Quantum oscillations of static displacements and of point-defect elastic interaction in metals

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Abstract. It is shown that the static displacement fields around point defects and the elastic interaction energy between defects in metals at distances exceeding the interatomic spacing have an oscillating quantum component (QC), besides the smoothly varying component obtained in the elastic continuum theory. This QC decreases as $R^{-n} \cos(2p_F R + \varphi)$ in directions normal to the Fermi surface (FS), where $2p_F$ is the FS diameter and $n = 1, 2$ and 3 for flat, cylindrical and spherical FS sections, respectively. The QC has its origin in long-range interatomic interactions of similar form, both impurity–host and host–host. It is pointed out that the existence of QC in the atomic displacements should produce anomalies in diffuse x-ray and neutron scattering from metallic solid solutions.

1. Introduction

Point defects in a crystal induce the static displacements $u(R)$ of host atoms. Elastic fields, caused by defects, interfere. This leads to the point-defect elastic interaction with energy $\mathscr{E}(R)$.

Within the continuum elastic theory [1, 2], we have displacements $u^{cont}(R) \propto R^{-2}$ and $\mathscr{E}^{const}(R) \propto R^{-3}$ (for the elastic anisotropic crystal). It is usually assumed that the continuum approximation for $u(R)$ and $\mathscr{E}(R)$ is correct at distances exceeding the interatomic separation $R \gg a$ (a is the lattice spacing) and is caused by the singularities of the Fourier transforms $u(q)$ and $\mathscr{E}(q)$ at $q \to 0$ (see e.g. [2]). Strictly speaking, to turn to the continuum theory, R is to exceed the range of the interatomic forces.

In metals, the interatomic host–host and impurity–host interactions due to conduction electron screening are long-range. Along the directions R, normal to the Fermi surface (FS), they decrease according to a power law and have Friedel oscillations [3, 4]

$$R^{-n} \cos(2p_F R + \varphi) \tag{1.1}$$

where $2p_F$ is the FS diameter, $\hbar = 1$ and $n = 1, 2$ and 3 for flat, cylindrical and spherical FS sections. Therefore one can expect that the asymptotic form of $u(R)$ and $\mathscr{E}(R)$ in metals will differ from the continuum approximation.

It will be shown in this work that in metals the expressions for $u(R)$ and $\mathscr{E}(R)$ at large distances $R \gg a$ contain, besides the usual continuum components (CC), oscillating terms like (1.1), which we call quantum components (QC) and denote $u^E(R)$ and $\mathscr{E}^E(R)$ indicating their electron origin.

Mathematically the presence of QC is due to the fact that $u(q)$ and $\mathscr{E}(q)$ have singularities at $q = q_F = 2k_F - G_0$, besides the long-wave singularities (here $2k_F$ is the vector connecting the 'parallel' parts of FS, and G_0 is a reciprocal lattice vector reducing $2k_F$ to the first Brillouin zone). Their existence is caused by the singularities at $q = q_F$ of the electron contributions to the dynamic matrix $V(q)$ of the ideal crystal and the Fourier transform $W(q)$ of the defect–lattice force.

It is well known that the singularities in $V(q)$ at $q = q_F$ cause the Migdal–Kohn anomalies in the phonon spectrum of metals [5–7]. The quantum oscillations $u(R)$ predicted in this work are the static analogue of these singularities (and the singularities of $W(q)$ as well).

Previously [8], the oscillating character of the asymptote of $\mathscr{E}(R)$ was pointed out for the simple case of atoms embedded into a free-electron gas.

To calculate QC, $u^E(R)$ and $\mathscr{E}^E(R)$, we use the lattice static method (or Kanzaki method) [2, 9]. The main formulae are briefly presented in section 2. In section 3 the electronic energy of the distorted metal, containing arbitrary point defects, is calculated in second-order perturbation theory. This makes it posible to find the electron contributions to $W(q)$ and $V(q)$. Such an approach within the scope of pseudopotential theory was frequently used for the description of different point defects in metals (see e.g. [10–14]). In this paper the generalisation of this approach was developed, taking into account the local field effects for arbitrary electron energy band structure and FS. These effects were analysed earlier when studying phonons in pure metals [15, 16].

The peculiar (or singular) parts of $W(q)$ and $V(q)$, and connected with them $u(q)$ and $\mathscr{E}(q)$, are derived and general expressions for $u^E(R)$ and $\mathscr{E}^E(R)$ are obtained in section 4. Specific calculations of QC for spherical, cylindrical and flat FS are carried out in section 5, and the analysis of the total atomic displacements and point-defect interaction energy in metals is done in section 6.

Finally, in section 7 the limitation of the model used and some physical consequences of quantum oscillations of $u(R)$ and $\mathscr{E}(R)$ are discussed. It is pointed out that QC of the atomic displacement fields should produce anomalies in diffuse x-ray and neutron scattering at diffraction vectors $Q = q_F + G$.

2. Lattice static method

We consider a metal with Bravais lattice, into which point defects of one kind with concentration c are introduced. Let us indicate the site position of the ideal 'average' lattice (i.e. uniformly deformed at random defect distribution) as R_s ($s = 1, 2, \ldots, N$) and their displacements u_s. Possible defect positions in the undeformed crystal are given by the vectors $L_s = R_s + h$, and their occupation numbers $c_s = 1, 0$ when unit cell s is occupied by the defect or not.

In the lattice static method [2] in harmonic approximation the displacements of the host atoms are taken into account and the change of the defect positions is neglected. The last is justified at small c and when the positions of the defects are the centres of symmetry in a crystal. Then the expansion of free energy in a power series of u_s can be written as

$$F = F_0 - \sum_{s,s'} [W_i(s, s')(c_{s'} - c)u_{si} - \tfrac{1}{2}V_{ij}(s, s')u_{si}u_{sj}]. \tag{2.1}$$

Here $W(s, s') \equiv W(R_s - L_{s'})$ is the force acting on the atom s from the defect located in the s' cell, and $V_{ij}(s, s')$ is the force constant matrix.

We introduce the Fourier components

$$u(q) = \frac{i}{N} \sum_s u_s \exp(-iq \cdot R_s)$$

$$W(q) = i \sum_s W(s, s') \exp[-iq \cdot (R_s - L_{s'})]$$

$$(2.2)$$

$$c(q) = \frac{1}{N} \sum_s (c_s - c) \exp(-iq \cdot L_s)$$

$$V_{ij}(q) = \sum_s V_{ij}(s, s') \exp[-iq \cdot (R_s - R_{s'})]$$

where vector q belongs to the first Brillouin zone. The function $W(q)$ is a real and antisymmetric function of q because the forces $W(s, s')$ are central. If the origin is chosen in the lattice cell, the functions $u(q)$, $V(q)$, $c(q) \exp(iq \cdot h)$ and $W(q) \exp(-iq \cdot h)$ will have translational symmetry in reciprocal space with period equal to the reciprocal lattice vector G. In q-representation

$$F = F_0 - N \sum_{q \neq 0} [W_i(q)c(q) - \tfrac{1}{2}V_{ij}(q)u_j(q)]u_i^*(q). \qquad (2.3)$$

After minimisation of F with respect to $u_i(q)$ one can find the connection between the displacements and concentration waves

$$u(q) = A(q)c(q) \qquad A(q) = V^{-1}(q)W(q). \qquad (2.4)$$

Substitution of (2.4) into (2.3) gives the equilibrium free energy of the solid solution

$$F = F_0 + \frac{N}{2} \sum_{q \neq 0} \mathscr{E}(q)|c(q)|^2 \qquad (2.5)$$

$$\mathscr{E}(q) = -W(q)V^{-1}(q)W(q) = -W(q)A(q). \qquad (2.6)$$

It follows from the above equations that the atomic displacements $u_s \equiv u(R)$, at distance $R = R_s - L_{s'}$ from a single defect located in the s' cell ($c(q) = N^{-1} \exp(-iq \cdot L_{s'})$), are defined as an integral over the Brillouin zone

$$u(R) = \frac{\Omega_0}{8\pi^3} \int_{BZ} A(q) \sin(q \cdot R) \, dq \qquad (2.7)$$

where Ω_0 is the atomic volume. If there are two point defects in cells s and s' at distance $R = L_s - L_{s'}$, then their elastic interaction energy is

$$\mathscr{E}(R) = \frac{\Omega_0}{8\pi^3} \int_{BZ} \mathscr{E}(q) \cos(q \cdot R) \, dq. \qquad (2.8)$$

The formulae (2.7) and (2.8) define $u(R)$ and $\mathscr{E}(R)$ at any distances R. It is usually assumed that at $R \gg a$ the behaviour of these integrals is determined by the region of small q, where $A(q)$ and $\mathscr{E}(q)$ are given by the formulae of the continuum elastic theory: $A(q) \sim a(n)q^{-1}$ and $\mathscr{E}(q) \sim b(n)$ when $q \to 0$ ($n = q/q$) [2]. However, it is known from the Fourier transformation theory that the asymptotes of integrals of type (2.7) and (2.8) are determined not only by the behaviour of the functions $A(q)$ and $\mathscr{E}(q)$ at $q \to 0$ but also by their singularities at finite q.

These singularities in metals exist at $q = 2k_F - G_0$ due to the electron contributions to $A(q)$ and $\mathscr{E}(q)$. To find explicit expressions for them, one should consider the electronic energy of the distorted solid solutions, which is additively included in the total free energy (2.3).

3. Electronic energy of the distorted solid solution

In the superpositional approach the potential energy of an electron in a metal containing point defects, when the relaxation of the host lattice is taken into account but the defect positions are unchanged, has the form

$$v(r) = \sum_s v_h(r - R_s - u_s) + c_s v_d(r - R_s - h) \tag{3.1}$$

where v_h and v_d are the interaction energies between the electron and host atom or defect, respectively. For a substitutional impurity, $h = 0$ and $v_d = v_{imp} - v_h$, where v_{imp} is the potential energy in the field of an impurity. In particular, for vacancies, $v_d = -v_h$. In the case of interstitial atoms, $h \neq 0$ and $v_d = v_{imp}$ (for self-interstitial atom, $v_d = v_h$).

We chose the potential energy in the ideal 'average' crystal as a zero-order approximation

$$v_0(r) = \sum_s \bar{v}(r - R_s) \qquad \bar{v}(r) = v_h(r) + cv_d(r - h) \tag{3.2}$$

and write E_p and $|p)$ for the electron spectrum and Bloch wavefunction in the extended zone for the potential $v_0(r)$. The potential energy

$$\Delta v(r) = v(r) - v_0(r) = \sum_k \Delta v(k) \exp(ik \cdot r) \tag{3.3}$$

will be considered as the disturbance. Within the accuracy of quadratic terms in displacements

$$\Delta v(k) = -v_h(k)\left(k_i u_i(q) - \tfrac{1}{2}k_i k_j \sum_{q'} u_i(q')u_j(q - q')\right) + \exp(iq \cdot h)c(q)v_d(k). \tag{3.4}$$

Here $k = q + G$ and

$$v_h(k) = \frac{1}{\Omega_0} \int dr\, v_h(r)\, e^{-ik \cdot r}$$

$$v_d(k) = \frac{1}{\Omega_0} \int dr\, v_d(r - h)\, e^{-ik \cdot r}. \tag{3.5}$$

The calculation of the electronic energy change ΔE due to the disturbance $\Delta v(r)$ will be performed within the scope of perturbation theory, taking into account the first- and second-order terms.

For the disturbance (3.3) we have

$$\Delta E = N\Omega_0 \sum_G \rho_0^*(G)\Delta v(G) + \frac{N\Omega_0}{2} \sum_{q,G,G'} \Delta v^*(q + G)\chi_{GG'}(q)\Delta v(q + G'). \tag{3.6}$$

Here $\rho_0(G)$ is the Fourier transform of the undisturbed electron density and $\chi_{GG'}(q)$ is

the density response function of the 'average' crystal. Following the definition of $\chi(q)$ and considering the shift of the 'average' crystal (3.2) on the whole one can find the relation [17]

$$G_i \rho_0(G) = \sum_{G'} \chi_{GG'}(0)G_i' \bar{v}(G').$$ (3.7)

At small defect concentration $\bar{v}(G) = v_h(G) + cv_d(G) \simeq v_h(G)$, and $\chi(q)$ can be regarded as the density response function of pure metal, not of the 'average' crystal. Then from the expressions (3.6), (3.7) and (3.4), taking into account the equation $u(G) = c(G) = 0$, we obtain (up to quadratic terms in $c(q)$ and $u(q)$)

$$\Delta E = \frac{N}{2} \sum_q U^E(q)|c(q)|^2 - N \sum_q [W_i^E(q)c(q) - \tfrac{1}{2}V_{ij}^E(q)u_j(q)]u_i^*(q).$$ (3.8)

Here

$$U^E(q) = \Omega_0 \sum_{G,G'} v_d(-q-G)v_d(q+G')\chi_{GG'}(q)$$ (3.9)

$$W^E(q) = \Omega_0\, e^{iq\cdot h} \sum_{G,G'} (q+G)v_h(-q-G)v_d(q+G')\chi_{GG'}(q)$$ (3.10)

and

$$\mathbf{V}^E(q) = \tilde{\mathbf{V}}^E(q) - \tilde{\mathbf{V}}^E(0)$$

$$\tilde{V}_{ij}^E(q) = \Omega_0 \sum_{G,G'} (q+G)_i(q+G')_j v_h(-q-G)v_h(q+G')\chi_{GG'}(q).$$ (3.11)

Comparison of expressions (3.8) and (2.3) shows that the first term in (3.8) determines the electronic energy of the system without deformations and should be included in F_0. It describes the pairwise indirect interaction between impurities via the conduction electrons. The values $W^E(q)$ and $\mathbf{V}^E(q)$ are the electron contributions to the total $W(q)$ and $\mathbf{V}(q)$. We note that the expression for the electron component of dynamic matrix $\mathbf{V}^E(q)$ coincides with previous results [15–17].

The density response function is connected with the inverse dielectric screening matrix $\varepsilon_{GG'}^{-1}(q)$ and polarisation matrix $\pi_{GG'}(q)$ by the relations [17, 18]

$$\chi_{GG'}(q) = [\Omega_0 v_c(q+G)]^{-1}[\varepsilon_{GG'}^{-1}(q) - \delta_{GG'}]$$

$$\varepsilon_{GG'}(q) = \delta_{GG'} + v_c(q+G)\pi_{GG'}(q) \qquad v_c(k) = 4\pi e^2/\Omega_0 k^2$$ (3.12)

and matrix $\pi(q)$ in self-consistent field approximation (or random-phase approximation) has the form

$$\pi_{G_1G_2}(q) = \frac{2}{N} \sum_{p,G} \gamma_{G_1G_2}(p, q, k) \frac{n(E_p) - n(E_{p+k})}{E_{p+k} - E_p}$$ (3.13)

$$\gamma_{G_1G_2}(p, q, k) = (p|e^{-i(q+G_1)\cdot r}|p+k)(p+k|e^{i(q+G_2)\cdot r}|p)$$

where $n(E_p)$ is the Fermi function and $k = q + G$.

4. Separation of singularities in electronic energy

The polarisation matrix $\pi(q)$ has singularities at $q = q_F$, for which $q_F + G_0 = 2k_F$. The set of the vectors q_F forms some surfaces in the Brillouin zone. The matrix $\chi(q)$ and

connected with it values $W^E(q)$ and $V^E(q)$ have singularities on these surfaces. Corresponding surfaces in extended reciprocal space are formed by the set of vectors $k = 2k_F$. In the vicinity of these surfaces, only one term in G from (3.13) with $G = G_0$ makes a contribution to the singular part of the polarisation matrix, which can be written as

$$\delta\pi_{GG'}(q) = \delta P(k)\gamma_{GG'}(2k_F) \qquad k = q + G_0 \tag{4.1}$$

where $\delta P(k)$ is the singular part of the function

$$P(k) = \frac{2}{N}\sum_p \frac{n(E_p) - n(E_{p+k})}{E_{p+k} - E_p}. \tag{4.2}$$

$\gamma_{GG'}(2k_F)$ is the averaged value of $\gamma_{GG'}(p, 2k_F - G_0, 2k_F)$ over p, for which $E_p = E_p + E_{p+2k_F} = E_F$, and the vector $2k_F$ close to k is chosen parallel to k for the sake of definiteness. Thus, $2k_F$ and $\gamma(2k_F)$ are functions of the direction of k but not its magnitude.

For isotropic band structure when $|p\rangle$ are plane waves

$$\gamma_{GG'}(2k_F) = \delta_{GG_0}\delta_{G'G_0}. \tag{4.3}$$

Supposing that the singular part of the dielectric matrix $\delta\varepsilon$ (but not its derivative) is much less than the value ε at $q = q_F$, one can write $\delta\varepsilon^{-1} = -\varepsilon^{-1}\delta\varepsilon\varepsilon^{-1}$ and find the singular part of the density response function from (3.12) and (4.1) as

$$\delta\chi_{GG'}(q) = -\frac{1}{\Omega_0}\delta P(k)\sum_{G_1,G_2}\varepsilon^{-1}_{G_1 G}(q_F)\gamma_{G_1 G_2}(2k_F)\varepsilon^{-1}_{G_2 G'}(q_F) \tag{4.4}$$

where the symmetry $\pi_{GG'}(q) = \pi_{G'G}(q)$ is used. After substituting (4.4) into (3.9)–(3.11) we obtain singular parts

$$\delta W^E(q) = -\delta P(k)C(2k_F) \qquad \delta V^E(q) = -\delta P(k)T(2k_F)$$
$$\delta U^E(q) = -\delta P(k)S(2k_F) \tag{4.5}$$

with

$$C(2k_F) = e^{iq_F \cdot h}\sum_{G,G'}(q_F + G)v^{sc}_h(-q_F - G)v^{sc}_d(q_F + G')\gamma_{GG'}(2k_F)$$

$$T_{ij}(2k_F) = \sum_{G,G'}(q_F + G)_i(q_F + G')_j v^{sc}_h(-q_F - G)v^{sc}_h(q_F + G')\gamma_{GG'}(2k_F) \tag{4.6}$$

$$S(2k_F) = \sum_{G,G'}v^{sc}_d(-q_F - G)v^{sc}_d(q_F + G')\gamma_{GG'}(2k_F)$$

and screened potentials are determined as

$$v^{sc}(q + G) = \sum_{G'}\varepsilon^{-1}_{GG'}(q)v(q + G'). \tag{4.7}$$

Finally, substituting (4.5) into (2.4) and (2.6) and taking into account that at small δV the value $\delta V^{-1} = -V^{-1}\delta VV^{-1}$, we obtain singular parts of $A(q)$ and $\mathscr{E}(q)$ due to the electron contributions to $W(q)$ and $V(q)$

$$\delta A(q) = -\delta P(k)D(2k_F) \qquad \delta\mathscr{E}(q) = \delta P(k)B(2k_F)$$
$$D = V^{-1}(C - TA) \qquad B = 2CA - ATA \tag{4.8}$$

where all coefficients are taken at $q = q_F = 2k_F - G_0$.

As follows from these expressions the singularities of $A(q)$ and $\mathscr{E}(q)$ arise from two causes: due to the conduction electron screening of the impurity–host interaction, which determines the singularities of $W(q)$; and due to the screening of the host–host interaction, which determines the singularities of $V(q)$. Accordingly, they are responsible for the first and the second terms in the expressions for D and B Let us estimate the relative value of these terms. At small q, as follows from continuum elastic theory, $A(q) \sim \alpha/q$, where α is the bulk coefficient of concentration lattice expansion [2]. Extrapolating this dependence up to $q \sim q_F$ we obtain

$$\frac{TA}{C} \sim \alpha \frac{v_h^{sc}(2k_F)}{v_d^{sc}(2k_F)} \qquad \alpha = \frac{1}{\Omega_0} \frac{d\Omega_0}{dc}. \qquad (4.9)$$

If $v_h^{sc}(2k_F) \sim v_d^{sc}(2k_F)$, then for interstitial atoms or vacancies when $\alpha \sim 1$ both terms are of the same order. For substitutional defects, where $\alpha \sim 0.01$–0.1, one can neglect the second terms in (4.8) and take into account only the singularities of $W(q)$.

5. Quantum components of the elastic interaction and of atomic displacements

The quantum components (QC) of the atomic displacements around the point defect $u^E(R)$ and elastic defect interaction energy $\mathscr{E}^E(R)$ at distances $R \gg a$ are determined by the singularities of $A(q)$ and $\mathscr{E}(q)$ at $q = q_F$. To find them one should integrate (2.7) and (2.8) over the neighbourhood of the surface $q = q_F$, retaining in $A(q)$ and $\mathscr{E}(q)$ only singular parts of these values. It is convenient to find an integral in extended k-space. The integrands in (2.7) and (2.8) do not change on the replacement $q \to q + G$. Therefore, instead of integrating over the regions $q \simeq q_F$ one can integrate with respect to $k = q + G_0$ over the neighbourhood of the surface $k = 2k_F$. Here vector G_0 is different for various regions of q and it is chosen such that $q_F + G_0 = 2k_F$. Hence

$$u^E(R) = -\frac{\Omega_0}{8\pi^3} \int' dk \, D(2k_F) \delta P(k) \sin(k \cdot R)$$

$$\mathscr{E}^E(R) = \frac{\Omega_0}{8\pi^3} \int' dk \, B(2k_F) \delta P(k) \cos(k \cdot R) \qquad (5.1)$$

where the prime means integration over $k \simeq 2k_F$.

5.1. Spherical Fermi surface

For spherical FS with radius p_F the surface $k = 2k_F$ is a sphere with radius $2p_F$. For $k \simeq 2k_F$ the singular part is

$$\delta P(k) = \frac{\nu_3}{4p_F} (k - 2p_F) \ln|k - 2p_F| \qquad \nu_3 = \frac{mp_F \Omega_0}{\pi^2} \qquad (5.2)$$

where m is the effective mass and $\nu_3 = \nu_3(E_F)$ is the electron density of states per atom.

Substituting this expression into (5.1), integrating it over angles and then after twofold integration by parts over k at $R \gg \pi/p_F$ we obtain

$$u^E(R) = -\frac{\nu_3\Omega_0}{4\pi} D(2k_F^0) \frac{\sin(2p_FR)}{R^3}$$

$$\mathscr{E}^E(R) = -\frac{\nu_3\Omega_0}{4\pi} B(2k_F^0) \frac{\cos(2p_FR)}{R^3} \qquad 2k_F^0 = 2p_F \frac{R}{R}. \tag{5.3}$$

Hence, $u(R)$ and $\mathscr{E}(R)$ for the spherical FS contain QC, oscillating with period π/p_F and decreasing as R^{-3}. The direction of the displacements is determined by the vector $D(2k_F^0)$, which depends on the direction R. Generally, $D(2k_F^0)$ is not parallel to R. But for high-symmetry directions (like [100], [110] and [111] in cubic crystals) one can prove that $D \parallel R$, and static displacements $u^E(R)$ are longitudinal. In the nearly-free-electron approach, according to (4.3) and (4.6), $C(2k_F^0) \parallel R$, $T_{ij}(2k_F^0) \propto R_iR_j$ and $D(2k_F^0)$ is parallel to the vector $V_{ij}^{-1}(q_F^0)R_j$, where $q_F^0 = 2k_F^0 - G_0$.

5.2. Cylindrical Fermi surface

Let the FS section be a circular cylinder with the height p_0 and radius p_F. In this case $2k_F = k_\parallel + 2p_Fk_\perp/k_\perp$, where $k_\parallel$ and $k_\perp$ are components of vector k along and normal to the cylinder axis, and $k_\parallel < p_0/2$. If $k_\parallel \ll p_0$, supposing that the electron spectrum near the FS is two-dimensional ($E_p = p_\perp^2/2m$) one can find from (4.2) (see also [19]) that

$$\delta P(k) = -\frac{\nu_2}{p_F^{1/2}} \mathrm{Re}(k_\perp - 2p_F)^{1/2} \qquad \nu_2 = \frac{mp_0\Omega_0}{2\pi^2} \tag{5.4}$$

where $\nu_2 = \nu_2(E_F)$ is the contribution of FS sections to the electron density of states per atom. At $k_\perp = 2p_F$ the function $\delta P(k)$ has root singularity.

Let $R = R_\parallel + R_\perp$. As the integrand in (5.1) has no singularities in $k_\parallel$, then $u^E(R)$ and $\mathscr{E}^E(R)$ will be exponentially decreasing functions of $R_\parallel$ (at distances of the order of the interatomic separation). Therefore, only the case $R_\parallel = 0$ is considered. At $R_\perp \gg \pi/p_F$ in (5.1) one can first integrate over the angle in the plane $k_\perp$, then by parts over $k_\perp$. As a result we obtain

$$u^E(R_\perp) = \frac{\nu_2\Omega_0p_0}{4\pi^2} \bar{D}(2p_F^0) \frac{\cos(2p_FR_\perp)}{R_\perp^2} \qquad p_F^0 = p_F \frac{R_\perp}{R_\perp}$$

$$\mathscr{E}^E(R_\perp) = \frac{\nu_2\Omega_0p_0}{4\pi^2} \bar{B}(2p_F^0) \frac{\sin(2p_FR_\perp)}{R_\perp^2} \tag{5.5}$$

where $\bar{D}(2p_F^0)$ and $\bar{B}(2p_F^0)$ are the average values of $D(2p_F^0 + k_\parallel)$ and $B(2p_F^0 + k_\parallel)$ over $k_\parallel$ in the region $k_\parallel < p_0/2$. It follows from these expressions that QC in the case of a cylindrical FS section along the normal to the cylinder axis are oscillating functions with amplitude decreasing as $R_\perp^{-2}$. For high-symmetry directions $u^E(R_\perp) \parallel R_\perp$.

5.3. Flat Fermi surface sections

We now consider FS that has flat sections of area $S_\perp$ separated by $2p_F$. Then $2k_F = k_\perp + 2p_Fk_\parallel/k_\parallel$, where $k_\perp$ and $k_\parallel$ are the components of k in the plane of FS and in the

normal direction. If $k_\perp$ is not close to the boundaries of the FS sections, supposing quasi-one-dimensionality of the electron spectrum ($E_p = p_\parallel^2/2m$) near FS, one can find from (4.2) (see also [4, 19]) that

$$\delta P(k) = -\frac{\nu_1}{2} \ln|(k_\parallel/2p_F) - 1| \qquad \nu_1 = mS_\perp \Omega_0/2\pi^3 p_F \qquad (5.6)$$

where $\nu_1 = \nu_1(E_F)$ is the contribution of the FS sections under consideration to the electron density of states per atom.

Since $\delta P(k)$ does not contain singularities in $k_\perp$, QC $u^E(R)$ and $\mathscr{E}^E(R)$ will be exponentially decreasing (at distances $\sim a$) functions of $R_\perp$ (the component of R in the plane $k_\perp$). The dependence of QC on $R_\parallel$ at $R_\parallel \gg \pi/p_F$ and $R_\perp = 0$ can be obtained from equation (5.1) after integration by parts over $k_\parallel$,

$$u^E(R_\parallel) = -\frac{\nu_1 \Omega_0 S_\perp}{8\pi^2} \bar{D}(2p_F^0) \frac{\sin(2p_F R_\parallel)}{R_\parallel} \qquad p_F^0 = p_F \frac{R_\parallel}{R_\parallel}$$

$$\mathscr{E}^E(R_\parallel) = \frac{\nu_1 \Omega_0 S_\perp}{8\pi^2} \bar{B}(2p_F^0) \frac{\cos(2p_F R_\parallel)}{R_\parallel}. \qquad (5.7)$$

Here $\bar{D}(2p_F^0)$ and $\bar{B}(2p_F^0)$ are obtained by averaging of the functions $D(2p_F^0 + k_\perp)$ and $B(2p_F^0 + k_\perp)$ over $k_\perp$ in the area $S_\perp$. It follows from (5.7) that along the normals to the flat FS sections $u^E(R_\parallel)$ and $\mathscr{E}^E(R_\parallel)$ decrease as $R_\parallel^{-1}$ and oscillate with period π/p_F. If $k_\parallel$ is a high-symmetry direction, then displacements are longitudinal ($u^E(R_\parallel) \parallel R_\parallel$).

For the flat FS sections $\delta P(k)$ at $k_\parallel = 2p_F$, and hence $\varepsilon(q)$ in (3.12) at $q = q_F$, has logarithmic divergence. To make sense of the inverse dielectric matrix $\varepsilon^{-1}(q_F)$, one should eliminate this divergence. It can be done through taking into account the nonzero temperature T or the damping Γ of the electron states due to the phonon scattering. Then in a small region $|k_\parallel - 2p_F| \lesssim k_0$ where $k_0 \sim p_F T/E_F, p_F \Gamma/E_F$, the expressions (5.6) for $\delta P(k)$ will change and the presented asymptotes of QC will be correct for not too large distances $\pi p_F^{-1} \ll R_\parallel \ll k_0^{-1}$.

6. Total atomic displacements and point-defect interaction energy

Total atomic displacements at large distances $R \gg a \sim \pi/p_F$ from a point defect are the sum of the above-discussed QC and a continuum component (CC)

$$u(R) = u^E(R) + u^{cont}(R). \qquad (6.1)$$

The order of magnitude of the latter is (see e.g. [2])

$$u^{cont}(R) \sim \frac{\alpha \Omega_0}{4\pi R^2} \qquad (6.2)$$

where α is determined in (4.9).

To estimate QC, we assume that for all considered FS $p_F \simeq \pi/a$ (a is the lattice spacing), and take into account that $V_{ij}(q_F) \sim \lambda a$, where λ is the elastic modulus of the host lattice.

Then using equations (5.3), (5.5) and (5.7) for $u^E(R)$ and (4.8) and (4.6) for D, one can estimate QC accordingly for spherical, cylindrical and flat FS sections as

$$u^E \sim \frac{g\Omega_0 a}{4\pi R^3} \qquad \frac{g\Omega_0}{4\pi R_\perp^2}\left(\frac{p_0}{p_F}\right)^2 \qquad \frac{g\Omega_0}{4\pi a R_\parallel}\left(\frac{S_\perp}{p_F^2}\right)^2$$

$$g = m|v_d^{sc}(2k_F)v_h^{sc}(2k_F)|/\lambda a\hbar^2.$$

(6.3)

In the expression for non-dimensional parameter g, Planck's constant is included although in the rest of this paper we assume $\hbar = 1$. The typical value of $g \sim 0.01\text{--}0.1$ is obtained. The comparison of (6.2) and (6.3) shows that at $R \gg a$ for spherical FS, $u^E \ll u^{cont}$ as a rule. But for cylindrical and flat FS, especially at small α and large p_0 and $S_\perp$, QC is comparable in magnitude with CC and even exceeds it. In the region $R \sim a$ where the asymptotic expressions give only the order of magnitude of displacements, in solid solutions with small $\alpha \sim g$ CC and QC are comparable in magnitude for all FS discussed (when $p_0 \sim p_F$ and $S_\perp \sim p_F^2$).

At large distances $R \gg a$ the total interaction energy of point defects in metals U_{tot} is the sum of the indirect interaction energy $U^E(R)$ and the elastic interaction $\mathscr{E}(R)$ containing CC and QC

$$U_{tot}(R) = U^E(R) + \mathscr{E}^E(R) + \mathscr{E}^{cont}(R).$$

(6.4)

In an elastic anisotropic crystal (see e.g. [2]) the order of magnitude is

$$\mathscr{E}^{cont}(R) \sim \lambda\alpha^2\Omega_0^2/4\pi R^3.$$

(6.5)

The indirect interaction $U^E(R)$ is determined by the singularities of $U^E(q)$ in the expressions (3.8) and (3.9) at $q = q_F$. (In the case of charged defects $U^E(q)$ also has singularities at $q \to 0$, which exactly cancel out with those of the direct Coulomb interaction of defects.) According to (3.8) and (4.5) the energy $U^E(R)$ is given by

$$U^E(R) = -\frac{\Omega_0}{8\pi^3}\int' dk \, \delta P(k)S(2k_F)\cos(k \cdot R)$$

(6.6)

i.e. is determined by an integral similar to that for $\mathscr{E}^E(R)$ in (5.1). Therefore $U^E(R)$ for any FS has the same form as $\mathscr{E}^E(R)$ with the constant $-S(2k_F)$ instead of $B(2k_F)$. Relative values are

$$\mathscr{E}^E/U^E \sim B(2k_F)/S(2k_F) \sim \alpha(v_h^{sc}(2k_F)/v_d^{sc}(2k_F))$$

(6.7)

and for $v_h^{sc} \sim v_d^{sc}$ and $\alpha \sim 1$, QC $\mathscr{E}^E(R)$ is comparable in magnitude with indirect interaction.

Using the example described above, the QC for the spherical, cylindrical and flat FS may be estimated as

$$\mathscr{E}^E \sim \frac{\lambda\alpha g\Omega_0^2}{4\pi R^3} \qquad \frac{\lambda\alpha g\Omega_0^2}{4\pi a R_\perp^2}\left(\frac{p_0}{p_F}\right)^2 \qquad \frac{\lambda\alpha g\Omega_0^2}{4\pi a^2 R_\parallel}\left(\frac{S_\perp}{p_F^2}\right)^2.$$

(6.8)

Comparison of the expressions (6.8) and (6.5) shows that at $\alpha \sim g$ QC is of the same order as CC (for spherical FS) or exceeds it (when $p_0 \sim p_F$, $S_\perp \sim p_F^2$). At $\alpha \sim 1$ (for interstitial atoms and vacancies) in the case of cylindrical and flat FS at large enough distances $\mathscr{E}^E(R)$ exceeds $\mathscr{E}^{cont}(R)$ because QC falls with R more slowly than does CC.

7. Discussion

The interatomic interactions in metals are screened by the conduction electrons. For this reason, the forces $W(s, s')$ acting on the host atom from the point defect and force constants $V(s, s')$ have Friedel oscillations (1.1). In this work it is shown that these long-range forces cause similar oscillations in the atomic displacement fields around the defect and in the elastic interaction of defects. The QC of the displacements found above are very similar in form and nature to the well known Friedel oscillations of electron density around a point defect or to RKKY oscillations of spin density around a magnetic impurity in a paramagnet [20, 21].

The magnitude of the QC of displacements can be comparable to or even exceed (especially in metals with cylindrical or flattened FS sections and small α) the CC. In these cases, if $u(R)$ is to be calculated, one cannot be confined to interactions in a few coordination spheres and should take into account long-range components of $W(s, s')$ and $V(s, s')$.

The oscillating character of the QC of displacements should manifest itself in the diffuse scattering of x-rays and neutrons in metallic solid solutions. When the diffraction vector $Q = q_F + G$, the scattering by the QC of displacements of a great number of atoms will all be in phase. Hence, anomalies in the intensity of the diffuse scattering should be observed at $Q = q_F + G$. Their positions will be in exact coincidence with Migdal–Kohn anomaly positions in the phonon spectrum of the host metal.

Perhaps, the sharp maximum of the diffuse neutron scattering observed in Nb with small concentrations of Zr, N or O impurities [22–24] can be explained in this way. The position of this maximum just coincides with the local minimum in the phonon spectrum of Nb [25].

The existence of anomalies at $Q = q_F + G$ presents the opportunity to obtain information about FS of metals by diffuse x-ray and neutron scattering data. A detailed analysis of the diffuse scattering anomalies will be carried out in a separate paper.

The QC $\mathscr{E}^E(R)$ can also make an essential contribution to the elastic energy of the defect interaction. It is particularly important in metals with low elastic anisotropy (for instance, tungsten) because $\mathscr{E}^{cont}(R) = 0$ in an elastically isotropic crystal for defects of cubic symmetry. Then at large R in equation (2.8) the region of small q will make a contribution to $\mathscr{E}(R) \propto R^{-5}$, connected with quadrupole moments [26] and decreasing much more abruptly than $\mathscr{E}^E(R)$.

It is noteworthy that the thermodynamic characteristics of a solid solution depend only upon the total defect interaction U_{tot} (equation (6.4)). It includes the indirect interaction $U^E(R)$, which is usually comparable with $\mathscr{E}^E(R)$ and has the same oscillating character. Hence, experimental proof of the existence of QC $\mathscr{E}^E(R)$ in U_{tot} may turn out to be rather difficult.

In this paper only point defects were considered. Similar reasoning must imply quantum oscillations in the atomic displacement fields around other defects in metals (e.g. dislocations, new phase particles, defect clusters). The elastic interaction between them should also contain the oscillating component.

As was shown in [27, 28], the indirect interaction of new phase particles in metals, due to the interference of interactions between different atoms, has oscillating character and depends drastically on the size, shape and orientation of the particles and distances between them. One can expect that the elastic interaction between particles in metals will have similar peculiarities due to the QC. Additional research is needed to clarify this question.

In conclusion let us consider one important limitation of the model, namely the validity of second-order perturbation theory for electronic energy calculation. The first two terms in the disturbed potential (3.4) contain atomic displacements. In higher orders of perturbation theory they would lead to anharmonic terms in the free energy. Consideration of the latter goes beyond the scope of this work. The third term in (3.4) can be assumed small if $v_d(2k_F) \ll E_F$. Otherwise, higher orders of perturbation theory in v_d will give rise to many-body forces in the electron part of $W(s, s')$ (i.e. $W(s, s')$ will depend on occupation numbers c_s). At small concentration of defects they can be neglected. Besides, terms of third and higher orders in perturbation theory renormalise pairwise forces $W(s, s')$, i.e. the expression (3.10) for $W^E(q)$ will be changed.

However, most likely, the character of the oscillations of $W(s, s')$ and consequently of QC $u^E(R)$ and $\mathscr{E}^E(R)$ will remain qualitatively unchanged (except for the special case when the potential $v_d(r)$ forms a localised energy level close to E_F). This can be concluded by analogy with the Friedel oscillations around a point defect, where exact results obtained from scattering theory coincide qualitatively with the expressions of perturbation theory [20]. It is also possible to point out the analogy with the indirect interaction of impurities, which has oscillations like (1.1) for exactly solvable models [29] as well as in second-order perturbation theory.

References

[1] Eshelby J D 1956 *Solid State Phys.* **3** 79–144, ed F Seitz and D Turnbull (New York: Academic)
[2] Krivoglaz M A 1969 *Theory of X-Ray and Thermal Neutron Scattering by Real Crystals* (New York: Plenum)
[3] Heine V and Weaire D 1970 *Solid State Physics* vol 24, ed H Ehrenreich, F Seitz and D Turnbull (New York: Academic) pp 249–463
[4] Gabovich A M, Ilchenko L G, Pashitsky E A and Romanov Yu A 1978 *Zh. Eksp. Teor. Fiz.* **75** 249
[5] Migdal A B 1958 *Zh. Eksp. Teor. Fiz.* **34** 1438
[6] Kohn W 1959 *Phys. Rev. Lett.* **2** 393
[7] Weiss L and Eschrig H 1982 *Phys. Status Solidi* b **114** 419
[8] Khalifen J and Gautier F 1982 *Phil. Mag.* B **46** 635
[9] Kanzaki H 1957 *J. Phys. Chem. Solids* **2** 24
[10] Ho P S 1971 *Phys. Rev.* B **3** 4035
[11] Popovic Z, Carbotte J P and Piercy G R 1973 *J. Phys. F: Met. Phys.* **3** 1008
[12] Singhal S P 1973 *Phys. Rev.* B **8** 3641
[13] Solt G and Zhernov A P 1979 *J. Phys. F: Met. Phys.* **9** 1013
[14] March N H 1973 *J. Phys. F: Met. Phys.* **3** 233
[15] Sham L J 1965 *Proc. R. Soc.* A **283** 33
[16] Pick R, Cohen M H and Martin R M 1970 *Phys. Rev.* B **1** 910
[17] Sham L J 1969 *Phys. Rev.* **188** 1431
[18] Sinha S K, Gupta R P and Price D L 1974 *Phys. Rev.* B **9** 2564
[19] Afanasiev A M and Kogan Yu 1962 *Zh. Eksp. Teor. Fiz.* **43** 1456
[20] Kittel C 1963 *Quantum Theory of Solids* (New York: Wiley)
[21] Harrison W A 1970 *Solid State Theory* (New York: McGraw-Hill)
[22] Wakabayashi N 1978 *Phys. Rev.* B **17** 3875
[23] Dosch H and Peisl J 1985 *Phys. Rev.* B **32** 623
[24] Dosch H, von Schwerin A and Peisl J 1986 *Phys. Rev.* B **34** 1654
[25] Nakagama Y and Woods A D B 1965 *Lattice Dynamics* ed R F Wollis (Oxford: Pergamon) pp 39–48
[26] Hardy J R and Bullough R 1967 *Phil. Mag.* **15** 237
[27] Vul D A, Krivoglaz M A and Martynenko O V 1988 *Fiz. Met. Metallov.* **66** 53
[28] Vul D A, Krivoglaz M A and Martynenko O V 1988 *Fiz. Met. Metallov.* **66** 455
[29] Veshcunov M S 1987 *Zh. Eksp. Teor. Fiz.* **92** 1485