$, (B) $\pi_c = (d\bar{\omega}_c/dT)_s$. Here $\bar{\omega}_{\mu} = \omega_{\mu}/\omega_p$, $\omega_p = (4\pi z^2 e^2/M\Omega)^{1/2}$ and the frequencies ω_c or ω_a correspond to vibrations of atoms with $k=0$ along or transverse to the hexagonal axis c .

It is also seen in figures 4 and 5 that the considered anomalies in $\pi_{ij}(x)$ are characterized by a considerable asymmetry of the concentration dependence with respect to the ETT point x_c . This seems to agree with the experimental data on the $\pi_{44}(x)$ anomalies in the Nb–Mo alloys shown in figure 1.

Figure 6 presents the calculated derivatives $\pi_a = d\bar{\omega}_a/dT$ and $\pi_c = d\bar{\omega}_c/dT$ for the HCP Cd–Mg alloys. The frequency values are given in units of the ion plasma frequency $\omega_p = (4\pi z^2 e^2/M\Omega)^{1/2}$, in which units the experimental ω_a and ω_c values in pure Cd are 0.41 and 0.79, respectively. It is seen that the form of the anomalies in π_{μ} is the same as that in π_{33} , though in the considered case of small ν they are much less than

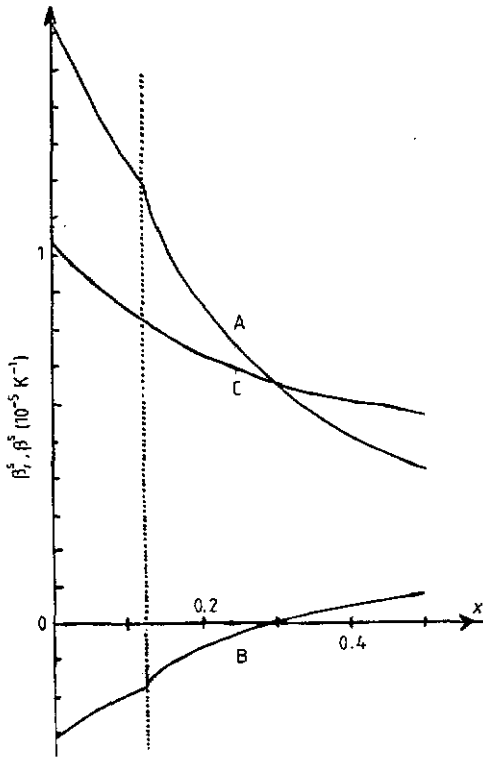


Figure 7. High-temperature values of the non-analytical contributions to the thermal expansion coefficients β_i for the $\text{Cd}_{1-x}\text{Mg}_x$ alloy model: (A) $\beta_{||}^s = (d \ln c/dT)_s$, (B) $\beta_{\perp}^s = (d \ln a/dT)_s$, (C) $\beta^s = \beta_{||} + 2\beta_{\perp}$.

those in π_{ss} . But since the π_{μ}^s term, as noted, rises with v as $v^{7/2}$, at not small v (e.g. in transition-metal alloys) the SDS anomalies in $d\omega_{\mu}/dT$ may be noticeable.

In figure 7 we present the calculated thermal expansion coefficients in anisotropic HCP Cd-Mg alloys: the longitudinal $\beta_{||} = d \ln c/dT$, transverse $\beta_{\perp} = d \ln a/dT$ and volume $\beta = \beta_{||} + 2\beta_{\perp}$ coefficients. In accordance with the remarks made in [11] and section 4, the singularities in $\beta(x)$ are very weak, while in $\beta_{||}^s$ and β_{\perp}^s they are more noticeable and are opposite in sign. Note also that in actual alloys the singularities in β_i can be much stronger than those in figure 7, see, e.g. [1, 11].

Experimental data on $\pi_{ij}(x)$, $\pi_{\mu}(x)$ and $\beta_i(x)$ values for the Li-Mg and Cd-Mg alloys discussed above are not known to us. However, there are some data on related characteristics of anharmonicity, namely microhardness and hardness. Let us discuss these data. In figure 8 we present data on microhardness $H_{\mu}(x)$ in the Li-Mg alloys at room temperature, taken from [12]. It is clear that $H_{\mu}(x)$ has a distinct anomaly near the point of the discussed ETT, $x_{c1} \approx 0.19$, as well as in the vicinity of $x_{c2} \approx 0.54$, which could correspond to the second ETT. For comparison, in figure 8 we also present the results of our model calculations of shear constants in the Li-Mg alloys taken from [2]. It is seen that the observed $H_{\mu}(x)$ and the calculated $B_{33}(x)$ and $B_{44}(x)$ dependences are very similar, differing mainly only by the scale factor H_{μ}/B_{33} , $H_{\mu}/B_{44} \sim 0.02$. Since the H_{μ} value characterizes the transition to an inelastic plastic flow in the stress-strain curve $\sigma(u_s)$, while the shear constants correspond to the initial part $\sigma, u_s \rightarrow 0$ of the

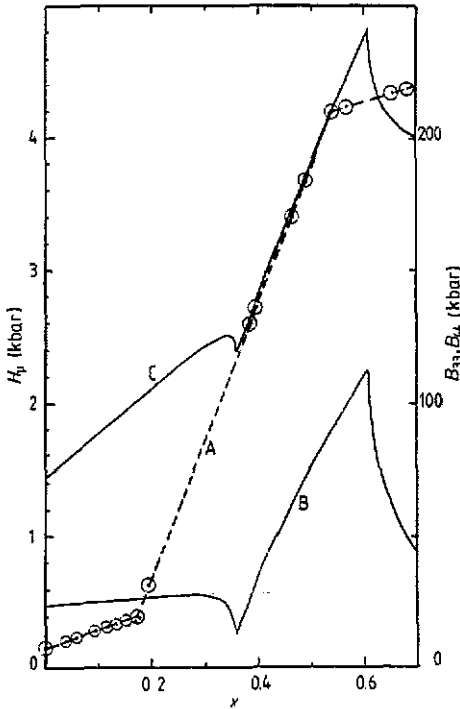


Figure 8. (A) Experimental values of microhardness $H_p(x)$ in the $\text{Li}_{1-x}\text{Mg}_x$ alloys from [12]. (B) The $B_{33}(x)$ values for the $\text{Li}_{1-x}\text{Mg}_x$ alloy model calculated in [2]. (C) The same as (B), but for $B_{44}(x)$.

same curve, the similarity of the concentration dependences seems to be natural and may be treated as a qualitative confirmation of the concepts discussed in [2] and in the present paper.

For the $\text{Cd}_{1-x}\text{Mg}_x$ alloys, the hardness $H(x)$ was recently measured by S V Varyukhin (private communication). Unfortunately, the microstructure and degree of homogeneity of the samples were not studied, so that the results are only qualitative. However, in the region of both the first and second ETT, $x \approx x_{c1}$ and $x \approx x_{c2}$, distinct singularities have been revealed in $H(x)$, which correspond to a stepwise increase of $H(x)$ with x by about 20% and 10%, respectively. These results also seem to confirm the importance of the SDS effects in anharmonic properties.

6. Concluding remarks

Let us make a remark about the effect of the BZ and ETT smearing in disordered alloys on the singularities under consideration. These effects were disregarded above. However, experiments on measuring analogous singularities in kinetic coefficients, in particular in the low-temperature thermopower $\alpha(x)$ (where the singular contributions, as in the π_{ij} values, are proportional to $\eta_{\pm}^{-1/2}$ [6]), have shown that the effects of smearing could be small and do not prevent observations of the SDS anomalies. Thus, in the $\text{Li}_{1-x}\text{Mg}_x$ [7] and $\text{Ti}_{1-x}\text{V}_x$ alloys [9], $\alpha(x)$ near the ETT increases by about an order of magnitude. Therefore, the SDS anomalies in the $\pi_{ij}(x)$ values in real alloys can also be that strong. Apparently, this is confirmed by the data on $\pi_{44}(x)$ in the

$\text{Nb}_{1-x}\text{Mo}_x$ alloys shown in figure 1. The data given in figure 8 also illustrate not too great 'alloy smearing' of the SDS anomalies in the plasticity characteristics.

Let us now summarize the main results of this work. We have studied the singular contributions ω_k^s to phonon frequencies ω_k in the vicinity of the ETT points, and have found that at not small $k > k_s \sim \eta_{\pm}^{1/2}$ they have the form $\omega_k^s \sim \eta_{\pm}^{3/2}$, while at $k < k_s$ the singularities become square root ones, $\omega_k^s \sim \eta_{\pm}^{1/2}$. If the effective pseudopotential v is small, then $k_s \sim (v\eta_{\pm})^{1/2}$, and for $k > k_s$ we present explicit expressions (8) and (9) for the non-analytical corrections \mathbf{D}_s to the dynamic matrix. The explicit expression has been obtained for the polarization operator $\Pi_{k+g_1, k+g}$ in the Williams–Weaire model (or at small v) in the form of one-dimensional integrals (16) convenient for the analysis of singularities. We have also shown that the Kohn anomalies in ω_k near the ETT can increase sharply and vary appreciably with changing k or η .

The mentioned low-frequency dispersion at $k \sim k_s$ gives rise to peculiarities in the temperature and η dependences of thermodynamic and anharmonic characteristics, the specific heat included, at low $T \sim T_s \sim T_D(v\eta_{\pm})^{1/2}$. It has also been shown that at $T > T_s$ the non-analytical contributions to the thermal expansion coefficients β_i are proportional to $\eta_{\pm}^{1/2}$, while in the temperature derivatives of the elastic constants, π_{ij} , and of the phonon frequencies at the BZ centre, π_{μ} , they are proportional to $\eta_{\pm}^{-1/2}$. The dependence of all the singular contributions on the magnitude of the pseudopotential v at small v is discussed; for this case explicit expressions (32) and (35) are obtained for the singular contributions β_i^s , π_{ij}^s and π_{μ}^s . Illustrative calculations of these contributions for the NFE models of the Li–Mg and Cd–Mg alloys have been carried out. Experimental data on the concentration dependence of microhardness $H_{\mu}(x)$ in the $\text{Li}_{1-x}\text{Mg}_x$ alloys and hardness $H(x)$ in the $\text{Cd}_{1-x}\text{Mg}_x$ alloys have been discussed, apparently suggesting a clear manifestation of the SDS effects in the plasticity characteristics, too.

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