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Tight-Binding Model for Transition Metal Electrons – 1

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Abstract. In a tight-binding model for the *d*-electrons of transition metals (Pd and its alloys, V, Nb) we calculate the shear-moduli, paramagnetic susceptibility, and electron–phonon coupling matrix elements and show how these quantities are interrelated. The starting point is a band-structure calculation which is performed up to second order in strain in the sheared crystals. The method of calculation is chosen such that the points in the Brillouin zone do not change under shear condition and thus do not contribute spurious terms to the band energies. A trace-method [9a], working in the high temperature limit, circumvents any diagonalization in calculating $E_n(\mathbf{k}, \gamma)$. Our electron–phonon coupling parameters enter directly the tight-binding form of the Eliashberg equations for superconductors.

1. Introduction

The electronic band structure of transition metals and some of their compounds are by now well within reach of numerical calculation.

Pettifor [1] introduced a procedure to make the matrix elements of the first-principle H–NFE–TB Hamiltonian,

$$\boldsymbol{H}_m = \left(\begin{array}{c|c} \boldsymbol{H}_{ss} & \boldsymbol{H}_{sd} \\ \hline \boldsymbol{H}_{ds} & \boldsymbol{H}_{dd} \end{array}\right), \tag{1}$$

independent of the energy to be calculated. The index '*s*' is used here for all those electrons which are to be represented by a nearly free electron approximation, whereas '*d*' stands for those electrons described by a tight-binding approximation. The hybridization does not extend beyond nearest neighbours in **k**-space, and the tight-binding overlap integrals are limited to nearest neighbours in **r**-space for face-centred cubic structures (or first and second neighbours for body-centred cubic structures). Following Pettifor, Posternak and Steinemann [2] calculated the band structure of Cu successfully by retaining only the $\boldsymbol{H}_{dd}$ block in (1).

For elements in the middle of the transition period, like Nb, this approximation might not be sufficient [3]: Whenever one is not interested in the resonance

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region of the spectrum, one might formally keep the H_{dd} block only by changing the numerical parameters in a sense of a perturbation expansion (W. B. Waeber, private communication). From Ref. [3a] we write

$$H_m \begin{pmatrix} \phi_s \\ \phi_d \end{pmatrix} = E \begin{pmatrix} \phi_s \\ \phi_d \end{pmatrix}$$

$$\{H_{dd} - H_{ds}(H_{ss} - E)^{-1} H_{sd}\} \phi_d = E\phi_d. \tag{2}$$

Replacing in (2) H_{ss} by the kinetic energy and E by the eigenvalue E_d of H_{dd} [3b] one can perform a perturbation expansion up to first order and use this result to receive a renormalized H_{dd}.

Starting from a quite different point of view and from another class of material, Weger, Goldberg and Barak [4] showed for A15-structures like V_3Ga that the tight-binding coupled linear chain model (Weger–Labbé–Friedel model; cf. Ref. [4a]) is a rather good approximation, and that for this structure covalency between the vanadium $3d$ and gallium bands, as well as admixture between $3d$ sub-bands, may be neglected as a first approximation, changing the numerical parameter eventually by some 30%.

In this and a subsequent paper we primarily study the electronic energy of transition metals as a function of shear deformation. This will not only provide a great deal of information about the elastic constants but will also give details of other electronic properties.

Good correlation between the temperature derivatives of the shear moduli and the paramagnetic susceptibility was established experimentally by Belmahi et al. [5] in polycrystalline Pd-alloys. Fischer et al. [6] extended this correlation throughout the transition metal series. They proposed a model to explain this correlation, which started from a nearly filled electron-band with d holes, and which included exchange interactions.

Measurements by Walker et al. [7] at low temperatures, as well as by Weinmann and Steinemann [3] at high temperatures, showed clearly from the behaviour of the shear modulus $G_2 = C_{44}$ (cf. equation (36)) in different Pd alloys that the d holes at the Fermi surface are near the point L of the Brillouin zone.

By calculating the band energies of a sheared crystal one has to carefully take account of differences between small and nearly equal quantities. Peter [9] suggested specially adapted perturbation methods. To circumvent the difficulty of a shear-dependent set of points $\mathbf{k}$ in the Brillouin zone, for which the diagonalizations leading to the band energies have to be made, he introduced a covariantly transformed reciprocal space, then independent of the shear-strain, so that the points $\mathbf{k}$ for the energy calculation remain fixed.

Since according to Heine et al. [10] the effective atomic potentials giving the correct band structure contain the same many-body corrections as the electron–phonon interaction constants, the study of uniform shear strains thus serves as a means of finding the numerical values of the electron–phonon matrix elements.

The correlation between shear-moduli, their respective temperature derivatives and the paramagnetic susceptibility certainly parallels the change of energy in both physical processes by conservation of volume.

In this part of our paper we shall derive explicitly the general features of our approach and give some first numerical results. In a later part we shall give more ample numerical results for various transition metal elements and compounds. To reduce the

numerical effort and to allow low temperature calculations in transition metals with a broad d-band, one should use an interpolation procedure, a procedure not necessary for the calculation of Pd and some of its alloys.

2. Tight-Binding Model

We shall consider only the physics of d-electrons in a transition metal and use $\hat{\mathscr{H}}$ as the Hamiltonian instead of $\mathbf{H}_{dd}$ as given in (1). Let the equilibrium positions of the lattice ions be $\mathbf{R}$ in simple (Bravais) lattices. The electrons are assumed to move in spherical symmetric atomic potentials $v(|\mathbf{r}-\mathbf{R}|)$; the atomic wave functions $\phi_a(\mathbf{r}-\mathbf{R})$ $(a=1,2,\ldots,5)$[3]) are degenerate at E_0, and are chosen as Löwdin functions (cf. Ref. [11]). The Bloch functions constructed with them are thus orthonormal

$$\langle \mathbf{k}', a|\mathbf{k}, b\rangle = \delta_{\mathbf{k}',\mathbf{k}} \cdot \delta_{a,b}$$

$$\langle \mathbf{r}|\mathbf{k}, a\rangle \equiv \psi_{\mathbf{k},a}(\mathbf{r}) := \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} \phi_a(\mathbf{r}-\mathbf{R}). \tag{3}$$

In calculating the matrix elements of the Hamiltonian

$$\hat{\mathscr{H}} = \hat{T} + \sum_{\mathbf{R}} v(|\mathbf{r}-\mathbf{R}|) \tag{4}$$

with the Bloch functions (3) to obtain the matrix form (1), one keeps, according to Slater and Koster [11], in the tight-binding limit, only one- and two-centre integrals where the atomic potential is located on one of the two atoms on which the atomic orbitals are located.

$$X_{ab}(R; lmn) = (\phi_a(\mathbf{r}-\mathbf{R}'), \quad \hat{\mathscr{H}}\phi_b(\mathbf{r}-\mathbf{R}'')). \tag{5}$$

l, m, n are the direction cosines of $\mathbf{R}=\mathbf{R}'-\mathbf{R}''$; $R=|\mathbf{R}|$. In Table I we repeat explicitly the reduction of the integrals (5) to three different ones given in Ref. [11].

$$d_0(R) \equiv dd\sigma$$

$$d_1(R) \equiv dd\pi$$

$$d_2(R) \equiv dd\delta. \tag{6}$$

The matrix elements of $\hat{\mathscr{H}}$ are (cf. Ref. [1]):

$$H_{ab}(\mathbf{k}) = (E_0 + d)\,\delta_{a,b} + \sum_{\mathbf{R}\neq 0} e^{i\mathbf{k}\mathbf{R}} X_{ab}(R; lmn) \tag{7}$$

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[3]) We fix the index a arbitrarily to the d-symmetries as follows: $a=1$ for xy; $a=2$ for zx; $a=3$ for yz; $a=4$ for x^2-y^2; $a=5$ for $3z^2-r^2$.

where:

$$d = -\Gamma \frac{5!!}{4\sqrt{\pi}} \sum_{s=0}^{\infty} \frac{\alpha^{2s-5}}{s!(2s-5)}$$

$$d_j = (k_0 R)^{-5} f_j(k_0 R, \alpha) \cdot \Gamma \quad (j = 0, 1, 2)$$

$$f_0 = -160\pi^{-1/2}(I_4 - 2I_2 + \tfrac{3}{4}I_0)$$

$$f_1 = 240\pi^{-1/2}(I_2 - \tfrac{1}{2}I_0)$$

$$f_2 = -120\pi^{-1/2} I_0$$

$$I_n = \int_{k_0 R/2\alpha}^{\infty} \eta^{4+n} \exp\{-\eta^2 + (k_0 R/2\eta)^2\}\, d\eta \quad (n = 0, 2, 4)$$

$$k_0^2 = 2mE/\hbar^2, \tag{8a–g}$$

α and Γ are adjustable parameters.

2.1. Crystal with uniform shear; band structure

The spirit of our approach is to assume that the tightly bound d-electrons follow, undistortedly, all motions of the lattice atoms. If $\delta\mathbf{R}(\gamma)$ characterizes the shear deformation of the lattice (cf. equations (23), (24)), the Hamiltonian (4) and the Bloch functions (3) will thus change to

$$\hat{\mathscr{H}}'(\gamma) = \hat{T} + \sum_{\mathbf{R}} v(|\mathbf{r} - \mathbf{R} - \delta\mathbf{R}(\gamma)|) \tag{9}$$

$$\langle \mathbf{r}|\mathbf{k}, a, \gamma\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} \phi_a(\mathbf{r} - \mathbf{R} - \delta\mathbf{R}(\gamma)). \tag{10}$$

In (10) we chose the reciprocal space in such a way that

$$\mathbf{k}'(\mathbf{R} + \delta\mathbf{R}) = \mathbf{k}\mathbf{R}.$$

The band structure of the sheared crystal follows from a Hamiltonian matrix similar to (7), but calculated with (9) and (10)

$$H'_{ab}(\mathbf{k}, \gamma) = \langle \mathbf{k}, a, \gamma|\hat{\mathscr{H}}'(\gamma)|\mathbf{k}, b, \gamma\rangle, \tag{11}$$

by applying a unitary transformation $\boldsymbol{U}'(\mathbf{k}\gamma)$ to (11),

$$\boldsymbol{U}'(\mathbf{k}, \gamma)\, \boldsymbol{H}'(\mathbf{k}, \gamma)\, \boldsymbol{U}'(\mathbf{k}, \gamma)^{-1} = (E'_n(\mathbf{k}, \gamma) \cdot \delta_{nm}), \tag{12}$$

$n = 1, 2, \ldots, 5$: band index.

In the tight-binding model $E'_n(\mathbf{k}, \gamma)$ are the correct eigenvalues ('bands') of $\hat{\mathscr{H}}'(\gamma)$. Since we consider only small shear-deformations we can develop $E'_n(\mathbf{k}, \gamma)$ into a series after γ, the parameter which characterizes the deformation (cf. (26) and (29)):

$$E'_n(\mathbf{k}, \gamma) = E_n(\mathbf{k}) + \gamma E_n^{(1)}(\mathbf{k}) + \tfrac{1}{2}\gamma^2 E_n^{(2)}(\mathbf{k}). \tag{13}$$

$E_n(\mathbf{k})$ is, of course, the band energy of the undistorted crystal found from (1) by

$$\boldsymbol{U}(\mathbf{k})\,\boldsymbol{H}\boldsymbol{U}(\mathbf{k})^{-1} =: \boldsymbol{A}(\mathbf{k}) = (E_n(\mathbf{k})\delta_{nm}). \tag{14}$$

As a result, one can find $E_n^{(1)}$, $E_n^{(2)}$ in (13) without performing unitary transformations $\boldsymbol{U}'(\mathbf{k},\gamma)$ for any γ. One only needs to know $\boldsymbol{U}(\mathbf{k})$ for the equilibrium crystals, which greatly simplifies the numerical calculations.

We introduce a matrix $\boldsymbol{V}(\mathbf{k},\gamma)$ which is unitary up to second order in γ:

$$\boldsymbol{V}(\mathbf{k},\gamma) = \boldsymbol{1} + \gamma\boldsymbol{W}(\mathbf{k}) + \tfrac{1}{2}\gamma^2\,\boldsymbol{Z}(\mathbf{k})$$
$$\boldsymbol{W}^+ = -\boldsymbol{W}; \quad \boldsymbol{Z} + \boldsymbol{Z}^+ = 2W^2 \tag{15}$$

and claim that

$$\boldsymbol{U}'(\mathbf{k},\gamma) = \boldsymbol{V}(\mathbf{k},\gamma)\cdot\boldsymbol{U}(\mathbf{k}). \tag{16}$$

Developing $\boldsymbol{H}'(\mathbf{k},\gamma)$ into a series up to terms in γ^2,

$$\boldsymbol{H}'(\mathbf{k},\gamma) = \boldsymbol{H}(\mathbf{k}) + \gamma\tilde{\boldsymbol{B}}(\mathbf{k}) + \tfrac{1}{2}\gamma^2\,\tilde{\boldsymbol{C}}(\mathbf{k}). \tag{17}$$

We find from (12), with (14) and (16),

$$(E_n'(\mathbf{k},\gamma)\,\delta_{nm}) = (E_n(\mathbf{k})\delta_{nm}) + \gamma(\boldsymbol{B} + \boldsymbol{W}\boldsymbol{A} - \boldsymbol{A}\boldsymbol{W}) + \tfrac{1}{2}\gamma^2\{(\boldsymbol{C} + 2(\boldsymbol{W}\boldsymbol{B} - \boldsymbol{B}\boldsymbol{W})$$
$$+ (\boldsymbol{Z}\boldsymbol{A} - \boldsymbol{A}\boldsymbol{Z}) + 2(\boldsymbol{A}\boldsymbol{W} - \boldsymbol{W}\boldsymbol{A})\,\boldsymbol{W})\}, \tag{18}$$

where

$$\boldsymbol{B} = \boldsymbol{U}\tilde{\boldsymbol{B}}\boldsymbol{U}^{-1}; \quad \boldsymbol{C} = \boldsymbol{U}\tilde{\boldsymbol{C}}\boldsymbol{U}^{-1}. \tag{19}$$

The non-diagonal elements of (18) have to be zero. From this condition we find

$$W_{nm}(\mathbf{k}) = \frac{B_{nm}(\mathbf{k})}{E_n(\mathbf{k}) - E_m(\mathbf{k})} \quad (n \neq m). \tag{20}$$

The diagonal part of $\boldsymbol{W}$ vanishes from (15).

Similarly one finds $\boldsymbol{Z}(\mathbf{k})$ but it does not contribute to the diagonal elements in (18). These are:

$$E_n'(\mathbf{k},\gamma) = E_n(\mathbf{k}) + \gamma B_{nn}(\mathbf{k}) + \tfrac{1}{2}\gamma^2\left\{C_{nn}(\mathbf{k}) + 2\sum_m{}' \frac{|B_{nm}|^2}{E_n(\mathbf{k}) - E_m(\mathbf{k})}\right\}. \tag{21}$$

Finally, we obtain, for $E_n \neq E_m$,

$$E_n^{(1)} = B_{nn}(\mathbf{k})$$
$$E_n^{(2)} = C_{nn}(\mathbf{k}) + 2\sum_m{}' \frac{|B_{nm}(\mathbf{k})|^2}{E_n(\mathbf{k}) - E_m(\mathbf{k})}. \tag{22}$$

As a result we found the perturbation expansion of $E_n'(\mathbf{k},\gamma)$ by performing only matrix multiplications, and not a diagonalization procedure for each separate γ. Degeneracies ($E_n \sim E_m, n \neq m$) require the usual special procedures. The corresponding thermodynamic expressions (equation (80)) remain finite. The transformation matrix $\boldsymbol{U}(\mathbf{k})$ is already known from the unsheared crystal.

2.2. Crystal with uniform shear; parameters

In order to derive $\boldsymbol{B}$ and $\boldsymbol{C}$ in (22) we go back to (19) and (7), where we have to develop $X'_{ab}(R';l'm'n')$ (all primed variables depend on γ).

There are two fundamental shear deformations, which we specify by special forms of the deformation tensor $\boldsymbol{\varepsilon}$:

$$\epsilon_{ij} = \begin{cases} \frac{1}{2}\left(\frac{\partial}{\partial x_i}\delta R_j + \frac{\partial}{\partial x_j}\delta R_i\right) & (i \neq j) \\ \frac{\partial}{\partial x_i}(\delta R_i) & (i = j) \end{cases}$$

$i,j = 1, 2, 3$, in such a way that $\mathrm{tr}\{\boldsymbol{\varepsilon}\} = 0$.

Case one: tetragonal shear

$$\epsilon_{11} = -2\epsilon_{22} = -2\epsilon_{33} = \gamma_1$$

$$\epsilon_{12} = \epsilon_{13} = \epsilon_{23} = 0. \tag{23}$$

Case two: trigonal shear

$$\epsilon_{11} = \epsilon_{22} = \epsilon_{33} = 0$$

$$\epsilon_{12} = \epsilon_{13} = \epsilon_{23} = \gamma_2. \tag{24}$$

1) Tetragonal shear. Since in the sheared lattice we have

$$\mathbf{R}' = \mathbf{R} + \delta\mathbf{R} = \mathbf{R} + \epsilon\mathbf{R} \tag{25}$$

we find from (23)

$$R'_i = R_i(1 + \epsilon_{ii})$$

$$\delta\mathbf{R} = \gamma_1 \mathbf{P}_1 := \gamma_1\{R_1; -\tfrac{1}{2}R_2; -\tfrac{1}{2}R_3\} \tag{26}$$

and from (26), by calculation,

$$R' = R\{1 + \gamma_1 \cdot \tfrac{1}{2}(3l^2 - 1) + \tfrac{1}{2}\gamma_1^2 \cdot \tfrac{9}{4} l^2(1 - l^2)\}$$

$$\frac{1}{R'} = \frac{1}{R}\{1 - \gamma_1 \cdot \tfrac{1}{2}(3l^2 - 1) + \tfrac{1}{2}\gamma_1^2 \cdot \tfrac{1}{4}(27l^4 - 21l^2 + 2)\}$$

$$l' = l\{1 + \gamma_1 \cdot \tfrac{3}{2}(1 - l^2) + \tfrac{1}{2}\gamma_1^2 \cdot \tfrac{3}{4}(9l^4 - 11l^2 + 2)$$

$$m' = m\{1 - \gamma_1 \cdot \tfrac{3}{2} l^2 + \tfrac{1}{2}\gamma_1^2 \cdot \tfrac{3}{4}(9l^4 - 5l^2)$$

$$n' = n\{1 - \gamma_1 \cdot \tfrac{3}{2} l^2 + \tfrac{1}{2}\gamma_1^2 \cdot \tfrac{3}{4}(9l^4 - 5l^2), \tag{27a–e}$$

where we have used l', m', n' for the direction cosines l'_i defined by

$$l'_i = \frac{R'_i}{R} \tag{28}$$

(equivalently for the unprimed quantities).

2) *Trigonal shear.* Starting again with (25), one finds from (24)

$$\delta\mathbf{R} = \varepsilon_2 \mathbf{R} = \gamma_2 \begin{pmatrix} R_2 + R_3 \\ R_1 + R_3 \\ R_1 + R_2 \end{pmatrix} =: \gamma_2 \mathbf{P}_2 \tag{29}$$

and from that

$$R' = R\{1 + \gamma_2(S^2 - 1) + \tfrac{1}{2}\gamma_2^2 S^2(3 - S^2)\}$$

$$\frac{1}{R'} = \frac{1}{R}\{1 - \gamma_2(S^2 - 1) + \tfrac{1}{2}\gamma_2^2(3S^4 - 7S^2 + 2)\}$$

$$l_i' = l_i + \gamma_2 S(1 - S l_i) + \tfrac{1}{2}\gamma_2^2 S[S(3S^2 - 5)\, l_i - 2(S^2 - 1)] \tag{30a–c}$$

where

$$S = l + m + n = \sum_i l_i . \tag{31}$$

2.3. *Crystal with uniform shear; transfer integrals*

To obtain finally the matrices $\tilde{B}$ and $\tilde{C}$, as defined in (17), we observe that the two-centre approximation (Table I) is valid for the deformed as well as for the undeformed crystal. We can write

$$X'_{ab}(R'; l'\, m'\, n') \equiv X'_{ab}[R'(\gamma);\, l'(\gamma), m'(\gamma), n'(\gamma)]$$
$$= \sum_{j=0}^{2} d_j[R'(\gamma)] \cdot g_{ab}^{j}[l'(\gamma), m'(\gamma), n'(\gamma)]. \tag{32}$$

Table I
Transfer integrals (5), (6) for cubic crystals (cf. [11])

$X_{ab}(R; lmn) = \sum_{j=0}^{2} d_j(R) \cdot g_{ab}^{(j)}(lmn)$

a, b	$g_{ab}^{(0)}(lmn)$	$g_{ab}^{(1)}(lmn)$	$g_{ab}^{(2)}(lmn)$
11	$3l^2 m^2$	$l^2 + m^2 - 4l^2 m^2$	$n^2 + l^2 m^2$
12	$3l^2 mn$	$mn(1 - 4l^2)$	$mn(l^2 - 1)$
13	$3lm^2 n$	$ln(1 - 4m^2)$	$ln(m^2 - 1)$
14	$\frac{3}{2}lm(l^2 - m^2)$	$2lm(m^2 - l^2)$	$\frac{1}{2}lm(l^2 - m^2)$
15	$\sqrt{3}lm[n^2 - \frac{1}{2}(l^2 + m^2)]$	$-2\sqrt{3}lmn^2$	$\frac{1}{2}\sqrt{3}lm(1 + n^2)$
22	$3l^2 n^2$	$n^2 + l^2 - 4n^2 l^2$	$m^2 + n^2 l^2$
23	$3ln^2 m$	$lm(1 - 4n^2)$	$lm(n^2 - 1)$
24	$\frac{3}{2}ln(l^2 - m^2)$	$ln[1 - 2(l^2 - m^2)]$	$-nl[1 - \frac{1}{2}(l^2 - m^2)]$
25	$\sqrt{3}ln[n^2 - \frac{1}{2}(l^2 + m^2)]$	$\sqrt{3}ln(l^2 + m^2 - n^2)$	$-\frac{1}{2}\sqrt{3}ln(l^2 + m^2)$
33	$3m^2 n^2$	$m^2 + n^2 - 4m^2 n^2$	$l^2 + m^2 n^2$
34	$\frac{3}{2}mn(l^2 - m^2)$	$-mn[1 + 2(l^2 - m^2)]$	$mn[1 + \frac{1}{2}(l^2 - m^2)]$
35	$\sqrt{3}mn[n^2 - \frac{1}{2}(l^2 + m^2)]$	$\sqrt{3}mn(l^2 + m^2 - n^2)$	$-\frac{1}{2}\sqrt{3}mn(l^2 + m^2)$
44	$\frac{3}{4}(l^2 - m^2)^2$	$l^2 + m^2 - (l^2 - m^2)^2$	$n^2 + \frac{1}{4}(l^2 - m^2)^2$
45	$\frac{1}{2}\sqrt{3}(l^2 - m^2)[n^2 - \frac{1}{2}(l^2 + m^2)]$	$\sqrt{3}n^2(m^2 - l^2)$	$\frac{1}{4}\sqrt{3}(1 + n^2)(l^2 - m^2)$
55	$[n^2 - \frac{1}{2}(l^2 + m^2)]^2$	$3n^2(l^2 + m^2)$	$\frac{3}{4}(l^2 + m^2)^2$

Now the Taylor series expansions of the factors $d_j(R')$ and $g^j_{ab}(l'm'n')$ give, respectively,

$$d_j[R'(\gamma)] = d_j^{(0)}(R) + d_j^{(1)}(R)\cdot\gamma + d_j^{(2)}(R)\cdot\frac{\gamma^2}{2}, \tag{32a}$$

where $d_j^{(0)}(R) \equiv d_j(R)$ is the radial factor given by equation (8a), while

$$d_j^{(1)}(R) = \frac{d}{d\gamma} d_j[R'(\gamma)]\bigg|_{\gamma=0}$$

and

$$d_j^{(2)}(R) = \frac{d^2}{d\gamma^2} d_j[R'(\gamma)]\bigg|_{\gamma=0}.$$

Similarly, we have

$$g^j_{ab}[l'(\gamma), m'(\gamma), n'(\gamma)] = g_{ab}^{(j,0)}(lmn) + g_{ab}^{(j,1)}(lmn)\,\gamma + g_{ab}^{(j,2)}(lmn)\cdot\frac{\gamma^2}{2}, \tag{32b}$$

where

$$g_{ab}^{(j,0)}(lmn) = g^j_{ab}(lmn)$$

are the terms shown in Table I, while

$$g_{ab}^{(j,1)}(lmn) = \frac{d}{d\gamma} g^j_{ab}[l', m', n']\bigg|_{\gamma=0}$$

$$g_{ab}^{(j,2)}(lmn) = \frac{d^2}{d\gamma^2} g^j_{ab}[l', m', n']\bigg|_{\gamma=0}.$$

Replacing in equation (32), we get

$$X'_{ab}(R'; l'm'n') = X_{ab}(R; lmn) + \gamma x_{ab} + \frac{\gamma^2}{2} y_{ab}, \tag{33}$$

where $X_{ab}(R;mn)$ is just the zeroth-order matrix element occurring in (7), while

$$x_{ab} = \sum_{j=0}^{2} [d_j^{(0)}(R)\, g_{ab}^{(j,1)}(lmn) + d_j^{(1)}(R)\, g_{ab}^{(j,0)}(lmn)] \tag{33a}$$

$$y_{ab} = \sum_{j=0}^{2} [d_j^{(0)}(R)\, g_{ab}^{(j,2)}(lmn) + 2d_j^{(1)}(R)\, g_{ab}^{(j,1)}(lmn) + d_j^{(2)}(R)\, g_{ab}^{(j,0)}(lmn)]. \tag{43b}$$

By the help of (33), one has

$$\tilde{B}_{ab}(\mathbf{k}) = \sum_{\mathbf{R}\neq 0} e^{i\mathbf{k}\mathbf{R}} x_{ab} \tag{34}$$

$$C_{ab}(\mathbf{k}) = \sum_{\mathbf{R}\neq 0} e^{i\mathbf{k}\mathbf{R}} y_{ab}. \tag{35}$$

In the calculation of the quantities x_{ab} and y_{ab}, equations (33a–b) deserve further consideration. The radial factors $d_j^{(1)}(R)$ and $d_j^{(2)}(R)$ can be factorized, each into a shear-independent and a shear-dependent part, as follows:

$$d_j^{(1)}(R) = R\frac{dd_j(R)}{dR}\cdot\left[\frac{d}{d\gamma}\left(\frac{R'(\gamma)}{R}\right)\right]\Bigg|_{\gamma=0}$$

$$d_j^{(2)}(R) = R^2\frac{d^2 d_j(R)}{dR^2}\left\{\left[\frac{d}{d\gamma}\left(\frac{R'(\gamma)}{R}\right)\right]\Bigg|_{\gamma=0}\right\}^2 + R\frac{dd_j(R)}{dR}\left[\frac{d^2}{d\gamma^2}\frac{R'(\gamma)}{R}\right]\Bigg|_{\gamma=0}.$$

The derivatives with respect to γ are obvious from equations (27a) and (30a), respectively, while the derivatives of $d_j(R)$ are to be obtained from equation (8a). One has, for example,

$$\frac{d}{dR}d_j(R) = \Gamma f_j(k_0 R,\alpha)\frac{d}{dR}(k_0 R)^{-5} + \Gamma(k_0 R)^{-5}\frac{d}{dR}f_j(k_0 R,\alpha)$$

and a similar expression for the second-order derivative. In the case of Cu and Fe, we known, from the paper by Pettifor [1], all the quantities E, Γ, α and R, and we can therefore estimate both terms of this sum. We expected, *a priori*, to get small values for the second term, as compared to the first. To our surprise this was not the case: the contributions of the terms arising from the derivatives of f_j to $(d/dR)d_j(R)$ and $(d^2/dR^2)\,d_j(R)$ ranged between 20 and 500% (with preference for 100%) as compared to those derived from the classical term $(k_0 R)^{-5}$. Moreover, they showed a remarkable stability over a wide range of values for the parameters E, α and R. Nevertheless, we dropped them for two reasons. First, because we believe they are spurious terms, introduced by the Gaussian cut-off procedure of Pettifor [1] (for the Lorentzian cut-off procedure such spurious terms do not occur). Our conviction is supported by the Grüneisen parameter data for the above metals. The second reason for dropping the above terms is aesthetical: values for E and α are not given for metals other than Cu and Fe, therefore we would be in the impossible position of having to give a unitary description for all the transition series. However, this second reason is quite secondary with respect to the first.

Concerning the calculation of the quantities $g_{ab}^{(j,1)}(lmn)$ and $g_{ab}^{(j,2)}(lmn)$, we observe simply from Table I that if we put

$$l_i' = l_i^{(0)} + l_i^{(1)}\gamma + l_i^{(2)}\frac{\gamma^2}{2}$$

we have at once

$$l_i' l_j' = l_{ij}^{(0)} + l_{ij}^{(1)}\gamma + l_{ij}^{(2)}\frac{\gamma^2}{2},$$

where

$$l_{ij}^{(0)} = l_i^{(0)} l_j^{(0)}$$

$$l_{ij}^{(1)} = l_i^{(0)} l_j^{(1)} + l_i^{(1)} l_j^{(0)}$$

$$l_{ij}^{(2)} = l_i^{(0)} l_j^{(2)} + 2l_i^{(1)} l_j^{(1)} + l_i^{(2)} l_j^{(0)}.$$

Using these rules, we get $g_{ab}^{(j,0)}(lmn)$, $g_{ab}^{(j,1)}(lmn)$ and $g_{ab}^{(j,2)}(lmn)$ on a computer immediately with the minimum number of operations and with minimum computing time.

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[4] If all factors were taken as their zeroth-order terms one would of course arrive at $X_{ab}(R;lmn)$ itself.

3. Thermodynamics of Shear Deformations

The experimentally established correlation between the paramagnetic susceptibility and the temperature derivation of the shear-moduli needs theoretical explanation. We first summarize the thermodynamics of shear deformation.

The shear-moduli for tetragonal and trigonal shear in cubic crystals are given as

$$G_1 = \tfrac{1}{2}(C_{11} - C_{12}); \quad G_2 = C_{44}, \tag{36}$$

where the $C_{\alpha\beta}$ are the elastic constants of the material.

The free energy of the system F' (prime for the strained crystal) is related to the elastic potential

$$F' = F(0) + \tfrac{1}{2} \sum_{\alpha,\beta=1}^{6} C_{\alpha\beta}\, \epsilon_\alpha\, \epsilon_\beta. \tag{37}$$

In (37) the Voigt notation of the indices is as usual for $\alpha = 1, \ldots, 6$, equivalent to 11; 22; 33; 23; 13; 12.

Inserting (23) or (24) into (37) and using the definitions (36), one finds for both shear deformations that

$$F'(\gamma_i) = F(0) + \tfrac{3}{2} G_i \gamma_i^2 \quad (i = 1, 2) \tag{38}$$

so that we may omit the index i for briefness. Equation (38) is a second-order derivation for $F'(\gamma)$ and we thus find

$$G = \frac{1}{3}\left(\frac{\partial^2 F'}{\partial \gamma^2}\right)_0. \tag{39}$$

In order to calculate $\partial\mu/\partial\gamma$, we list the following three conditions:

1) As is already implicitly used in (37) one has the *condition of equilibrium*:

$$\left(\frac{\partial F'(\gamma, n)}{\partial \gamma}\right)_{n,\gamma=\gamma_0} = 0. \tag{40}$$

2) *Particle conservation*

In a given substance the number of electrons n is independent of shear angle γ:

$$\frac{\partial n}{\partial \gamma} = 0. \tag{41}$$

3) *Symmetry conservation*

Through (40) is defined the equilibrium shear angle $\gamma_0(n)$ as a function of n. γ_0 could vary with n or could remain constant over a finite domain of n, in particular γ_0 could remain $\gamma_0 = 0$ (cubic symmetry). In this latter case we can write

$$\frac{\partial}{\partial n}\left[\left(\frac{\partial F'(\gamma, n)}{\partial \gamma}\right)_{n,\gamma=\gamma_0}\right] = 0. \tag{42}$$

From these three equations it follows that $([\partial\mu(n,\gamma)]/\partial\gamma)_{\gamma=\gamma_0} = 0$. In the case where γ measures the compression, γ_0 is expected to vary with n. Hence the expression for the expression for the compression modulus includes a term in $(\partial\mu/\partial\gamma)_{\gamma=\gamma_0}$.

We shall also include in our consideration of Bloch electrons of energies (21) an exchange interaction between particles with equal spin. For the sake of simplicity we place all electron quantum numbers into one index only:

$$(\mathbf{k}, n; s) \equiv (l; s), \tag{43}$$

where s is the spin variable ± 1. The single-particle energies are

$$E_l'(J) = E_l' - \sum_{l'} J(l,l') f'(l'). \tag{44}$$

The Fermi function $f(l)$, is, as usual,

$$f(l) = \frac{1}{\exp[(E_l - \mu)/k_B T] + 1}, \tag{45a}$$

or, in the sheared crystal,

$$f'(l) = \frac{1}{\exp[(E_l' - \mu')/k_B T] + 1}, \tag{45b}$$

where the chemical potential μ also depends on γ.

$$n = 2\sum_l f(l) = 2\sum_l f'(l) \tag{46}$$

is the total number of electrons in the crystal.

The free energy of the electrons is given by Ref. [12]:

$$F' = n\mu' - 2k_B T \cdot \sum_l \ln\{1 + \exp[(\mu' - E_l'(J))/k_B T]\} + \sum_{l,l'} J(l,l') f'(l) f'(l') \tag{47}$$

or in equal form for the unstrained crystal. Defining a new Fermi energy by

$$z_l' = \mu' + \sum_{l'} J(l,l') f'(l'). \tag{48}$$

One can rewrite (47) as:

$$F' = 2\sum_l \{f_l'(E_l')\, z_l' - k_B T \ln\{1 + \exp[(z_l' - E_l')/k_B T]\} - \tfrac{1}{2}\sum_{l'} J(l,l') f_l'(E_l') f_l'(E_l')\}, \tag{49}$$

where the index at f_l' indicates the explicit form of the new Fermi energy (48). E_l' are the single-particle energies without exchange as given in (21).

We find from (49)

$$\frac{\partial F'}{\partial\gamma} = 2\sum_l f_l'(E_l')\frac{\partial E_l'}{\partial\gamma} \tag{50}$$

$$G = \tfrac{2}{3}\sum_l \left\{ f_l(E_l)\left(\frac{\partial^2 E_l'}{\partial\gamma^2}\right)_0 + \left(\frac{\partial f_l'(E_l')}{\partial\gamma}\right)_0 \left(\frac{\partial E_l'}{\partial\gamma}\right)_0 \right\}. \tag{51}$$

Notice that from (40), (50) and (48) one also finds $(\partial\mu'/\partial\gamma)_0 = 0$. Indeed, from (42),

$$\frac{\partial}{\partial\mu}\left(\frac{\partial F}{\partial\gamma}\right)_0 = 2\sum \frac{\partial f(E_k)}{\partial E_k}\left(\frac{\partial E_k}{\partial\gamma}\right)_0 = 0.$$

From (41),

$$\frac{\partial n}{\partial\gamma} = \sum \frac{\partial f(E_k)}{\partial E_k}\left[\left(\frac{\partial E_k}{\partial\gamma}\right)_0 - \left(\frac{\partial z_k}{\partial\gamma}\right)_0\right] = 0.$$

Hence,

$$\sum_k \frac{\partial f(E_k)}{\partial E}\left(\frac{\partial z_k}{\partial\gamma_0}\right) = 0.$$

From (48),

$$\left(\frac{\partial\mu}{\partial\gamma}\right)_0 = \left(\frac{\partial z_k}{\partial\gamma}\right)_0 - \sum_{k'} J(k,k')\left(\frac{\partial f(E_{k'})}{\partial\gamma}\right)_0.$$

Summing over $\partial f(E_k)/\partial E$ we get

$$\frac{\partial\mu}{\partial\gamma_0}\sum \frac{\partial f(E_k)}{\partial E_k} = -\sum_{k'}\left[\sum_k J(k,k')\frac{\partial f(E_k)}{\partial E_k}\right]\left(\frac{\partial f(E_k)}{\partial\gamma}\right)_0.$$

Now, $\sum J(k',k)\,[\partial f(E_{k'})/\partial E_{k'}] = g(k)$ is of cubic symmetry and the other factor, $(\partial f(E_k)/\partial\gamma)_0$, is of tetragonal (or trigonal) symmetry, hence $(\partial\mu/\partial\gamma)_0 = 0$.

a) $J(l,l') = J = \text{const.}$

In this simple case the exchange cannot have any influence on F', as can be seen from (44): the energy is renormalized by the additive constant of $\frac{1}{2}Jn$. The shear-moduli (51) then becomes:

$$G = \tfrac{2}{3}\sum_l \left\{ f_l(E_l)\left(\frac{\partial^2 E_l'}{\partial\gamma^2}\right)_0 + \frac{\partial f_l}{E_l}\left(\frac{\partial E_l'}{\partial\gamma}\right)^2\right\}. \tag{52}$$

b) $J(l,l') = J\cdot\Delta(l-l')\,;\ \Delta(0) = 1$

In this case $J(l,l')$ describes a short-range exchange force in **k**-space. One finds an explicit influence of the exchange force:

$$\begin{aligned}
\sum_l \left(\frac{\partial f_l'(E_l')}{\partial\gamma}\right)_0 \cdot \left(\frac{\partial E_l'}{\partial\gamma}\right)_0 &= \sum_l \frac{\partial f_l}{\partial E_l}\left(\frac{\partial E_l'}{\partial\gamma}\right)_0^2 + \sum_l \frac{\partial f_l}{\partial z_l}\cdot\left(\frac{\partial z_l}{\partial\gamma}\right)_0\left(\frac{\partial E_l'}{\partial\gamma}\right)_0 \\
&= \sum_l \frac{\partial f_l}{\partial E_l}\left(\frac{\partial E_l'}{\partial\gamma}\right)_0^2 + \sum_{ll'} \frac{\partial f_l}{\partial z_l} J(ll')\left(\frac{\partial f_{l'}(E_l')}{\partial\gamma}\right)_0\left(\frac{\partial E_l'}{\partial\gamma}\right)_0 \\
&= \sum_l \frac{\partial f_l}{\partial E_l}\left(\frac{\partial E_l'}{\partial\gamma}\right)_0^2 + \sum_{ll'}\left(-\frac{\partial f_l'}{\partial E_l'}\right) J(l'l)\left(\frac{\partial E_l'}{\partial\gamma}\right)_0 \cdot \left(\frac{\partial f_l'(E_l')}{\partial\gamma}\right)_0 \\
&= \sum_l \frac{\partial f_l}{\partial E_l}\left(\frac{\partial E_l'}{\partial\gamma}\right)_0^2 + \sum_l \left(\frac{\partial f_l'(E_l')}{\partial\gamma}\right)_0 \cdot J \cdot \left(\frac{\partial E_l'}{\partial\gamma}\right)_0 \cdot \bar{N}.
\end{aligned}$$

Thus

$$\sum_l \left(\frac{\partial f_l'(E_l')}{\partial \gamma}\right)_0 \left(\frac{\partial E_l'}{\partial \gamma}\right)_0 = (1 - J\bar{N})^{-1} \sum_l \frac{\partial f_l}{\partial E_l} \left(\frac{\partial E_l'}{\partial \gamma}\right)_0^2 .$$

The shear-moduli then come out as:

$$G = \tfrac{2}{3} \sum_l \left\{ (1 - J\bar{N}(E_F))^{-1} \frac{\partial f_l}{\partial E_l} \left(\frac{\partial E_l'}{\partial \gamma}\right)_0^2 + f_l(E_l) \left(\frac{\partial^2 E_l'}{\partial \gamma^2}\right)_0 \right\}. \tag{53}$$

As we observe, (52) and (53) are determined by (14), (13) and (22), since $(\partial E'/\partial\gamma)_0 \equiv E^{(1)}$, $(\partial^2 E'/\partial\gamma^2) = E^{(2)}$.

4. Paramagnetic Susceptibility

We start from the same free-energy expression as in (49), augmented by the spin index s:

$$F = \sum_{l,s} \{f_{ls} z_{ls} - k_B T \ln[1 + \exp((z_{ls} - E_l + s\mu_B \cdot B))/kT] + \tfrac{1}{2} \sum_{l'} J(l,l') f_{ls} f_{l's}\},$$

where μ_B is the Bohr magneton and B the magnetic induction. On taking derivatives with respect to B we find:

$$\frac{\partial F}{\partial B} = -\mu_B \sum_{l,s} s f_{ls}$$

$$\chi = -\left(\frac{\partial^2 F}{\partial B^2}\right)_0 = -2\mu_B \sum_l \frac{\partial f_{l1}}{\partial E} \left(1 + \frac{1}{\mu_B} \frac{\partial z_{l1}}{\partial B}\right)_0 .$$

Using particle conservation in the B-field, as well as (48) in the form

$$\mu = z_{ls} - \sum_{l'} J(l,l') f_{l's}.$$

One finally arrives for J at an expression

$$\chi = -2\mu_B^2 \sum_l \frac{\partial f_l}{\partial E_l} \left[1 + \frac{1}{\mu_B} \sum_{l'} J(l,l') \left(\frac{\partial f_{l'1}}{\partial B}\right)_0\right]. \tag{55}$$

a) $J(l,l') = J = \text{const.}$

Since in a magnetic field the energy for spin up and down particles is different, we expect – contrary to the shear strain – an influence of the exchange field on J. Since

$$\frac{1}{\mu_B} \sum_{l'} J(l,l') \left(\frac{\partial f_{l'1}}{\partial B}\right)_0 = J \cdot \frac{1}{\mu_B} \sum_{l'} \left(\frac{\partial f_{l'1}}{\partial B}\right)_0 = J \cdot \frac{1}{\mu_B} \cdot \tfrac{1}{2} \sum_{ls} s \left(\frac{\partial f_{ls}}{\partial B}\right)_0$$

$$= J \cdot \frac{1}{2\mu_B^2} \left(-\left(\frac{\partial^2 F}{\partial B^2}\right)_0\right) = J \frac{\chi}{2\mu_B^2}$$

we find from (55)

$$\chi = \frac{-2\mu_B^2}{1 + J \sum_l \frac{\partial f_l}{\partial E_l}} \sum_l \frac{\partial f_l}{\partial E_l}. \tag{56}$$

b) $J(l,l') = J\Delta(l - l')\,;\, \Delta(0) = 1$

Applying a similar procedure as that leading to (56), we find for short-range exchange in **k**-space

$$\chi = \frac{-2\mu_B^2}{1 - \bar{N}(E_F) \cdot J} \sum_l \frac{\partial f_l}{\partial E_l}. \tag{57}$$

5. Electron–Phonon Coupling

We shall now show that the parameters $\boldsymbol{B}$, introduced in (19), also appear in the electron–phonon coupling Hamiltonian

$$\hat{\mathscr{H}}_{\text{el-ph}} = \sum_{\mathbf{k}} \sum_{\mathbf{q},t} \sum_{n,m} \mathbf{q}_{nm}(\mathbf{k},\mathbf{q};t)\, c^+_{\mathbf{k}+\mathbf{q},n}\, c_{\mathbf{k},m'} \cdot (a_t^+(\mathbf{q}) + a_t(-\mathbf{q})), \tag{58}$$

thus connecting also the effects depending on electron–phonon coupling, as for example the superconducting transition temperature, on the potential parameters found by shear experiments, band structures and the paramagnetic susceptibility.

In (58) we have used the usual notation of electron operators c_k^+, c_k in second quantization, $a(\mathbf{q})$ for the phonon operators, $\mathbf{q}$ for the phonon momentum exchanged in an electron–phonon collision. t is the polarization index.

Phonons produce lattice deformations

$$\delta\mathbf{R} = \sum_{\mathbf{q},t} Q_t(\mathbf{q})\, \mathbf{e}_t(\mathbf{q})\, e^{i\mathbf{q}\mathbf{R}} \tag{59}$$

which vary locally. We extend our previously introduced model to a situation where, locally, the electron **k**-space is adjusted to the deformation to keep $\mathbf{k}\cdot\mathbf{R} = \text{const}$. In (59) we have, as usual, the polarization vector $\mathbf{e}_t(\mathbf{q})$ and

$$Q_t(\mathbf{q}) = \left(\frac{\hbar}{2NM\omega_t(\mathbf{q})}\right)^{1/2} (a_t^+(\mathbf{q}) + a_t(-\mathbf{q})). \tag{60}$$

When we insert (59) into the Hamiltonian (9) we find the electron–phonon coupling matrix element by first-order perturbation theory starting from

$$H'_{ab}(\mathbf{k}',\mathbf{k}) = \langle \mathbf{k}', a, \mathbf{R} | \hat{\mathscr{H}}' | \mathbf{k}, b, \mathbf{R} \rangle. \tag{61}$$

Here we use the wave functions (10). We find:

$$H'_{ab}(\mathbf{k}',\mathbf{k}) = \frac{1}{N} \sum_{\mathbf{R}_1 \mathbf{R}_2} \exp[i(\mathbf{k} - \mathbf{k}')\mathbf{R}_2] \exp[i\mathbf{k}(\mathbf{R}_1 - \mathbf{R}_2)] \cdot \tilde{I}'_{ab}(\mathbf{R}_1,\mathbf{R}_2) \tag{62}$$

$$\begin{aligned}\tilde{I}'_{ab}(\mathbf{R}_1,\mathbf{R}_2) = {} & (\phi_a(r), v(\mathbf{r})\, \phi_b(\mathbf{r} - (\mathbf{R}_1 - \mathbf{R}_2) - (\delta\mathbf{R}_1 - \delta\mathbf{R}_2))) \\ & + (\phi_a(\mathbf{r} + (\mathbf{R}_1 - \mathbf{R}_2) + (\delta\mathbf{R}_1 - \delta\mathbf{R}_2)), v(\mathbf{r})\, \phi_b(\mathbf{r})).\end{aligned} \tag{63}$$

We develop (62) into a series after $(\delta\mathbf{R}_1 - \delta\mathbf{R}_2)$ up to first order and find

$$\tilde{I}'_{ab}(\mathbf{R}_1, \mathbf{R}_2) = I^{(0)}_{ab}(\mathbf{R}_1 - \mathbf{R}_2) + \tilde{I}^{(1)}_{ab}(\mathbf{R}_1 - \mathbf{R}_2) \cdot (\delta\mathbf{R}_1 - \delta\mathbf{R}_2). \tag{64}$$

With (64) we can reduce (61) considerably. In the $I^{(0)}$ term one may perform the $\mathbf{R}_2$ summation since $(\mathbf{R}_1 - \mathbf{R}_2)$ may be introduced as a new variable. In the $I^{(1)}$ term one can use (59) and perform also one of the $\mathbf{R}$ summations. The result is given in (65):

$$H'_{ab}(\mathbf{k}', \mathbf{k}) = \delta_{\mathbf{k}',\mathbf{k}} H_{ab}(\mathbf{k}) + \sum_{\mathbf{q},t} \sum_{\mathbf{R}} \delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}} e^{i\mathbf{k}\mathbf{R}} Q_t(\mathbf{q}) \, (e^{i\mathbf{q}\mathbf{R}} - 1) \, \mathbf{e}_t(\mathbf{q}) \, \tilde{I}^{(1)}_{ab}(\mathbf{R}). \tag{65}$$

We can transform (65) with the unitary matrix $\boldsymbol{U}(\mathbf{k})$ given in (14). This transforms the atomic states ϕ_a into band states and allows us to determine the electron–phonon matrix element $g_{nm}(k, q; t)$ from (58):

$$\boldsymbol{U}(\mathbf{k}') \, \boldsymbol{H}'(\mathbf{k}', \mathbf{k}) \, \boldsymbol{U}^{-1}(\mathbf{k}) = \delta_{\mathbf{k}',\mathbf{k}} \, \boldsymbol{A}(\mathbf{k}) + \sum_{\mathbf{q},t} \sum_{\mathbf{R}} \delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}} e^{i\mathbf{q}\mathbf{R}} Q_t(\mathbf{q}) \, (e^{i\mathbf{q}\mathbf{R}} - 1) \cdot \mathbf{x}^t(\mathbf{k}', \mathbf{k}; \mathbf{R}), \tag{66}$$

thus

$$g_{nm}(\mathbf{k}, \mathbf{q}, t) = \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} Q_t(\mathbf{q}) \, (e^{i\mathbf{q}\mathbf{R}} - 1) \cdot \mathbf{x}^t_{nm}(\mathbf{k}', \mathbf{k}; \mathbf{R}). \tag{67}$$

The matrix notation $\boldsymbol{x}^t(\mathbf{k}', \mathbf{k}; \mathbf{R})$ used in (66) and (67) can be connected to previously introduced quantities which, in fact, show the general utility of our approach.

We find from (65) and (66):

$$\mathbf{x}^t(\mathbf{k}', \mathbf{k}; \mathbf{R}) = \boldsymbol{U}(\mathbf{k}') \, ((\mathbf{e}_t \, \tilde{I}^{(1)}_{ab}(\mathbf{R}))) \, \boldsymbol{U}^{-1}(\mathbf{k}). \tag{68}$$

Now, from (64), we see by inspection that

$$\tilde{I}^{(1)}_{ab}(\mathbf{R}) = (\nabla_R \, \phi_a(\mathbf{r} + \mathbf{R}), v(\mathbf{r}) \, \phi_b(\mathbf{r})) - (\phi_a(\mathbf{r}), v(r) \, \nabla_R \, \phi_b(\mathbf{r} - \mathbf{R})).$$

Going back to (11) and (17) we find, as a result of the two-centre approximation, that

$$\tilde{B}_{ab}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} \mathbf{P} \cdot \tilde{I}^{(1)}_{ab}(\mathbf{R}), \tag{69}$$

with $\mathbf{P}$ either taken from (26) or (29), corresponding to the shear mode applied.

Thus we see that both the electronic contributions to the elastic coefficients and the electron–phonon coupling are determined by the quantities $\tilde{I}^{(1)}_{ab}(\mathbf{R})$.

6. Discussion

The shear moduli (51)–(53),

$$G = \tfrac{2}{3} \sum_l \left\{ S \frac{\partial f_l}{\partial E_l} (E^{(1)}_l)^2 + f_l(E_l) \, E^{(2)}_l \right\}, \tag{70}$$

or

$$G = G^{(1)} + G^{(2)} + G^{(3)}$$

$$G^{(1)} = \tfrac{2}{3} \sum_l S \frac{\partial f_l}{\partial E_l} B_{ll}^2(\mathbf{k}) \tag{71a}$$

$$G^{(2)} = \tfrac{2}{3} \sum_l f_l(E_l)\, C_{ll}(\mathbf{k}) \tag{71b}$$

$$G^{(3)} = \tfrac{2}{3} \cdot 2 \sum_{l,m}{}' f_l(E_l) \frac{|B_{lm}|^2}{E_l(\mathbf{k}) - E_m(\mathbf{k})} \tag{71c}$$

(S = Stoner factor) may be compared to the changes in energy by a magnetic field

$$\Delta E(\mathbf{k}) = b_1 \cdot \mu_B \cdot \mathbf{B} \cdot \boldsymbol{\sigma} + b_2 \cdot \mathbf{j} \cdot \mathbf{A} + c\mathbf{A}^2. \tag{72}$$

$G^{(1)}$ in (71a) corresponds to the magnetic term propertional to b_1. Both are diagonal in $\mathbf{k}$ and l and we might call $G^{(1)}$ the 'Pauli term'. $G^{(3)}$ in (71c) is non-diagonal in l and corresponds to the b_2 term in (72), and is therefore possibly named the 'van-Vleck term' (orbital paramagnetism).

The term (71b) corresponding to the quadratic term in the magnetic field acts like the core diamagnetism.

This classification parallels the one given by A. H. Wilson for tightly bound electrons.

Since under shear-deformation we also find $(\partial\mu'/\partial\gamma)_0 = 0$ (as mentioned with (50) and generally proved quite earlier [13]), the effect of shear is simply a rearrangement of electrons: some are shifted to higher, some to lower energies. Observing that the matrix $\boldsymbol{B}(\mathbf{k})$ in (18) is equivalent to the 'deformation potential' of Bardeen and Shockley [14], we might find a very simple expression in analogy with magnetic polarization and susceptibility.

Let

$$\langle \boldsymbol{B}(\mathbf{k}) \rangle = \boldsymbol{B}$$

and let us only use the diagonal terms. Then (cf. also Refs. [6] and [8a]) the mechanical 'polarization' is

$$\P = \int \{f(E - B\gamma) - f(E + B\gamma)\} N(E)\, dE$$

$$\P \cong 2D\gamma N(T); \quad N(T) = -\int \frac{\partial f}{\partial E} N(E)\, dE. \tag{73}$$

The total energy stored in the shear deformation is

$$\Delta F = -\tfrac{1}{2}\gamma B \cdot \P$$

and

$$G = \frac{1}{3}\left(\frac{\partial^2 \Delta F}{\partial \gamma^2}\right)_0 = -\tfrac{2}{3} B^2 N(T)$$

or, with inclusion of the exchange factor of Stoner (71),

$$G = -\tfrac{2}{3} B^2 S N(T). \tag{74}$$

The spin susceptibility $\chi = 2\mu_B^2 N(T)\bar{S}$ is thus directly equivalent to G, as was also used extensively to describe some anomalous properties in A15 compounds (cf. Ref. [15]).

It would be very tempting to also compare (71a) with the electron-polarization part which screens the bare phonon propagator which is given by

$$\int |g(\mathbf{q})|^2 G_0(k)\, G_0(k+q)\, d^4 k,$$

where $g(\mathbf{q})$ is given by (67) and $G_0(k)$ is the free electron propagator. But since $g(\mathbf{q})$ vanishes in the limit $q \to 0$, and as we mentioned in finding (70), $g(\mathbf{q})$ is proportional, not to $B(q)$, but to $B(q) \cdot q$.

We should remark here that for a thorough calculation of the electron–phonon matrix elements one should take into account numerical information about the phonon-spectrum, as for example found by neutron-diffraction experiments [16].

Another point to be made concerns the validity and perturbation approach leading to $E_n^{(1)}$ and $E_n^{(2)}$ in (22). Indeed, it is not hard to see that (22) corresponds exactly to a second-order quantum-mechanical perturbation treatment of the Hamiltonian (9). As already stated, the point in our formulation is from the view of numerical calculations in the undeformed and deformed lattice. By relying on the same fix-points in the Brillouin zone we are able to avoid uncertainties arising from only choosing different $\mathbf{k}$'s, with $\gamma = 0$ or $\neq 0$.

For high temperatures one can even avoid any diagonalization procedure ([9a]) by a trace method. This allows a reasonably simple numerical procedure with not too many points in the Brillouin zone in cases like Nb, where the band-width is very large.

We start from (50) and make use of (22). For simplicity we neglect exchange effects.

$$\frac{\partial F'}{\partial \gamma} = 2 \sum_{\mathbf{k}} \mathrm{tr}\{\boldsymbol{D}'(\mathbf{k};\gamma)\,[\boldsymbol{B}(\mathbf{k}) + \gamma \boldsymbol{C}(\mathbf{k})]\}, \tag{75}$$

where

$$\boldsymbol{D}'(\mathbf{k};\gamma) = \{1 + \exp[(\boldsymbol{H}'(\mathbf{k};\gamma) - \mu'\,\boldsymbol{1})/k_B T]\}^{-1}. \tag{76}$$

Since $\mathrm{tr}\{\ldots\}$ is independent of the system of states, one can return directly to (17).

We use this procedure only for $10 k_B T \gtrsim |\mu - E_{\mathrm{extr}}|$, where E_{extr} is the highest (lowest) energy in the band (electron-hole symmetry). With (39) we find, from (75),

$$G = \tfrac{2}{3} \sum_{\mathbf{k}} \mathrm{tr}\left\{ \left(\frac{\partial \boldsymbol{D}'}{\partial \gamma} \right)_0 \tilde{\boldsymbol{B}}(\mathbf{k}) + \boldsymbol{D}(\mathbf{k})\, \tilde{\boldsymbol{C}}(\mathbf{k}) \right\}. \tag{77}$$

The $\tilde{C}(\mathbf{k})$ in (77) is easily recognized. The differentiation of $\boldsymbol{D}'$ needs some care since $\boldsymbol{D}'$ is a sum of non-commuting matrices $\tilde{\boldsymbol{A}}$, $\tilde{\boldsymbol{B}}$, $\tilde{\boldsymbol{C}}$. Instead of making a series expansion of D' we use

$$\exp[(\boldsymbol{H}' - \mu'\,\boldsymbol{1})/k_B T] = \lim_{L \to \infty} \left(1 + \frac{1}{L} (\boldsymbol{H}' - \mu'\,\boldsymbol{1}) \right)^{L/k_B T}$$

$$\approx \left(1 + \frac{1}{L} (\boldsymbol{H}' - \mu'\,\boldsymbol{1}) \right)^{L/k_B T} =: \boldsymbol{K}^{L/k_B T}.$$

Up to first order in γ we have

$$(\boldsymbol{K}+\gamma\tilde{\boldsymbol{B}})^{L/k_BT}=\boldsymbol{K}^{L/k_BT}+\gamma\boldsymbol{P},$$

where

$$\boldsymbol{P}=[\ldots[[[\boldsymbol{K},\tilde{\boldsymbol{B}}]_+,\boldsymbol{K}^2]_+,\boldsymbol{K}^4]_+,\ldots K^{(L/k_BT)/2}]_+. \tag{78}$$

Further, taking the definition (76),

$$\begin{aligned}\boldsymbol{D}'&=[\boldsymbol{1}+\boldsymbol{K}^{L/k_BT}+\gamma\boldsymbol{P}]^{-1}=[(\boldsymbol{1}+\gamma\boldsymbol{PD})\,(1+\boldsymbol{K}^{L/k_BT})]^{-1}\\&=\boldsymbol{D}[1+\gamma\boldsymbol{PD}]^{-1}\cong\boldsymbol{D}-\gamma\boldsymbol{DPD},\end{aligned}$$

thus

$$\boldsymbol{D}'-\boldsymbol{D}=-\gamma\boldsymbol{DPD}.$$

Equation (79) gives to first order the derivation of $\boldsymbol{D}'$ after γ. We thus have, for (77),

$$G=\tfrac{1}{3}\sum_{\mathbf{k}}\mathrm{tr}\{\boldsymbol{D}(\mathbf{k})\,\tilde{\boldsymbol{C}}(\mathbf{k})-\boldsymbol{PD}\tilde{\boldsymbol{B}}\boldsymbol{D}(\mathbf{k})\}. \tag{80}$$

The equivalence of (80) with (52) is seen from an explicit expression for $\boldsymbol{P}$ coming directly from (78), now taken in the representation (12),

$$P_{nm}=-\frac{1}{\beta}\int_0^1\exp[-\lambda E_n/k_B\,T]\,B_{nm}\exp[-(1-\lambda)\,E_n/k_B\,T],$$

so that

$$\begin{aligned}\mathrm{tr}\{\boldsymbol{PDBD}\}&=\sum_{n,m}\frac{B_{nm}^2}{E_n-E_m}\,(f(E_n)\,f(E_m)\cdot(\exp(-E_n/k_B\,T)-\exp(-E_m/k_B\,T))\\&=\sum_{n,m}\frac{B_{nm}^2}{E_n-E_m}\,(f(E_n)-f(E_m)).\end{aligned}$$

This expression remains finite if $E_n\to E_m$. Quite similarly one expresses directly dG/dT by

$$\frac{dG}{dT}=\frac{2}{3k_B\,T^2}\sum_{\mathbf{k}}\mathrm{tr}\{\boldsymbol{D}(\boldsymbol{1}-\boldsymbol{D})\,\tilde{\boldsymbol{A}}\tilde{\boldsymbol{C}}-\boldsymbol{PD}[(\tilde{\boldsymbol{A}}-\tilde{\boldsymbol{A}}\boldsymbol{D},\boldsymbol{B}]_+\,\boldsymbol{D}+[\boldsymbol{P},\tilde{\boldsymbol{A}}]_+\,\boldsymbol{D}\tilde{\boldsymbol{B}}\boldsymbol{D}\}.^{5}) \tag{81}$$

7. Superconductors

Expression (67) for the matrix element of interaction between electrons and transversal phonons allows a discussion of the influence of transverse phonons on superconductivity. Since transition metal superconductors are of the strong coupling type we use directly the form of the theory given by Scalapino [16].

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[5]) It might be worthwhile mentioning that (75) has been calculated for $L=64$, this means 6 commutators in (76) on a simple HP 35 calculator with sufficient accuracy.

Since our interaction potentials are – when they lead to the correct band structure of the metal – already renormalized [10], we find the electron self-energy as (we work in units with $\hbar = 1$)

$$\hat{\Sigma}_{\mathrm{ph}}(\mathbf{k}; i\omega_n) = -k_B T \sum_{\mathbf{k}', n'} \sum_{t} |g_{\mathbf{k}\mathbf{k}'t}|^2 \cdot D\,(\mathbf{k}-\mathbf{k}', i(\omega_n - \omega_n))\, \tau_3 \hat{G}(\mathbf{k}', i\omega_n')\, \tau_3, \quad \omega_n = k_B T(2n+1)\cdot\pi \tag{82}$$

for electrons at the Fermi surface (we omitted the band index). $D_t(\mathbf{q}, i\omega_m)$ is the phonon Green function ($\mathbf{q} = \mathbf{k} - \mathbf{k}', \omega_m = \omega_n - \omega_n'$):

$$D_t(\mathbf{q}, i\omega_m) = \int_0^\infty d\Omega\, L_t(\mathbf{q}, \Omega)\, \frac{2\Omega}{(i\omega_m)^2 - (\Omega)^2}.$$

Since the electron Green function $\hat{G}$ in (82) contains $\hat{\Sigma}_{\mathrm{ph}}$, (82) is actually an integral equation.

One can perform the n' summation and find, on analytical continuation, $i\omega_n \to \omega(\mathrm{Im}\,\omega = 0^+)$:

$$\hat{\Sigma}_{\mathrm{ph}}(\mathbf{k}, \omega) = \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \int_0^\infty d\Omega \sum_{\mathbf{k}', t} \tau_3\, \mathrm{Im}\, \hat{G}(\mathbf{k}', \omega' + i\delta)\, \tau_3 \cdot L_t(\mathbf{k}-\mathbf{k}', \Omega) |g_{\mathbf{k}\mathbf{k}'t}|^2 \left[\frac{f(-\omega') + n(\Omega)}{\omega' + \Omega - \omega} + \frac{f(\omega') + n(\Omega)}{\omega' - \Omega - \omega} \right]. \tag{83}$$

[$f(\omega), n(\Omega)$ are the electron and phonon distributions respectively.] In the usual way, one writes $\hat{\Sigma}_{\mathrm{ph}}(\mathbf{k},\omega)$ as

$$\hat{\Sigma}_{\mathrm{ph}}(\mathbf{k}, \omega) = (1 - Z(\mathbf{k}, \omega))\, \omega 1 + \phi(\mathbf{k}, \omega)\, \tau_1. \tag{84}$$

By combining (84) with Dyson's equation,

$$\hat{G}^{-1}(\mathbf{k}, \omega) = \hat{G}_0^{-1}(\mathbf{k}, \omega) - \hat{\Sigma}_{\mathrm{ph}}(\mathbf{k}, \omega_n)$$

one gets the one-electron Green's function

$$\hat{G}(\mathbf{k}, \omega) = \frac{\omega Z(\mathbf{k}, \omega)\, 1 + \epsilon_k \tau_3 + \phi(\mathbf{k}, \omega)\, \tau_1}{\omega^2 Z^2(\mathbf{k}, \omega) - \epsilon_{\mathbf{k}}^2 - \phi^2(\mathbf{k}, \omega)}, \tag{85}$$

which, upon insertion into (83), leads to the well-known coupled integral equations for the mass renormalization parameter $Z(\mathbf{k}, \omega)$ and the energy gap parameter

$$\Delta(\mathbf{k}, \omega) = \phi(\mathbf{k}, \omega)/Z(\mathbf{k}, \omega).$$

Contrary to the often discussed approximation for nearly free electrons, in our tight-binding region we cannot simply solve for $Z(\mathbf{k}, \omega)$, but have to solve the corresponding integral equation. This already indicates the strong influence of the tight-binding properties on superconductivity in a strong coupling superconductor as described here.

Solutions of the coupled system of equations will also allow us to make a comparison of the nearly free electron approximation of the electron–phonon interaction constant entering T_c as given by McMillan [17] and Hopfield [18]. These authors observe that in

$$\lambda = \frac{N(0)\langle J^2\rangle}{M\langle\omega^2\rangle}, \tag{86}$$

where J is the electron–phonon matrix element, $N(0)\langle J^2\rangle$ is remarkably constant over a whole series of superconductors, although $N(0)$ itself varies considerably.

This behaviour could be explained if only part of the electrons in transition metals were engaged in the superconducting phase transition and if, according to a rigid band assumption, this part at the Fermi surface remained the same for certain families of metals.

In such a case the shear moduli were easy to find from (51) and (74) as

$$G = p \cdot G(k_0) = -\tfrac{2}{3} p B^2 N(T) S.$$

p is the number of equivalent electron – or hole – 'pockets', contributing to G and λ. Since B^2 corresponds to $\langle J^2\rangle$ we have $\lambda \sim G$. Generalizing, and observing $pN(T) \sim N(0)$, we suggest for λ,

$$\lambda = \sum \frac{G}{G_{\text{total}}}. \tag{87}$$

If there was only a small electron contribution to shear, we would expect an equally small contribution to electron–phonon coupling. As Bongi [19] points out, in A15 phases there may be a contribution from the compressibility also added to (82).

8. Numerical Results

The approach described in the preceding paragraphs has already yielded some preliminary results which tend to show that numerical result swill be obtained in finite computing time. The results reported here are obtained on a HP 9830A calculator with an 8K R-W memory, and were checked on a fast program on a CII 10070 calculator. The first task consists of fitting the tight-binding parameters.

In the case of Cu and Fe, the TB constants are derived from the parameters β, Γ, k_0, and R, given by Hubbard and Dalton [20], with the use of our equations (8) and $\beta = (k_0/\alpha)^2$.

For the case of Pd and Nb we had to adapt the existing band calculations: for Pd we used the calculation of Mueller [23] and for Nb that of Mattheiss [24].

For the FCC elements, Cu and Pd, we used one shell of neighbours and for the BCC elements two shells of neighbours. In this way we obtained the following parameters:

Element	R (A.U.)	$dd\sigma$	$dd\pi$	$dd\delta$
Cu	4.8302	–0.022831	0.012887	–0.002046
Fe	4.6813	–0.023947	0.008324	–0.000824
Fe	5.4055	–0.006716	0.001779	–0.000137
Pd	$a_0/\sqrt{2}$	–0.0494	0.0265	–0.0034
Nb	$a_0/\sqrt{3}$	–0.0547	0.0662	–0.0406
Nb	a_0	–0.0435	0.0319	0.0156

With these parameters we have obtained the band structures given in Figure 1a–d.

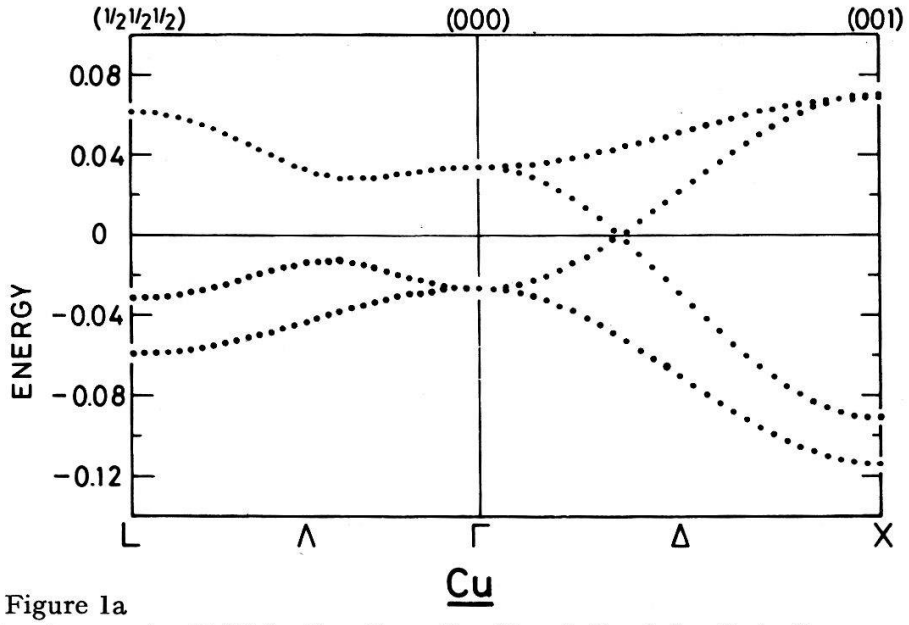

Figure 1a
Electronic energies $E_n(\mathbf{k})$ in directions $\Gamma - X$ and $\Gamma - L$ for Cu in Ry.

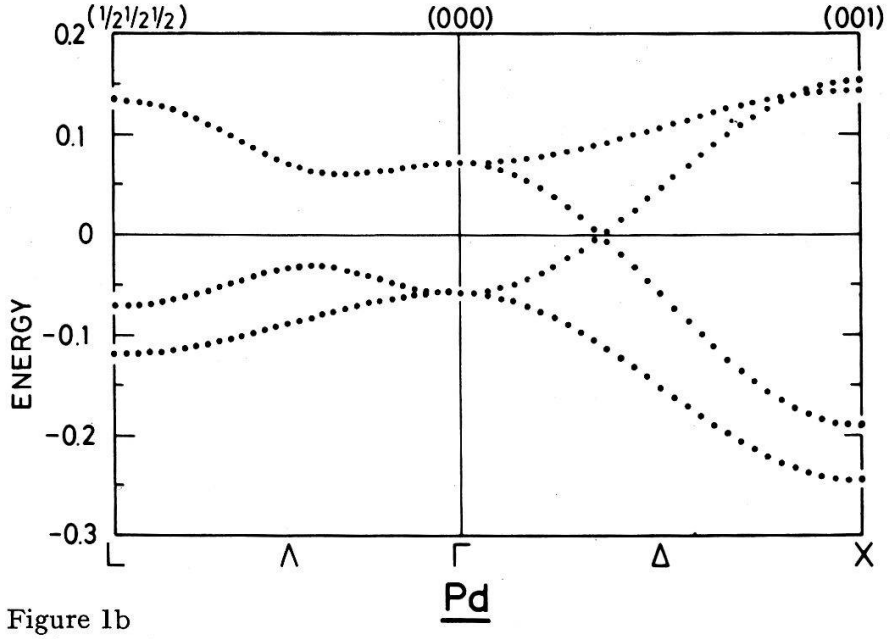

Figure 1b
Electronic energies $E_n(\mathbf{k})$ in directions $\Gamma - X$ and $\Gamma - L$ for Pd in Ry.

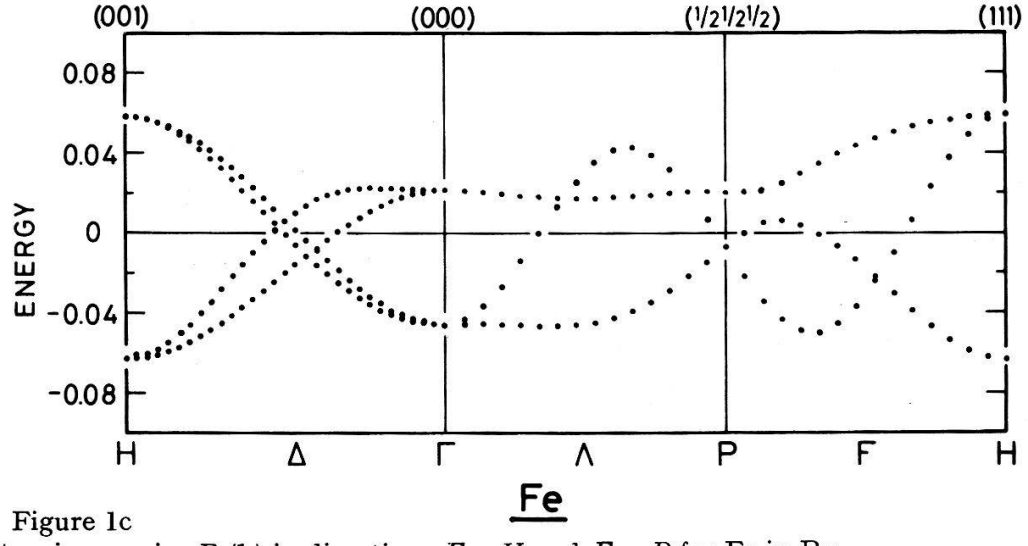

Figure 1c
Electronic energies $E_n(\mathbf{k})$ in directions $\Gamma - H$ and $\Gamma - P$ for Fe in Ry.

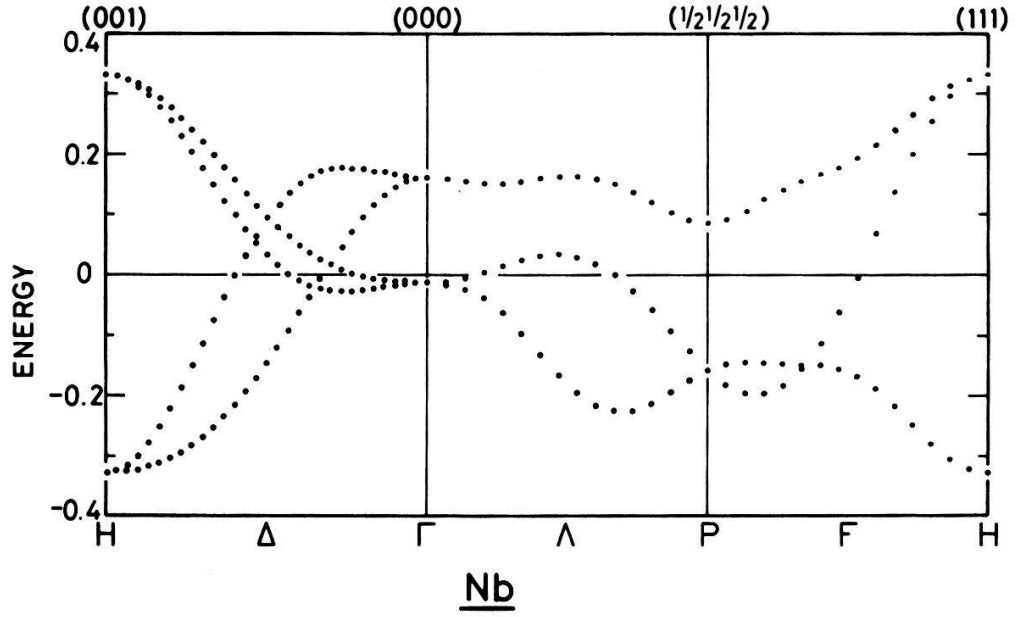

Figure 1d
Electronic energies $E_n(\mathbf{k})$ in directions $\Gamma - H$ and $\Gamma - P$ for Nb in Ry.

By an analogous procedure, the phonon structure can be obtained by adjusting the Born–von Karman parameters. In the case of Nb, these parameters for the first eight shells are given by Nakagawa and Woods [22], from which the spectrum shown in Figure 2 is deduced.

Finally, Figure 3a–d shows the susceptibility and the shear moduli G_1 and G_2 and their temperature derivatives for the four elements considered here. The temperature selected is 600°K (900°K for Nb). The fact that the curves are approximately smooth shows that at these temperatures the derivatives of the Fermi function extend a sufficient energy domain to interpolate between the (approximately 90) points in the irreducible Brillouin zone selected for calculation.

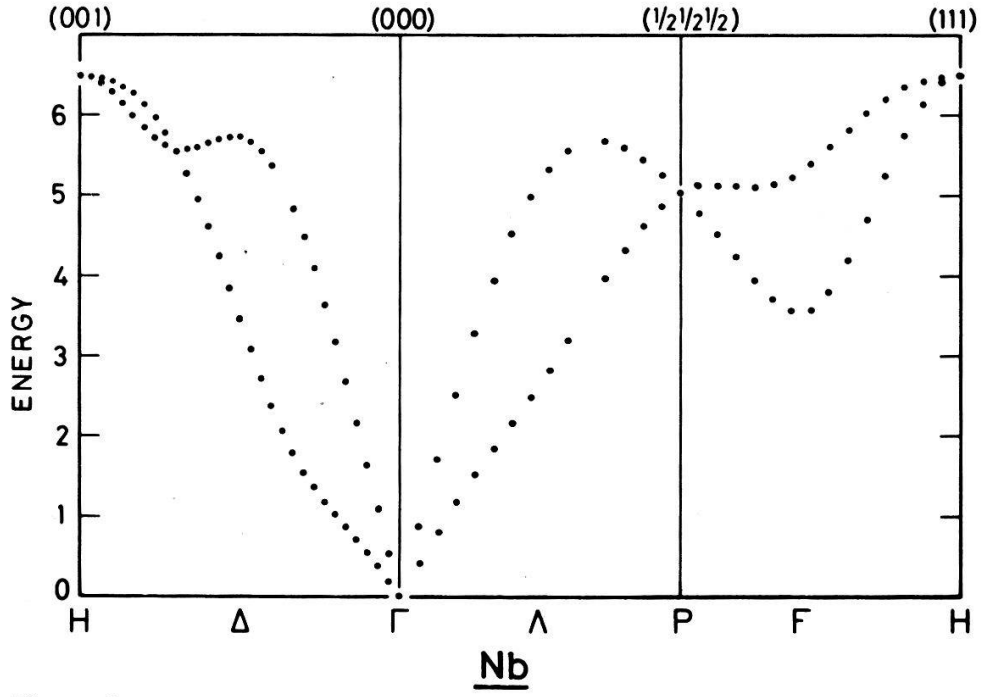

Figure 2
Phonon spectrum for Nb in directions $\Gamma - H$ and $\Gamma - P$, in 10^{12} c.p.s.

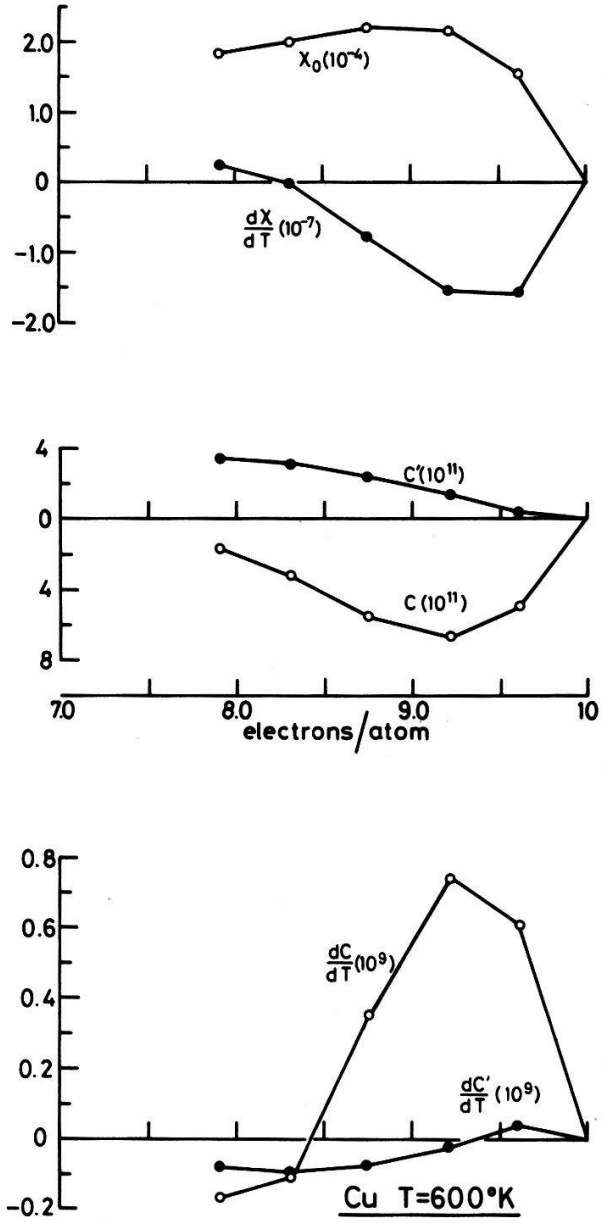

Figure 3a

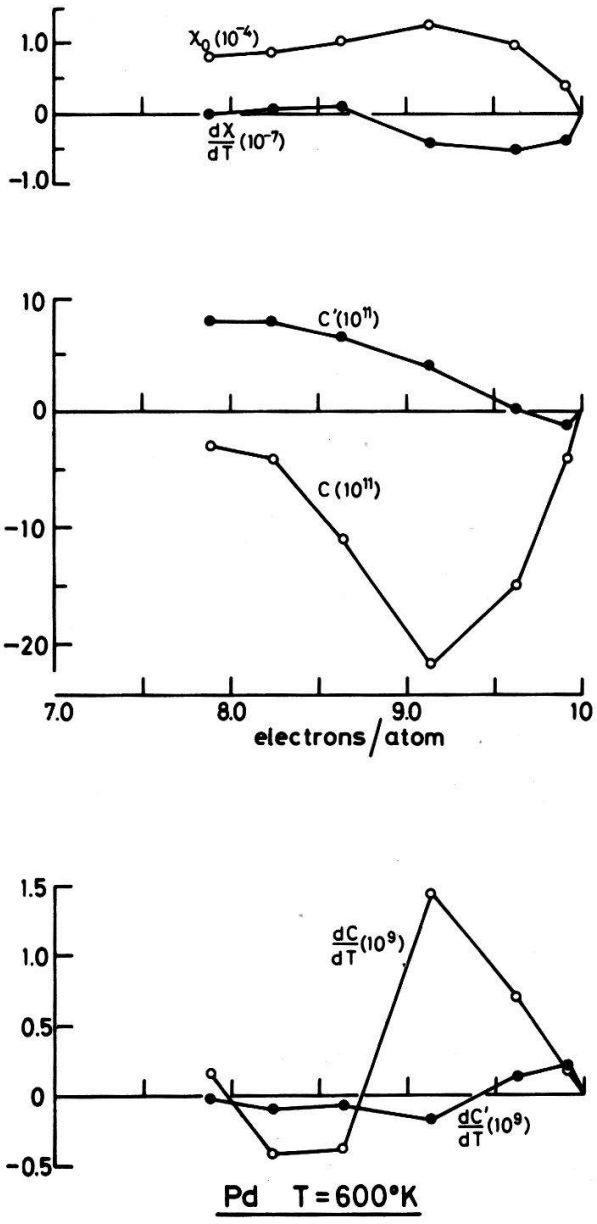

Figure 3b

Figure 3a
Paramagnetic bare susceptibility and electronic contribution to shear moduli for Cu, and their temperature derivatives, in c.g.s. units ($T = 600°K$).

Figure 3b
Paramagnetic bare susceptibility and electronic contribution to shear moduli for Pd, and their temperature derivatives, in c.g.s. units ($T = 600°K$).

For calculation at lower temperatures (in particular for the superconducting properties, equation (83)), additional smoothing procedures are required. Either the natural width of the electron and phonon propagators is chosen to be large, or more sophisticated interpolation procedures, such as the ones given by Raubenheimer and Gilat [25], are used.

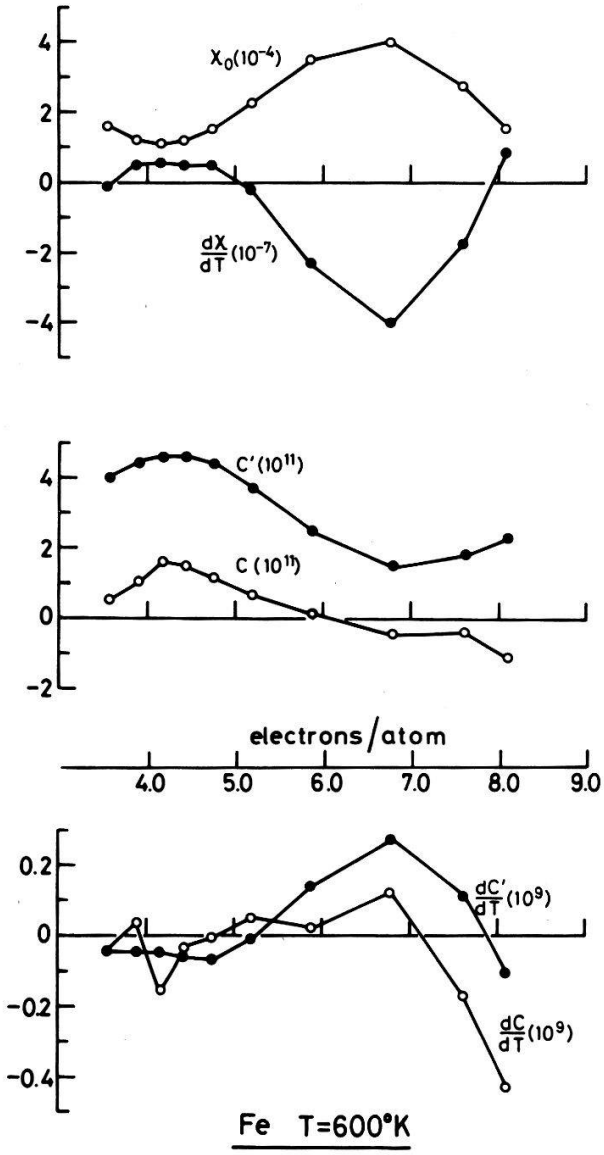

Figure 3c

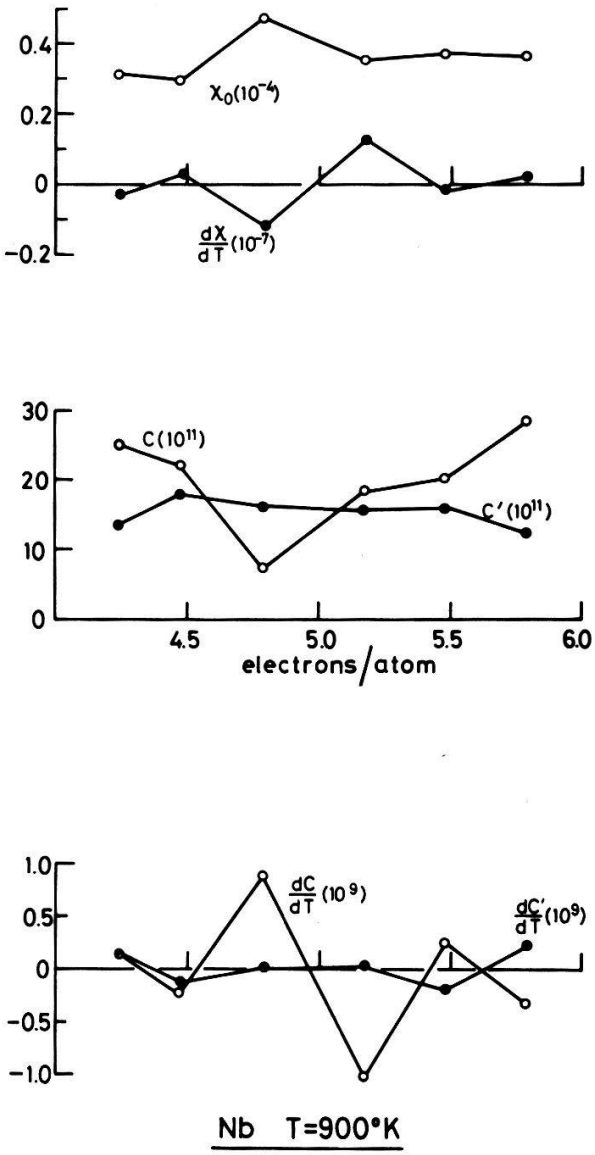

Figure 3d

Figure 3c
Paramagnetic bare susceptibility and electronic contribution to shear moduli for Fe, and their temperature derivatives, in c.g.s. units ($T = 600°K$).

Figure 3d
Paramagnetic bare susceptibility and electronic contribution to shear moduli for Nb, and their temperature derivatives, in c.g.s. units ($T = 900°K$).

Figure 3 shows that not only the bare paramagnetic susceptibility but also the electronic contribution to the shear moduli are estimated by the procedures outlined here in such a way as to give reasonable agreement with experiment (for elastic constants, see Refs. [7] and [8][6]). Thus we also dispose of a set of reasonable electron–phonon coupling parameters with which we may estimate superconducting properties from a gap equation, which is solved without averaging over energy shells, as has been done by McMillan [17] and by Klein et al. [26]. That angular anisotropy plays a role in superconductivity is now clear, both experimentally [27] and theoretically [28], [4]. In a forthcoming paper we will give results on the superconducting properties derived from the band structure parameters presented in this section.

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[6]) The convergency of our method is determined by the energy density of sampling points compared with $1/k_B T$. Hence it is best for Cu and worse for Nb. More accurate results obtained for combined *s-d* bands will be given in a forthcoming paper.

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