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# *Ab initio* calculation of the tetragonal shear moduli of the cubic transition metals

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A new approach for ground-state-energy calculations, based on the density-functional formalism, is proposed. It enables us to express a shear modulus as a sum of two simple terms, a one-electron "band term," based on a "frozen-potential" condition, and a "Madelung term" based on an effective ionic charge. This method is applied for the tetragonal shear moduli of the thirteen nonferromagnetic cubic transition metals, using the linear muffin-tin orbital—atomic sphere approximation band method. The results agree fairly well with experiment. To our knowledge, this is the first successful *ab initio* calculation of shear moduli in transition metals, and the results for Rh preceded the experimental measurement.

*Ab initio* calculations of the ground-state energy in solids have been considerably advanced with the development of fast computers. A powerful scheme for such calculations is the density-functional formalism.[1] This approach was found successful in its local-density approximation[2] for self-consistent calculations of the cohesive energy, the bulk modulus, and the equilibrium interatomic distances of both simple and transition metals[3] and of metallic compounds.[4] It gave correct value also for the heat of formation of such compounds.[5]

In this work we are interested in ground-state-energy variations under symmetry removing change of the lattice. To calculate shear moduli, one must know the effect of strains on total ground-state energy. In Sec. I we present, within the density-functional formalism, two stationarity properties which allow us to define and use, in Sec. II, model electronic density and effective potential. From them we deduce an expression for total-energy differences which enables us to formulate in Sec. III the tetragonal shear moduli as a sum of two contributions: the band contribution (studied in Sec. IV) and the Madelung contribution (Sec. V). Finally, in Sec. VI we present and compare with experiment results for the tetragonal shear moduli of all the cubic, nonferromagnetic, transition metals.

The theoretical approach of this work is based on a generalization of the force theorem of Andersen,[6] which is worked out in details, and published in a parallel paper by one of the authors.[7] In that paper it is shown that this approach can be applied to calculate shear moduli for symmetry removing strains.

## I. STATIONARITY PROPERTIES

Within the density-functional approach,[1,2] the total ground-state energy $\mathscr{E}$ of a system of electrons (with a fixed total number), under the influence of an "external" potential $v(\vec{r})$, is the minimum among the admissible electronic densities: $n(\vec{r})$, of a unique functional of $v$ and $n$:

$$\mathscr{E}\{v,n\}=F\{n\}+\int v(\vec{r})n(\vec{r})d^3r\ , \tag{1}$$

where $F$ is a universal functional of the density. The minimum property could be expressed by the relation,[7]

$$\frac{\delta\mathscr{E}\{v,n\}}{\delta n(\vec{r})}=E_F,\quad \forall\vec{r}\in\Omega \tag{2}$$

where $E_F$ is the Fermi energy and $\Omega$ is the Wigner-Seitz (WS) cell volume. Then this functional (1) has a stationarity property, under first-order density variations,

$$\mathscr{E}\{v,n\}=\mathscr{E}\{v,\tilde{n}\}+O((\tilde{n}-n)^2)\ , \tag{3}$$

where $\tilde{n}$ is a slightly varied density.

Considering electrons in a crystal, $v$ is the Coulomb potential of the nuclei, and the energy functional must be renormalized to include the Coulomb interaction between the nuclei. The exact form of $F\{n\}$ in Eq. (1) is unknown; however, Kohn and Sham[2] have shown that the energy functional (neglecting lattice vibrations) can also be expressed as a sum of three terms:

$$\mathscr{E}\{v,n\}=T_n\{n\}+U_c\{v,n\}+\mathscr{E}_{\mathrm{xc}}\{n\}\ , \qquad (4)$$

where $U_c$ is the total classical Coulomb energy of the crystal, $T_n$ is the ground-state kinetic energy of an equivalent [i.e., having the same ground-state density $n(\vec{r})$] system of noninteracting electrons, and $\mathscr{E}_{\mathrm{xc}}$ is the effective exchange-correlation energy, which includes the exchange and many-body effects of the interaction $U_{\mathrm{xc}}$ and the difference between the real kinetic energy $T$ and $T_n$:

$$\mathscr{E}_{\mathrm{xc}}\{n\}=T\{n\}-T_n\{n\}+U_{\mathrm{xc}}\{n\}\ . \qquad (5)$$

Let us now consider this system of noninteracting electrons in a crystal represented here by a periodic potential $v_n(\vec{r})$. The electrons have, in this system, one-electron wave functions $\phi_{\vec{k}}(\vec{r})$ and a spectrum of band energies $E(\vec{k})$, in the Brillouin zone (BZ). The ground-state energy of this system can be expressed as a functional of $v_n$:

$$\begin{aligned}\mathscr{E}_n\{v_n\}&=\int_{\mathrm{BZ}}d^3k\ \Theta(E_F-E_{\vec{k}})\\ &=\int_{-\infty}^{E_F}EN(E)dE\ , \qquad (6)\end{aligned}$$

where $E_F$ is the Fermi energy, and $N(E)$ the density of states corresponding to the one-electron potential $v_n(\vec{r})$. (The BZ integration also includes a summation on a band index which is omitted here for simplicity.) Let us define, for any $v_n(\vec{r})$ and $n(\vec{r})$, the functional

$$T_n\{n,v_n\}=\mathscr{E}_n\{v_n\}-\int v_n(\vec{r})n(\vec{r})d^3r\ . \qquad (7)$$

It coincides with the ground-state kinetic energy $T_n\{n\}$ for the density

$$n(\vec{r})=\int_{\mathrm{BZ}}d^3k\ \Theta(E_F-E_{\vec{k}})\,|\,\phi_{\vec{k}}(\vec{r})\,|^2\ . \qquad (8)$$

Furthermore, Eq. (1) can be applied to the system of noninteracting electrons, where the functional $F\{n\}$ is replaced by $T_n\{n\}$. An energy functional $\mathscr{E}_n\{v_n,n\}$ is then obtained, whose functional derivative with respect to $v_n$ is given by

$$\delta\mathscr{E}_n\{v_n,n\}/\delta v_n(\vec{r})=n(\vec{r})\ , \qquad (9)$$

and which has a minimum with respect to *density* variations around the ground state.

The functional $T_n\{v_n,n\}$ introduced in Eq. (7) could be interpreted as the Legendre transform of $\mathscr{E}_n\{v_n\}$. Thus its minimum property will be with respect to *potential* variations around the ground state. This can be written as:

$$T_n\{\tilde{n}\}=T_n\{v_n,\tilde{n}\}+O((\tilde{v}_n-v_n)^2)\ , \qquad (10)$$

where $\tilde{v}_n$ is the potential which yields $\tilde{n}$ through (8), and $v_n$ is a band-structure potential which should be close to it. Then, with the use of these two stationarity properties, the total ground-state energy can be expressed as follows:

$$\begin{aligned}\mathscr{E}=\ &U_c\{v,\tilde{n}\}+\mathscr{E}_{\mathrm{xc}}\{\tilde{n}\}+\mathscr{E}_n\{v_n\}\\ &-\int v_n(\vec{r})\tilde{n}(\vec{r})d^3r+O((\tilde{n}-n)^2)\\ &+O((\tilde{v}_n-v_n)^2)\ , \qquad (11)\end{aligned}$$

which can be used for an approximate energy calculation with the use of a density $\tilde{n}$ and a one-electron potential $v_n$ which are simpler than the exact physical ones.

## II. TOTAL-ENERGY DIFFERENCES, CONDITIONS ON DENSITIES, AND POTENTIALS

In order to calculate shear constants, total-energy differences between two crystals with the same atoms but with slightly different structures are to be evaluated. Let us consider a volume conserving lattice strain characterized by a strain parameter $\gamma$ and introduce $n_\gamma(\vec{r})$ and $v_n^\gamma(\vec{r})$, the electronic density and the equivalent one-electron potential, respectively, of the sheared crystal. One can then define

$$\delta_\gamma\mathscr{E}\equiv\mathscr{E}\{v_\gamma,n_\gamma\}-\mathscr{E}\{v,n\}\ , \qquad (12)$$

and, with the use of Eq. (4), express this difference as a sum of three contributions,

$$\delta_\gamma\mathscr{E}=\delta_\gamma T_n+\delta_\gamma U_c+\delta_\gamma\mathscr{E}_{\mathrm{xc}}\ . \qquad (13)$$

The problem will then be to calculate those terms. Following the idea of the first paragraph, we now impose conditions on the densities and potentials. Let us assume that our densities $n(\vec{r})$ and $n_\gamma(\vec{r})$ are close to model densities $\tilde{n}(\vec{r})$ and $\tilde{n}_\gamma(\vec{r})$ satisfying the following conditions.

(i) They are muffin-tin densities (i.e., spherically symmetric around the WS cell center up to the smallest MT radius, chosen so as to avoid the overlap between spheres in both crystals, and flat from it up to the boundaries).

(ii) They are identical within the WS cells (frozen density).

Similarly, let us introduce conditions on the effective potentials $v_n(\vec{r})$ and $v_n^\gamma(\vec{r})$ of the one-electron system:

(iii) They are muffin-tin potentials.

(iv) They are identical within the WS cell (frozen potential).

Working now with spherically averaged quantities, we denote them replacing the variable $\vec{r}$ by $r$, the distance from the WS cell center. Before discussing these conditions, let us examine what are their consequences on Eq. (13). For this purpose the quantity $Z_0$, which is essentially an electric charge, is defined as follows:

$$Z_0 = \Omega n(s) , \tag{14}$$

where $n(s)$ is the value of the density at the Wigner-Seitz radius $s$,

$$s = \left[ \frac{3\Omega}{4\pi} \right]^{1/3} . \tag{15}$$

Condition (i) makes the crystal similar to a system of charge point (or spherical) ions in a uniform neutralizing background. Then $\delta_\gamma U_c$ may simply be written as

$$\delta_\gamma U_c = Z_{\mathrm{eff}}^2 \delta_\gamma \mathscr{E}_M , \tag{16}$$

where $\mathscr{E}_M$ is the Madelung energy of unit point charges[8] and $Z_{\mathrm{eff}}$ is, following Eq. (14), defined as

$$Z_{\mathrm{eff}} = \Omega \tilde{n}(s) . \tag{17}$$

(The change in the self-Coulomb energy within the spheres has vanished by the frozen-density condition.)

Conditions (ii) and (iv) give

$$\delta_\gamma \int_{\mathrm{WS}} v_n(\vec{r}) \tilde{n}(\vec{r}) d^3 r = 0 , \tag{18}$$

since both $v_n$ and $\tilde{n}$ are identical within the WS cell in both crystals, and $\delta_\gamma T_n$ becomes

$$\delta_\gamma T_n = \delta_\gamma \mathscr{E}_n = \delta_\gamma \int_{-\infty}^{E_F} E N(E) dE , \tag{19}$$

the difference between the total ground-state energies of the one-electron systems.

The last term in Eq. (13) $\delta_\gamma \mathscr{E}_{\mathrm{xc}}$ vanishes by condition (ii). This is because $\mathscr{E}_{\mathrm{xc}}\{n\}$ can be expressed as a sum of a local term (function of $\tilde{n}$) and a nonlocal term, expanded in gradients of $\tilde{n}(\vec{r})$[1], which are zero [condition (i)] in the region where the WS cells match.

To sum up, with the use of conditions on the densities and potentials of both sheared and unsheared crystals, it is possible to reduce the total-energy difference to a simple expression,

$$\delta_\gamma \mathscr{E} = \delta_\gamma \mathscr{E}_n + Z_{\mathrm{eff}}^2 \delta_\gamma \mathscr{E}_M , \tag{20}$$

which contains two terms: a "band term" (the first one), and a "Madelung term" (the second one). These terms cannot be calculated analytically and numerical work is needed, which is presented in the next section.

In the monoatomic crystals we are interested in, condition (i) is automatically satisfied for free-electron wave functions, and, to a great extent, for simple metals. But this is not in principle the case for transition metals, where it requires a radial density variation. The "frozen-potential condition" was first pointed out for homogeneous pressure on the basis of the virial theorem,[9,10] and then for more general cases[6] on the basis of stationarity properties. It is closely related to the modified tight-binding approximation.[11,12]

Expressions for $\delta_\gamma \mathscr{E}$ of a similar form have also been suggested in previous works,[13–15] using a pseudopotential technique for simple metals.

## III. ELASTIC CONSTANTS CALCULATION

In this section small volume-conserving lattice changes are treated, and the energies of two crystals are to be compared. Following the idea of the linear muffin-tin orbital (LMTO)—atomic sphere approximation—(ASA) method, the crystal is considered to be composed of WS cells of volume $\Omega$ which are assumed to be close to spheres of radius $s$, as happens in dense structures (bcc, fcc, and hcp metals). In order to calculate the energy change, one has to use, in this case, two calculations around the equilibrium position. Equation (20) is applied here for the calculation of the tetragonal shear moduli $C' = \frac{1}{2}(C_{11} - C_{12})$ of the bcc and fcc transition metals through the expression

$$C' = \frac{2}{3} \lim_{\gamma \to 0} \delta_\gamma \mathscr{E} / \gamma^2 . \tag{21}$$

From this expression it is obvious that $\gamma$ is to be sufficiently small, and it has been chosen to be a $z$-symmetric tetragonal strain[12] under which the point $\vec{r} = (x,y,z)$ of the cubic crystal is transformed into $\vec{r}_\gamma = (x_\gamma, y_\gamma, z_\gamma)$ by the vectorial equation

$$\begin{bmatrix} x_\gamma \\ y_\gamma \\ z_\gamma \end{bmatrix} = \begin{bmatrix} e^{-\gamma/2} & 0 & 0 \\ 0 & e^{-\gamma/2} & 0 \\ 0 & 0 & e^{\gamma} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} . \tag{22}$$

This transformation keeps the volume constant to all orders in $\gamma$ and has a tetragonal nature.

The cubic crystal is interpreted as a tetragonal lattice with two atoms per unit cell. The $c/a$ ratio of such a lattice is $\sqrt{2}$ for fcc and 1 for bcc. The tetragonal strain expressed in Eq. (22) conserves the symmetry of this lattice, changing the $c/a$ ratio to

$$c_\gamma/a_\gamma = c/a \exp(\tfrac{3}{2}\gamma) \ . \tag{23}$$

$\delta_\gamma \mathscr{E}$ is calculated by comparing results for crystals with $\gamma$ values of zero and of $\pm 2\%$ and $\pm 4\%$.

With the use of Eqs. (20) and (21), $C'$ is expressed as a sum of two terms

$$C' = C'_b + C'_M \ , \tag{24a}$$

a band term defined as

$$C'_b = \tfrac{2}{3} \lim_{\gamma \to 0} \delta_\gamma \mathscr{E}_n / \gamma^2 \ , \tag{24b}$$

and a Madelung term,

$$C'_M = \tfrac{2}{3} Z_{\mathrm{eff}}^2 \lim_{\gamma \to 0} \delta_\gamma \mathscr{E}_M / \gamma^2 \ . \tag{24c}$$

Expressions of the type of Eqs. (24) have been suggested in the past for calculations of elastic constants, but without condition (iv) for $\delta_\gamma \mathscr{E}_n$ and condition (i) for $Z_{\mathrm{eff}}$. Such a work has been carried out by Harrison[13] who calculated the elastic constants of Na, Mg, and Al with the use of the pseudopotential method.

Our calculation of the band term is described in Sec. IV and of the Madelung term in Sec. V. The discussion of the results and the conclusion are given in Sec. VI.

## IV. THE BAND TERM

The band term $C'_b$ is calculated by Eqs. (19) and (24b) with the use of the frozen-potential condition (iv) for its variation under shear. This is done with the LMTO-ASA band method,[6,16] which has the advantage in being able to separate between the structure and the potential dependences of the band problem. The former is represented in terms of structure matrix which contains all the information about the lattice; the latter is represented in terms of potential parameters which characterize the potential within a WS sphere. The application of the frozen-potential condition under shear can be easily interpreted within the LMTO-ASA method, by keeping the potential parameters constant, while the structure matrix is varied. As we have already said, we use a structure matrix of a tetragonal lattice with two atoms per unit cell (discussed in Sec. III) and a $c/a$ ratio given for any value of $\gamma$ by Eq. (23). The potential parameters are those obtained by self-consistent band calculations for the bcc and fcc transition metals,[17] based on the "scalar" Dirac equation[16] (i.e., including the Darwin and the mass-velocity shifts, but neglecting the effect of spin-orbit coupling).

We introduce a variable $n = n(E)$ which is the number of electrons with band energies below $E$, and replace Eq. (19) by

$$\delta_\gamma \mathscr{E}_n = \delta_\gamma \int_0^{n_e} E(n) dn \ , \tag{25}$$

where $n_e$ should be in principle the total number of electrons per atom, but in practice we assume that the core electrons are not affected by the strain and consider only the valence electrons. The density of states $N(E)$ is calculated in discrete equidistant energy points $E_r$ with intervals $E_{r+1} - E_r = \Delta E$, and $r = R$ is the index of the highest energy point below $E_F$. Then Eq. (25) is approximated by

$$\delta_\gamma \mathscr{E}_n \cong \delta_\gamma \left[ \sum_{r=1}^{R-1} E_r (n_{r+1} - n_r) + \tfrac{1}{2} \Delta E n_R + \int_{n_R}^{n_e} E(n) dn \right] , \tag{26}$$

where we denote $n_r = n(E_r)$. One has the identity

$$\frac{dE}{dn} = \frac{1}{N(E)} \tag{27}$$

TABLE I. Results for $\delta_\gamma \mathscr{E}_n$ in mRy/atom for fcc transition metals.

| | Metal | | | | | | |
|---|---|---|---|---|---|---|---|
| $\gamma$ | Cu | Rh | Pd | Ag | Ir | Pt | Au |
| $l = 0,1,2$ | | | | | | | |
| $\gamma = -4\%$ | $-0.310$ | $+0.654$ | $-0.861$ | $-0.198$ | $+1.235$ | $-1.108$ | $-0.603$ |
| $-2\%$ | $-0.087$ | $+0.161$ | $-0.270$ | $-0.057$ | $+0.304$ | $-0.336$ | $-0.163$ |
| $2\%$ | $-0.118$ | $+0.088$ | $-0.100$ | $-0.067$ | $+0.201$ | $-0.215$ | $-0.192$ |
| $4\%$ | $-0.505$ | $+0.287$ | $-0.671$ | $-0.284$ | $+0.733$ | $-1.049$ | $-0.821$ |
| $l = 0,1,2,3$ | | | | | | | |
| $-4\%$ | $-0.449$ | $+0.402$ | $-0.918$ | $-0.365$ | $+0.825$ | $-1.051$ | $-0.992$ |
| $-2\%$ | $-0.123$ | $+0.089$ | $-0.279$ | $-0.099$ | $+0.195$ | $-0.307$ | $-0.260$ |
| $2\%$ | $-0.171$ | $-0.064$ | $-0.190$ | $-0.134$ | $-0.050$ | $-0.303$ | $-0.337$ |
| $4\%$ | $-0.721$ | $-0.340$ | $-0.977$ | $-0.553$ | $-0.285$ | $-1.363$ | $-1.394$ |

TABLE II. Results for $\delta_\gamma \mathscr{E}_n$ in mRy/atom for bcc transition metals.

|  | Metal |  |  |  |  |  |
|---|---|---|---|---|---|---|
| $\gamma$ | V | Cr | Nb | Mo | Ta | W |
| $l=0,1,2,3$ |  |  |  |  |  |  |
| $-4\%$ | $+0.266$ | $+1.854$ | 0.305 | 2.849 | 0.193 | 2.847 |
| $-2\%$ | 0.062 | 0.443 | 0.098 | 0.829 | 0.128 | 0.759 |
| $2\%$ | 0.116 | 0.497 | 0.216 | 0.954 | 0.194 | 0.855 |
| $4\%$ | 0.293 | 2.199 | 1.073 | 3.201 | 0.951 | 3.351 |

and denoting $N_r = N(E_r)$, one gets by linear interpolation for $n_R \le n \le n_{R+1}$:

$$\frac{dE}{dn} \simeq N_R^{-1} + (n-n_R)\frac{N_{R+1}^{-1}-N_R^{-1}}{n_{R+1}-n_R} , \tag{28}$$

which can be used in a quadratical approximation for $E(n)$ in the integral

$$\int_{n_R}^{n_e} E(n)dn = (n_e-n_R)E_R + \tfrac{1}{2}(n_e-n_R)^2 N_R^{-1} + \tfrac{1}{6}(n_e-n_R)^3 \frac{N_{R+1}^{-1}-N_R^{-1}}{n_{R+1}-n_R} . \tag{29}$$

With the use of Eq. (26), one then gets

$$\delta_\gamma \mathscr{E}_n \cong \sum_{r=1}^{R-1} E_r(\delta_\gamma n_{r+1} - \delta_\gamma n_r) + \tfrac{1}{2}\Delta E \delta_\gamma n_R + \delta_\gamma \int_{n_R}^{n_e} E(n)dn , \tag{30}$$

where the last integral is calculated by (29), and by $\delta_\gamma$ we denote the difference between the results for $\gamma$ and $\gamma=0$ based on the same energy scale, and the frozen-potential condition (i.e., different structure matrices but the same potential parameters). We use a fine energy scale ($\Delta E \simeq 0.5$ mRy) for good numerical accuracy in Eqs. (29) and (30).

In order to test the accuracy of $\delta_\gamma \mathscr{E}_n$, we have calculated it for fcc metals once for a band structure based on the values $l=0,1,2$ for the orbital quantum number, and once for the values $l=0,1,2,3$. The results for $\gamma = \pm 2\%, \pm 4\%$ for fcc metals are represented in Table I. There turns out to be a considerable effect due to the inclusion of the $l=3$ value. This seems surprising at first sight, because band-structure results based on $l=0,1,2$ are known to be quite accurate for the fcc transition metals.[17-20] However, we should not forget that the sum in Eq. (30) contains contributions from all the valence bands with considerable mutual cancellation, while the error effect due to the neglect of $l>2$ is additive. In Table II we represent the results for bcc metals calculated with $l=0,1,2,3$ and for $\gamma = \pm 2\%$ and $\pm 4\%$.

Another test of these results is on the problem of how accurately they can be used for the reproduction of $C_b'$ by Eq. (24b). For this purpose, we represent in Tables III and IV the averages $(\delta_\gamma \mathscr{E}_b + \delta_{-\gamma}\mathscr{E}_b)/2$, eliminating the odd $\gamma$ power terms in a series expansion of the results for $\delta_\gamma \mathscr{E}_n$. It turns out that the ratios between the values for $\gamma = 4\%$ and $\gamma = 2\%$ (also represented in Table III) are always close to 4 for fcc (except for one case, Rh, where the values divided are very small) indicating that the $\gamma^2$ term is dominant, and that the effect of the "computation noise" is small. However, this test on bcc metals is less satisfactory, and the error on the band term is not as well evaluated for this structure. One reason could be that bcc is

TABLE III. Results for $(\delta_\gamma \mathscr{E}_n + \delta_{-\gamma}\mathscr{E}_n)/2$ in mRy/atom for fcc transition metals.

|  | Metal |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| $\gamma$ | Cu | Rh | Pd | Ag | Ir | Pt | Au |
| $l=0,1,2$ |  |  |  |  |  |  |  |
| $4\%$ | $-0.407$ | $+0.470$ | $-0.766$ | $-0.241$ | $+0.984$ | $-1.078$ | $-0.712$ |
| $2\%$ | $-0.102$ | $+0.124$ | $-0.185$ | $-0.062$ | $+0.252$ | $-0.275$ | $-0.177$ |
| Test | 3.99 | 3.79 | 4.14 | 3.89 | 3.90 | 3.92 | 4.02 |
| $l=0,1,2,3$ |  |  |  |  |  |  |  |
| $4\%$ | $-0.585$ | $+0.031$ | $-0.947$ | $-0.459$ | $+0.270$ | $-1.207$ | $-1.193$ |
| $2\%$ | $-0.147$ | $+0.012$ | $-0.234$ | $-0.116$ | $+0.072$ | $-0.305$ | $-0.298$ |
| Test | 3.98 | 2.58 | 4.04 | 3.96 | 3.75 | 3.96 | 4.00 |

TABLE IV. Results for $(\delta_\gamma\mathscr{E}_n+\delta_{-\gamma}\mathscr{E}_n)/2$ in mRy/atom for bcc transition metals.

| | Metal | | | | | |
|---|---|---|---|---|---|---|
| $\gamma$ | V | Cr | Nb | Mo | Ta | W |
| $l=0,1,2,3$ | | | | | | |
| 4% | 0.280 | 2.027 | 0.689 | 3.025 | 0.572 | 3.099 |
| 2% | 0.089 | 0.470 | 0.157 | 0.892 | 0.161 | 0.807 |
| Test | 3.14 | 4.31 | 4.39 | 3.39 | 3.55 | 3.84 |

less close packed than fcc, so a change of symmetry is more sensible and the corner corrections,[16] which are neglected here, may be important for this structure. By the above averaging we have mainly eliminated the $\gamma^3$ contribution to $\delta_\gamma\mathscr{E}_n$, which is quite large here. It should be noted also that this contribution does not represent a real anharmonic effect because Eq. (20) is valid only up to the order $\gamma^2$ (see Ref. 7). Using a polynomial decomposition up to $\gamma^4$ of these results we can uniquely determine the $\gamma^2$ term, and calculate $C_b'$ (in Ry/atom) by Eq. (24b). The obtained values are represented in Tables V and VI. They turn out to be negative for most fcc (except for the metals of the IXth column of the Periodic Table, Rh, Ir), and positive for bcc metals. Negative values of similar band terms in elastic moduli have been obtained in calculations for simple metals in the past, as the pseudo potential calculations of Harrison[13] for Na, Mg, and Al.

The calculation errors in our results for $C_b'$ come mainly from inaccuracies in the band-structure method (and not from the numerical work). The errors in the results for $l=0,1,2$ are (comparing them to the $l=0,1,2,3$ results (of order 200 mRy/atom, and the absence of the correction term has an effect on the accuracy of the results for the bcc metals.

## V. THE MADELUNG TERM

In order to determine $C_M'$ [see Eq. (24c)] both the effective charge $Z_{\rm eff}$ and the $\gamma$ dependence (around $\gamma=0$) of $\delta_\gamma\mathscr{E}_M$ are to be calculated. $\delta_\gamma\mathscr{E}_M$ is the change under strain in the Madelung energy of unit charge point ions in a homogeneous neutralizing background. Similar to the band term, we calculate $\delta_\gamma\mathscr{E}_M$ for $\gamma=\pm2\%$, $\pm4\%$, and determine the $\gamma^2$ term in a power series expansion, by polynomial decomposition up to $\gamma^4$. The Madelung energies are calculated very accurately by the method proposed by Harris and Monkhorst,[21] based on a modification of the Ewald method, with the use of a summation in the reciprocal space only and omitting an infinitesimal sphere around $\vec{k}=0$. The results depend here only on the structure and not on a particular metal (up to the inverse linear dimensions). Making the above polynomial decomposition, one gets, for

$$\frac{2}{3}\lim_{\gamma\to0}\delta_\gamma\mathscr{E}_M/\gamma^2\ ,$$

$0.0750e^2/a$ for fcc and $0.0576e^2/a$ for bcc, where $a$ is the cubic lattice constant. These results are similar to the ones calculated by Fuchs.[22]

To evaluate the effective charge $Z_{\rm eff}$, let us define the spherically averaged electronic density as given by the LMTO-ASA (within a WS cell):

$$n(r)=\frac{1}{4\pi}\sum_l\int_{-\infty}^{E_F}N_l(E)\,|\phi_l(E,r)|^2dE\ , \qquad (31)$$

where $N_l(E)$ and $\phi_l(E,r)$ are, respectively, the $l$th partial density of states and the solution, for $l$ and $E$, of the radial Schrödinger (or Dirac) equation for the spherical band-structure potential, normalized within a cell. Equation (17) has defined what is the effective charge but $\tilde{n}(s)$, which is the value of the model density at the WS cell, is not defined. So noting that $n^{(1)}(s)$ (the first $r$ derivative) is zero due to crystal symmetry, one can write down an expansion in $n^{(2)}(s)$ of $Z^2$ (since we want to minimize the energy which depends on $Z^2$ and not on $Z$) and keep only the first term:

$$Z_{\rm eff}^2=Z_0^2-n^{(2)}(s)\left.\frac{d(Z^2)}{dn^{(2)}(s)}\right|_{Z=Z_0}\ , \qquad (32)$$

TABLE V. Results for $C_b'$ in Ry/atom for the two calculations for fcc transition metals.

| | Metal | | | | | | |
|---|---|---|---|---|---|---|---|
| $C_b'$ | Cu | Rh | Pd | Ag | Ir | Pt | Au |
| $l=0,1,2$ | −0.17 | +0.21 | −0.30 | −0.10 | +0.42 | −0.46 | −0.30 |
| $l=0,1,2,3$ | −0.25 | +0.02 | −0.38 | −0.20 | +0.12 | −0.51 | −0.50 |

TABLE VI. Results for $C_b'$ in Ry/atom for the bcc transition metals.

|  | Metal |  |  |  |  |  |
|---|---|---|---|---|---|---|
| $C_b'$ | V | Cr | Nb | Mo | Ta | W |
| $l=0,1,2,3$ | $+0.16$ | $+0.76$ | $+0.25$ | $+1.56$ | $+0.28$ | $+1.36$ |

knowing $n^{(2)}(s)$ and the derivative of

$$\frac{d(Z^2)}{dn^{(2)}(s)}\ ,$$

one gets $Z_{\rm eff}^2$. This calculation is again based on the self-consistent LMTO-ASA band-structure results for the fcc and bcc transition metals.[17]

There remains the question of how to calculate the derivative $d(Z^2)/dn^{(2)}(s)$ appearing in Eq. (32). For this purpose we use the expression (31) for the spherically averaged electronic density. We are looking here for small variations around the band-structure result, and there are many ways of varying $n$. Variation of $n(r)$ contain a "Fermi-surface (FS) term" due to the variation in the occupation of one-electron states close to the FS, and a BZ term due to mixtures of states lying close to the Fermi level from both sides.[7,12] Variations due to the FS term can be expressed as variations of $N_l(E_F)$ in Eq. (31). Variations due to the BZ term can be expressed as combinations of products of the form $\phi_l(E_1,r)\phi_l(E_2,r)$, where $E_1$ and $E_2$ are the energies lying close to $E_F$ from both sides. If such a product is approximated by $\phi_l(E_F,r)^2$, then also the BZ term can be expressed by an effective variation of $N_l(E_F)$ in Eq. (31). But we want to keep the number of particles constant. Certainly if $N(E)$ is not varied this condition is satisfied. So, following this discussion, to vary $n$ one can use the possibility offered by the LMTO-ASA method to vary the partial density of states $N_l(E)$ at $E_F$. Such variations are then done with the two restrictions: (a) the sum $\sum_l N_l(E)$ is kept constant, (b) the first $r$ derivative $n^{(1)}(s)$ is kept close to zero. In transition metals, $N_l(E_F)$ are important for essentially three $l$ values ($l\geq 2$), so restrictions (a) and (b) leave almost one degree of freedom for such variations and the derivative is then sharply defined.

For the fcc metals we compare here results for $l=0,1,2$ and for $l=0,1,2,3$. The spherically averaged density and its $r$ derivatives at $r=s$ are calcu-

TABLE VII. Results for the effective charge and for the various quantities involved in its calculation; the units are in powers of $a_0$, the Bohr radius; the results for $dn^{(2)}(s)/dZ\mid_{Z=Z_0}$ are based on assumptions (a) and (b), respectively; $Z_{\rm eff}$ is calculated by Eq. (32), and rounded to two digits; it coincides (up to 0.1) with both (a) and (b) results. Here only for fcc transition metals.

|  |  |  | Metal |  |  |  |  |
|---|---|---|---|---|---|---|---|
| Quantity | Cu | Rh | Pd | Ag | Ir | Pt | Au |
| $\Omega$ | 79.6 | 92.8 | 99.3 | 113.7 | 95.4 | 101.8 | 113.3 |
| $l=0,1,2$ |  |  |  |  |  |  |  |
| $n(s)\times 100$ | 3.51 | 4.14 | 3.34 | 2.53 | 4.73 | 4.03 | 3.12 |
| $n^{(1)}(s)\times 100$ | $-1.86$ | $-3.29$ | $-2.82$ | $-1.95$ | $-4.14$ | $-3.64$ | $-2.78$ |
| $n^{(2)}(s)\times 100$ | 19.8 | 23.2 | 27.2 | 24.5 | 27.5 | 34.1 | 34.5 |
| $Z_0$ | 2.79 | 3.84 | 3.32 | 2.88 | 4.51 | 4.10 | 3.53 |
| $dn^{(2)}(s)/dZ$ (a) | $-0.098$ | $-0.112$ | $-0.081$ | $-0.104$ | $-0.140$ | $-0.109$ | $-0.115$ |
| $dn^{(2)}(s)/dZ$ (b) | $-0.107$ | $-0.117$ | $-0.085$ | $-0.108$ | $-0.154$ | $-0.117$ | $-0.122$ |
| $Z_{\rm eff}$ | 4.3 | 5.5 | 5.7 | 4.7 | 6.1 | 6.4 | 5.7 |
| $l=0,1,2,3$ |  |  |  |  |  |  |  |
| $n(s)\times 100$ | 3.25 | 4.05 | 3.21 | 2.44 | 4.74 | 3.96 | 3.03 |
| $n^{(1)}(s)\times 100$ | $-0.78$ | $-1.68$ | $-1.27$ | $-0.79$ | $-2.17$ | $-1.74$ | $-1.18$ |
| $n^{(2)}(s)\times 100$ | 23.2 | 29.8 | 32.9 | 28.7 | 35.3 | 41.4 | 40.6 |
| $Z_0$ | 2.59 | 3.76 | 3.19 | 2.77 | 4.52 | 4.03 | 3.43 |
| $dn^{(2)}(s)/dZ$ (a) | $-0.113$ | $-0.122$ | $-0.090$ | $-0.120$ | $-0.153$ | $-0.124$ | $-0.130$ |
| $dn^{(2)}(s)/dZ$ (b) | $-0.119$ | $-0.129$ | $-0.092$ | $-0.126$ | $-0.170$ | $-0.128$ | $-0.135$ |
| $Z_{\rm eff}$ | 4.2 | 5.7 | 5.8 | 4.6 | 6.4 | 6.6 | 5.8 |

TABLE VIII. Calculated values of $Z_0$, $Z_{\text{eff}}$, and the relative difference between them in percents.

| Element | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Z_0$ | 1.126 | 2.16 | | | 3.28 | 3.36 | | 3.13 | | 2.84 | 2.59 |
| $Z_{\text{eff}}$ | 1.106 | 2.08 | | | 3.34 | 3.72 | | 4.5 | | 4.8 | 4.2 |
| $\frac{Z_{\text{eff}}-Z_0}{Z_0}$ | −1.8% | −3.7% | | | 1.8% | 11% | | 44% | | 69% | 62% |
| | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag |
| | 1.123 | 2.18 | | | 3.92 | 4.25 | | | 3.76 | 3.19 | 2.77 |
| | 1.111 | 2.13 | | | 3.95 | 4.54 | | | 5.7 | 5.8 | 4.6 |
| | −1.1% | −2.3% | | | 0.8% | 6.8% | | | 52% | 82% | 66% |
| | Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au |
| | 1.123 | 2.17 | | | 4.3080 | 4.78 | | | 4.52 | 4.03 | 3.43 |
| | 1.101 | 1.99 | | | 4.3084 | 5.00 | | | 6.4 | 6.6 | 5.8 |
| | −2.0% | −8.3% | | | 0.01% | 4.6% | | | 42% | 64% | 69% |

lated by Eq. (31), making an integration (by Simpson's method) based on 99 energy points in the valence band, with a variable energy interval proportional to $N(E)^{-1}$. The wave functions $\phi_l(E,r)$ are calculated by solving the "scalar" Dirac equation (see explanation before) with the self-consistent potential. The first $r$ derivatives $\phi_l^{(1)}(E,s)$ are calculated by accurate interpolation (they are related to the logarithmic derivatives which play an essential role in the LMTO-ASA method). The second $r$ derivatives $\phi_l^{(2)}(E,s)$ are calculated directly on the basis of the radial Schrödinger equation, which relates $\phi_l^{(2)}(E,s)$ to a combination of $\phi_l(E,s)$ and $\phi_l^{(1)}(E,s)$ (relativistic effects on the wave functions are not expected to be important close to the WS cell boundaries).

Let us denote

$$n_l^{(i)}(E,s)=\frac{d^i}{dr^i}[\,|\phi_l(E,r)|^2]_{r=s}\ . \tag{33}$$

By multiplying these quantities (for $i=0,1,2$) by $N_l(E)/4\pi$, and carrying out the $l$ summation and the integration of Eq. (31), we calculate $n(s)$, $n^{(1)}(s)$, and $n^{(2)}(s)$, and the obtained values for the $l=0,1,2$ and the $l=0,1,2,3$ cases are represented in Table VII for fcc metals. We also represent in this table the values of the WS volume[23] $\Omega$ and of $Z_0$ obtained by (14). The calculated value of $n^{(1)}(s)$ deviates somewhat from zero (mainly due to incomplete convergence of the band calculation, especially for $l=0,1,2$). For monoatomic crystals one should get by crystal symmetry that the sum $\sum_l N_l(E)n_l^{(1)}(E,s)$ is close to zero for any $E$; so the derivative $dn^{(2)}(s)/dZ\,|_{Z=Z_0}$ needed in Eq. (32), is calculated by the formula

$$\left.\frac{dn^{(2)}(s)}{dz}\right|_{Z=Z_0}=\frac{\sum\limits_l \delta N_l(E_F)n_l^{(2)}(E_F,s)}{\Omega\sum\limits_l \delta N_l(E_F)n_l(E_F,s)}\ , \tag{34a}$$

where $n_l(E,s)=n_l^{(0)}(E,s)$ and $\delta N_l(E_F)$ are calculated by restrictions (a), (b):

$$\sum_l \delta N_l(E_F)=0\ , \tag{34b}$$

$$\sum_l \delta N_l(E_F)n_l^{(1)}(E_F,s)\simeq 0\ . \tag{34c}$$

The value obtained in (34a) is determined sharply, for transition metals, but not uniquely, due to

TABLE IX. Results for $C_M'$ in Ry/atom for the two calculations for fcc transition metals. Also represented are the inverse cubic lattice constants $a$ in Bohr radius units $a_0$ used in this calculation.

| | Cu | Rh | Pd | Ag | Ir | Pt | Au |
|---|---|---|---|---|---|---|---|
| $a_0/a$ | 0.1464 | 0.1391 | 0.1360 | 0.1300 | 0.1379 | 0.1349 | 0.1302 |
| $C_M'$ for $l\le 2$ | 0.41 | 0.63 | 0.66 | 0.43 | 0.77 | 0.83 | 0.63 |
| $C_M'$ for $l\le 3$ | 0.39 | 0.68 | 0.68 | 0.41 | 0.85 | 0.88 | 0.65 |

TABLE X. Results for $C'_M$ in Ry/atom for bcc transition metals; $a_0/a$ is also presented.

| | V | Cr | Nb | Mo | Ta | W |
|---|---|---|---|---|---|---|
| $a_0/a$ | 0.0924 | 0.0971 | 0.0848 | 0.0891 | 0.0849 | 0.0884 |
| $C'_M$ for $l \leq 3$ | 0.12 | 0.15 | 0.15 | 0.21 | 0.18 | 0.25 |

the inaccuracy in (34c), and to the small contribution from $l > 2$. In practice we have carried out two approximate calculations of (34a), based on values of $\delta N_l(E_F)$ determined uniquely (up to a proportionality factor) as follows.

(a) We have assumed that $\delta N_l(E_F)$ is zero for $l > 2$ [which concerns in our case just the $\delta N_3(E_F)$ value for the calculation with $l = 0,1,2,3$], and determined $\delta N_l(E_F)$ for $l \leq 2$ by Eqs. (34b) and (34c), where (34c) is considered as an exact equation.

(b) We have applied Eq. (34b) involving $\delta N_l(E_F)$ for the $l$ values involved in the band calculation, and in addition assumed that

$$[N_l(E_F)+\delta N_l(E_F)]/N_l(E_F)\ , \quad \text{for } l > 2$$

and that

$$\frac{\sum_l [N_l(E_F)+\delta N_l(E_F)]n_l^{(1)}(E_F,s)]}{\sum_l N_l(E_F)n_l^{(1)}(E_F,s)}$$

are both equal to

$$[N_2(E_F)+\delta N_2(E_F)]/N_2(E_F)\ .$$

This assumption is based on the linkage of the high-$l$ (greater than 2) components, and of the deviation of the calculated $n^{(1)}(E_F,s)$ from zero with the $d$ band (for transition metals).

The values obtained for fcc metals for

$$dn^{(2)}(s)/dZ\,|_{Z=Z_0}$$

under assumptions (a) and (b) are represented in Table VII. These derivatives can now be used together with $Z_0$ and $n^{(2)}(s)$ to calculate $Z_{\text{eff}}$ by Eq. (32). It turns out that the $Z_{\text{eff}}$ values obtained under assumptions (a) and (b) coincide with each other up to about 0.1 (i.e., about 2%). So we represent in Table VII the $Z_{\text{eff}}$ values up to two decimal digits, which agree with both assumptions (a) and (b) up to a theoretical dispersion error $\Delta Z_{\text{th}} \lesssim 0.1$.

By comparing the results of Table VII for $l = 0,1,2$ and $l = 0,1,2,3$, we find that the change in $Z_{\text{eff}}$ between the two cases is up to about 5%. Since the LMTO-ASA band method[6,16] is based on the determination of the band energies through a tail-cancelation condition, obtained by expansion in $l$ around the WS cell center, and does not emphasize the convergence of the density close to the cell boundaries, it is not possible to assume, as for $C'_b$, that the error in $Z_{\text{eff}}$ for $l = 0,1,2$ is considerably larger than the error for $l = 0,1,2,3$.

In Table VIII we show the results we got for both $Z_0$ and $Z_{\text{eff}}$ for all cubic metals and the relative change in percent between $Z_0$ and $Z_{\text{eff}}$. It turns out that $Z_{\text{eff}}$ is greater than $Z_0$ by a factor of $1.5-2$ for the fcc transition metals, whereas the charge is minimal in the first and the fifth columns of the Periodic Table (especially for Ta). The physical meaning of the transformation between $Z_0$ and $Z_{\text{eff}}$ is that it represents energy effects through the variation procedure. And this concerns, among other effects, nonlocal exchange-correlation effects. So a large difference between $Z_{\text{eff}}$ and $Z_0$ might indicate that such effects (on the strain energy) are important. As was mentioned earlier, in the free-electron limit, $Z_{\text{eff}}$ coincides with $Z_0$, and Eq. (20) with $Z_{\text{eff}}$ replaced by $Z_0$ should not be a bad approximation for simple metals,[13–15] with only $s$ and $p$ valence bands. So pseudopotential calculations with a Madelung term

TABLE XI. Results for $C'$ in $10^{10}$ N/m$^2$ compared with experiments for fcc transition metals.

| | Cu | Rh | Pd | Ag | Ir | Pt | Au |
|---|---|---|---|---|---|---|---|
| $C'_b$ | $-4.6$ | $+0.3$ | $-5.6$ | $-2.6$ | $+1.8$ | $-7.4$ | $-6.4$ |
| $C'_M$ | $+7.2$ | $+10.7$ | $+10.0$ | $+5.3$ | $+13.0$ | $+12.7$ | $+8.4$ |
| $C'_{\text{calc}}$ | 2.6 | 11.0 | 4.4 | 2.7 | 14.8 | 5.3 | 2.0 |
| $C'_{\text{exp}}$ | 2.56 | 11.5 | 2.9 | 1.71 | 17.2 | 5.22 | 1.6 |

TABLE XII. Results for $C'$ in $10^{10}$ N/$\mathrm{m}^2$ compared with experiments for bcc transition metals.

| | V | Cr | Nb | Mo | Ta | W |
|---|---|---|---|---|---|---|
| $C'_b$ | +2.5 | +13.9 | +3.1 | +21.8 | +3.3 | +18.8 |
| $C'_M$ | +1.9 | +2.8 | +1.9 | +2.9 | +2.2 | +3.5 |
| $C'_{\mathrm{calc}}$ | 4.4 | 16.6 | 5.0 | 24.7 | 5.5 | 22.3 |
| $C'_{\mathrm{expt}}$ | 5.86 | 15.3 | 5.98 | 15.6 | 5.4 | 16.4 |

based on $Z_0$ turned out to be successful for such metals.[13]

For fcc transition metals, it will be seen later that the transformation from $Z_0$ to $Z_{\mathrm{eff}}$ is essential for the calculated value of $C'$, and that it even determines their positive sign (except for Ir and Rh where $C'_b$ is positive).

The values of $C'_M$ (in Ry/atom) are obtained with the use of Eq. (24c), multiplying the result of $\frac{2}{3}\lim_{\gamma\to 0}\delta_\gamma \mathscr{E}_M/\gamma^2$ by the calculated $Z_{\mathrm{eff}}^2$ (Table VIII) and by $a_0/a$, the ratio between the Bohr radius and the cubic lattice constant. The obtained values (for $l=0,1,2$ and $l=0,1,2,3$) are represented for fcc in Table IX, together with the values of $a_0/a$ calculated from Ref. 23 and for $l=0,1,2,3$ only for bcc metals in Table X.

## VI. DISCUSSION AND CONCLUSION

In Tables XI and XII results for $C'_b$ and $C'_M$ based on the $l=0,1,2,3$ calculations are shown in units of $10^{10}$ N/$\mathrm{m}^2$ for fcc and bcc, respectively. And by summing them, one obtains the calculated tetragonal shear modulus $C'_{\mathrm{calc}}$, which is compared with $C'_{\mathrm{expt}}$, the experimental results extrapolated to $T=0$ K [Pd,[24] Cu,[25] Au and Ag,[26] Pt and Ir,[27] Rh,[28] V,[29] Nb,[12] Cr,[30] Ta, Mo, W (Ref. 31)].

The experimental result for Rh was measured recently,[28] after the calculation was completed, and its value was correctly predicted. All the theoretical results agree fairly well with experiment considering that it is a parameterless calculation and that there is some uncertainty on the experimental results. The only data actually needed are the crystal structure and the electronic structure of the atoms, all other quantities are calculated. For bcc metals the results are less accurate. We have already noted that the band term for these metals did not satisfy well the parabolic behavior. We think that the main source of error comes here from the evaluation of this term. The results, though, are still in the right order of magnitude.

This work represents, to our knowledge, the first successful *ab initio* calculation of shear moduli in transition metals, and proves the validity of the theoretical method presented above. Conceptually this work completes previous works on shear moduli in transition metals, based on a tight-binding parametrization[12,32] (where only the band term $\delta_\gamma \mathscr{E}_n$ was actually calculated) explaining anomalies in the temperature and the composition dependence of the shear moduli in Nb-Zr and Nb-Mo alloys. In Ref. 12 we have found for the band contribution of the tetragonal shear modulus of Nb $C'_b=0.16$ Ry/atom. It was also positive consistently with what we find here 0.25 Ry/atom. The difference may be coming from all the contributions to the band-structure calculation which were not included in these earlier works. But the band contribution to the trigonal shear modulus as ($C_{44}^b$) was negative. Since the Madelung contribution to $C_{44}$ is almost 1 order of magnitude larger for trigonal shear ($C_{44}^M=0.4286e^2/a$ instead of $C'_M=0.0576e^2/a$ for bcc, it is reasonable to think that we also should find a negative contribution with this approach.

In the present work we also calculate the Madelung term, which is essential for the magnitude (and even for the right sign for some fcc metals) of the moduli, but whose behavior is typical of the crystal structure and is not expected to be anomalous for a particular substance.

The use of the LMTO-ASA method enables us to develop a perturbative expansion for $\delta_\gamma \mathscr{E}_n$ (considering only the structure constant matrix, due to the frozen-potential condition) similar to the tight-binding one.[12,32,33] The use of the method of Harris and Monkhorst enables a similar expansion for $\delta_\gamma \mathscr{E}_M$ also. Since we have made no assumption on the type of deformation considered here (except that it should be small), such a representation of the method becomes adequate also for phonon calculations, where again tight-binding calculations were found successful explaining anomalies in the phonon spectra of transition metals and their compounds.[23,34,35] The effective charge $Z_{\mathrm{eff}}$, introduced in our approach, being the same for all volume-conserving deformation of the lattice, might be used for any phonon.

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