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Augmented-Plane-Wave Calculation of the Total Energy, Bulk Modulus, and Band Structure of Compressed Aluminum*

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This paper reports the results of self-consistent calculations on aluminum of the total energy, bulk modulus, and band structure by the augmented-plane-wave method. Using a Kohn-Sham free-electron exchange we calculate a 0°K equilibrium volume 5.8% greater than observed and a compressibility too large by 16%. We find that a free-electron exchange factor of 0.713 ± 0.01 would predict the correct 0°K equilibrium density.

I. INTRODUCTION

In this paper we report the results of calculations for aluminum of the total energy, bulk modulus, and band structure under compression, using the augmented-plane-wave (APW) method and utilizing the local exchange approximation. A similar calculation has been reported recently by Rudge for lithium,[1] also using the APW method, and by Liberman[2] for lithium, beryllium, aluminum, and iron. Liberman uses a modified Korringa-Kohn-Rostoker (KKR) method and a spherical unit cell.

We have used the standard APW method described in detail elsewhere.[3] Since some variations of the original method have appeared recently,[4] it is worthwhile to state explicitly that we treat the charge density and the crystal potential as constants in the space between the touching spheres and apply the treatment of Slater and DeCicco[5] to calculating the Coulomb-potential discontinuity at the sphere boundary.

II. CALCULATION OF PRESSURE AND ENERGY

The band calculations were made for 256 points in the full Brillouin zone. All ten inner (core) electrons were also treated self-consistently, but in an atomiclike fashion by using the Noumerov method to solve the Schrödinger equation, and requiring the wave functions to be zero at the muffin-tin boundary. The Fermi energy used in the band calculations was determined, using the method described by Snow and Waber,[6] by filling in the lowest states until the sum of the weights of these states equaled the number of electrons in the band.

The total energy may be expressed as

$$E=E_k+\int d\mathbf{r}\,\rho(\mathbf{r})[V_{\rm ne}(\mathbf{r})+\tfrac{1}{2}V_{\rm ee}(\mathbf{r})+\tfrac{3}{4}fV_{\rm ex}(\mathbf{r})]+E_{\rm nn}. \tag{1}$$

E_k is the total kinetic energy and the remaining terms represent the total potential energy U. $\rho(\mathbf{r})$ is the total electron density, $V_{\rm ne}$ is the electron nuclear potential, $V_{\rm ee}$ is the electron-electron potential, $V_{\rm ex}$ is the exchange potential, and $E_{\rm nn}$ is the interaction energy of the nuclei. We use the free-electron exchange approximation such that

$$V_{\rm ex}(\mathbf{r})=-3[(3/\pi)\rho(\mathbf{r})]^{1/3}; \tag{2}$$

f is the exchange factor and is a constant.

If the eigenvalues satisfy the one-electron equations

$$\epsilon_i\mu_i(\mathbf{r})=[-\nabla^2+V_{\rm ne}(\mathbf{r})+V_{\rm ee}(\mathbf{r})+fV_{\rm ex}(\mathbf{r})]\mu_i(\mathbf{r}), \tag{3}$$

then the variational principle is obeyed and the virial theorem

$$PV=\tfrac{2}{3}E_k+\tfrac{1}{3}U \tag{4}$$

is satisfied.[1,7] PV is the product of pressure and volume. All of the computations presented here were set up to satisfy the virial theorem. Details of these calculations are given in the Appendix.

The criteria for self-consistency were such that consecutive iterations yielded variations in total energy less than 5×10^{-4} Ry. The computed pressure and energy as a function of volume is shown in Figs. 1 and 2. These calculations were done with an $f=\frac{2}{3}$, variously referred to as the Kohn-Sham-Gaspar or Dirac exchange. The pressures were calculated by the virial

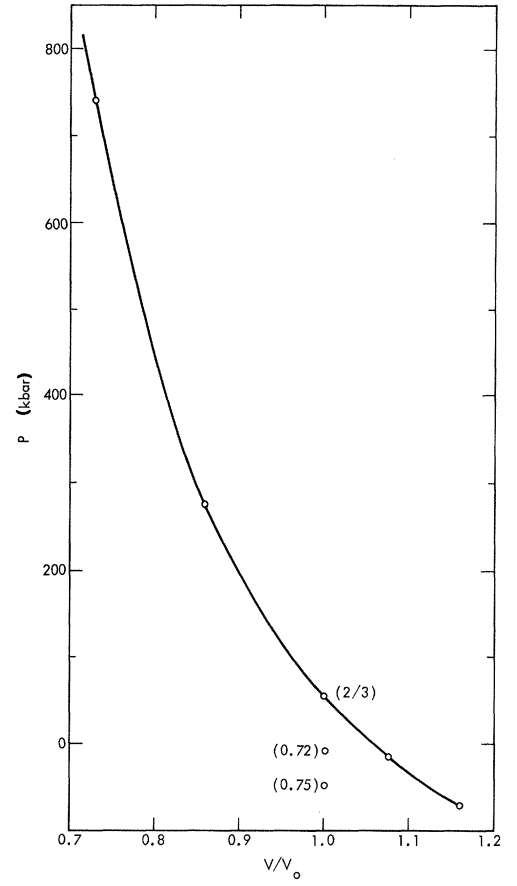

FIG. 1. Calculated pressure (kbar) versus volume ratio.

theorem. The energy curve was drawn in the bowl by fitting the energy to a polynomial expansion in volume and interpolating. The pressures calculated by differentiating this expansion in energy agreed with pressures from the virial theorem to within 3 kbar. The dashed lines in Fig. 2 are the derivatives as obtained from the virial theorem.

The calculations were made using a potential grid of up to 500 points rather than the 200 points usually used in the APW calculations. It was only by so doing that the resultant energy-volume curve would agree with pressures from the virial theorem to the accuracy we believed they should. We used a mesh doubling scheme similar to Herman and Skillman[8] with doubling occurring at grid points 80, 160, 240, 320, and 370. The major limitation in the exact calculation of the energy is the accuracy to which the core electrons can be computed, and we estimate this to lead to an over-all error of about 0.01 Ry and 15 kbar.

The number of APW's used in constructing the wave functions varied for each state. However, care was taken that halving the number used changed the eigenvalue by less than the self-consistency requirement. All of the APW'S were truncated at $l=12$ of the angular momentum sum.

The computed equilibrium volume ratio V/V_0 at $P=0$ kbar is 1.058 within the accuracy of both methods. V_0, the experimental 0°K equilibrium volume, is 10.00 cm^3/mole. $-V(dP/dV)_T$, the bulk modulus at $P=0$ bar, is 0.92 Mbar when calculated from the $P-V$ results and is 0.94 Mbar when calculated from the polynomial expansion of the energy that was used to draw in the solid curve in the bowl of Fig. 2. The good agreement between these two calculations is another measure of the degree to which these calculations satisfy the virial theorem. The experimental bulk modulus is 0.794 Mbar.[9]

These results are in good agreement with the recent calculations of Liberman.[2] He calculates a compressibility of 0.93 Mbar and an equilibrium volume ratio of 1.070. Liberman uses the KKR method with a muffin potential to calculate the band structure and then uses a spherical unit cell as in the Wigner-Seitz model. This approximation allows him to compute the pressure by evaluating a surface integral. The greatest difference between his calculation and ours is in his model of the exchange interaction. It is a variant of the free-electron exchange model with $f=\frac{2}{3}$. For a detailed discussion the interested reader should see Liberman's paper.

These comparisons with experiment neglect the zero-point vibrational properties. We can estimate these by using the Grüneisen model.[10] In this approximation the

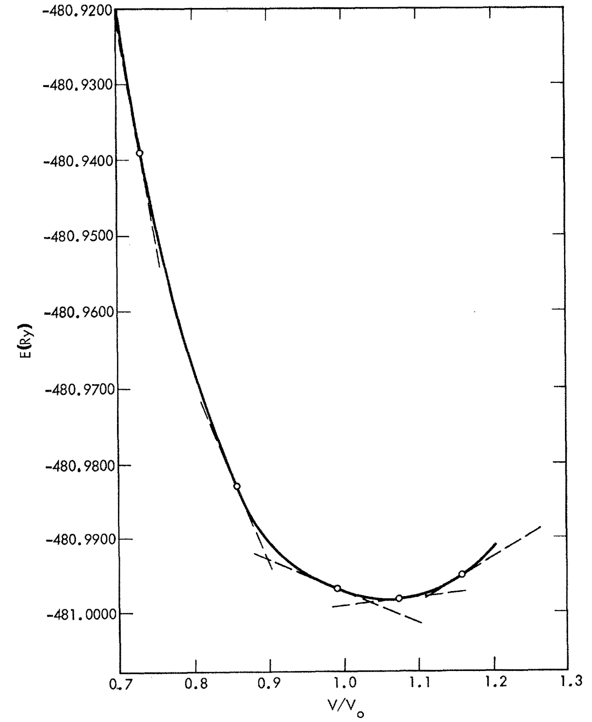

FIG. 2. Calculated total electronic energy (Ry) versus volume ratio. Dashed lines are derivatives obtained using the virial theorem.

zero-point energy E^0 and pressure P^0 are

$$E^0 = (9/8)Nk\Theta, \tag{5}$$

$$P^0 = (\gamma/V)E^0. \tag{6}$$

γ is Grüneisen's parameter, equal to 2.19 for aluminum[9]; Θ, the Debye temperature, equals 430.3°K [9]; and V equals 10.0 cm^3/mole.[9] From this we obtain a P^0 of 9 kbar. At the highest density, $V/V_0 = 0.729$, P^0 is about 16 kbar. These corrections are within the order of our numerical accuracy and will be neglected. An additional uncertainty arises from our use of 256 points in the full Brillouin zone. We have made no attempt to assess the magnitude of this error.

The same calculations were made using exchange factors of $\frac{3}{4}$ and 0.72. These results are shown by the two unconnected points in Fig. 1. Interpolating we find that the exchange factor which predicts the correct 0°K density is 0.713 ± 0.01. The uncertainty is based on the error estimate. This figure is close to the "optimized exchange" factor of 0.72 determined by Kmetko[11] for atomic aluminum. Kmetko solved the atomic problem using the atomic analogs of Eqs. (1)–(3) for a number of exchange factors. The eigenfunctions were then used in the Hartree-Fock equations and the exchange factor which gave the lowest energy was referred to as the "optimized exchange" factor. The results of recent unpublished work on calcium by the authors suggest that the agreement in the optimized exchange factors for aluminum atom and solid may be fortuitous.

Using the exchange factor of 0.713 we have calculated the energy of cohesion to be 0.32 ± 0.02 Ry. The experimental value is 0.25 Ry.[9] The energy of the atom was calculated with the Herman-Skillman program.[8] The results for other exchanges are given in Table I. Liberman reports a figure of 0.20 Ry.

The calculation of cohesive energy is fraught with at least two uncertainties. First, we are seeking the small difference between two large numbers obtained from two models which are not strictly comparable. Second, it is not clear that the proper exchange factor for the atom will be the same as in the solid. For example, if we assume that the correct exchange factor is 0.715 for the atom and 0.713 for the solid, we arrive at a cohesive energy in excellent agreement with the experiment. We suspect that the latter may be the case since none of the exchanges appear to give the correct cohesive energies. For these reasons it appears that from the thermodynamic point of view the best empirical method of obtaining the exchange factor would be from the solid properties alone and not from cohesive energies.

TABLE I. Pressure and energy versus exchange factor at $V/V_0 = 1.0$.

f	P (kbar)	E_{solid} (Ry)	E_{cohesion} (Ry)
0.75	−44	-485.174 ± 0.01	0.35 ± 0.02
0.72	9	−483.667	0.33
0.713[a]	0.0[a]	−483.13[a]	0.32
$\frac{2}{3}$	56	−480.997	0.30
Experiment (Ref. 9)			0.25

[a] Obtained by interpolation.

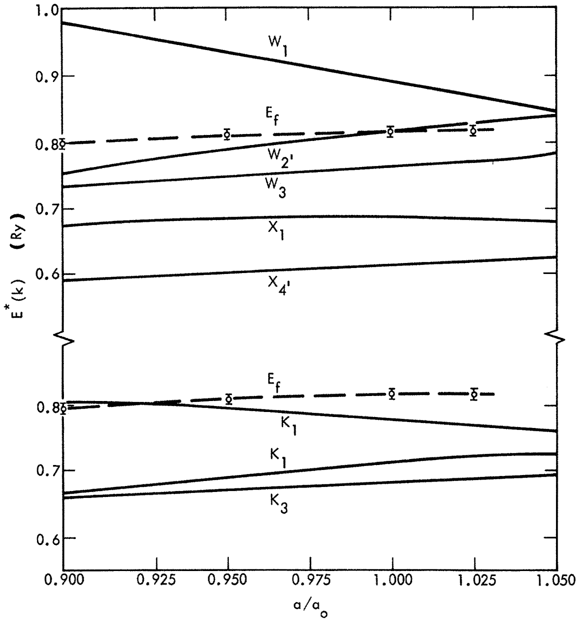

FIG. 3. Change in reduced energy $E^*(k)$ with lattice parameter.

III. BAND STRUCTURE UNDER COMPRESSION

Figure 3 shows the variation of the band structure with lattice parameter at some points of high symmetry in the Brillouin zone. The calculations were made with the $\frac{2}{3}$ exchange factor. The energies are expressed in the reduced units $E^*(\bar{K}) = [E(\bar{K}) - E(0)](a/a_0)^2$, with $E(0)$ equal to the energy of the lowest state (Γ_1) of the conduction band. For free-electron states with a constant effective mass, $E^*(K)$ is a constant at all a/a_0. The Fermi energies shown in Fig. 3 were obtained by first fitting the energy levels near the Fermi energy to within 0.001 Ry with an Ashcroft-type pseudopotential,[12] an adjusted effective mass, and a wave function of nine plane waves. A random set of points inside the Brillouin zone was generated at which the eigenvalues were calculated by the pseudopotential method. The energy of the Fermi surface enclosing three electrons could then be determined. The estimated accuracy of our Fermi energy is ± 0.008 Ry as shown by the bars. These are not the Fermi energies that were obtained in the self-consistent band calculations by the method of Snow and Waber.

Changes in the band structure in going from $\frac{2}{3}$ to 0.72 exchange are small, the maximum change being 0.003 Ry in the relative energy of W_2' above Γ_1. No

TABLE II. Pseudopotentials calculated from energies at W for $a/a_0=1.0$.

	Exchange factor			$a/a_0=1.0$		
	1.0	0.75	0.72	$\frac{2}{3}$	Ashcroft (Ref. 12)	Segall (Ref. 13)
V_{111}	0.0073	0.0167	0.0178	0.0197	0.0179	0.023
V_{200}	0.0384	0.0430	0.0435	0.0443	0.0562	0.043

change occurs in the ordering of the levels, and the Fermi energy decreases by less than 0.001 Ry. We therefore assume that qualitative remarks concerning changes in the $\frac{2}{3}$ exchange band structure apply equally to other exchange factors in this range.

Ashcroft, on the basis of a very careful analysis of the Fermi surface using pseudopotential theory to interpret de Hass–van Alphen experiments at normal density, concluded that W_2' was above but very close to the Fermi surface. Our results also indicate that W_2' is very close to the Fermi surface but we cannot make a finer distinction, due to the inaccuracy in our Fermi surface. In this paper we make no attempt to examine the details of the Fermi surface using the present theory. Our objective is to predict what qualitative changes will occur under pressure. It is clear, for example, that the W_2' is moving below the Fermi surface at about normal density.

It is possible to get some idea as to which exchange factor gives best agreement with Fermi surface data by comparing the pseudopotentials obtained from each band structure with the empirically determined pseudopotentials of Ashcroft. Ashcroft used a wave function made of four plane waves. The energies at W are related to pseudopotential coefficients V_{111} and V_{200} by

$$W_1-W_2'=4V_{111}$$

and

$$W_2'-W_3=2V_{200}-2V_{111}.$$

In order to make a consistent comparison with Ashcroft the pseudopotential coefficients in Table II were obtained by solving these equations using the actual band-structure points at W. Comparison with Ashcroft's results indicates that the best exchange factor in terms of Fermi surface experiments lies very close to the best exchange factor from thermodynamic stability and very accurately predicts the splitting between the W_1 and W_2'. Tables III and IV list the band-structure calculations at a number of points of high symmetry. Shown for comparison are the results of Segall.[13] It may be noted that the exchange factor has relatively little effect on the band structure. The most sensitive point being the W_2' state. We have compared the results in Table IV at $f=0.72$ and $f=1.0$ with recent unpublished calculations of Snow.[14] Our results differ on the average by ±0.0002 Ry. The largest difference occurs in the W_2' state and is 0.0007 Ry. This state is obviously very sensitive to the potential.

Melz[15] has recently explored the effect of pressure on the Fermi surface of aluminum with de Haas–van Alphen experiments. He measured the changes with pressure in the γ cross section, which is the extremal orbit around the point U. This cross section is the Fermi surface area S_u, in the third zone near the U point. Melz measured the change in this cross section $\Delta S/S_0$ up to 7 kbar where S_0 is the 1 atm, 4.2°K value and obtained the pressure derivative $d(\Delta S/S_0)/dP=-(4.7\pm0.6)\times10^{-3}/\text{kbar}$. As a model of this region of the zone he assumed this cross section to be approximated by $S_u=C(E_u-E_f)$. C is assumed to be a constant. E_f and E_u are the Fermi energy and the energy at U nearest to E_f. He then used the experimentally deter-

TABLE III. Conduction band energies relative to Γ_1 variation with lattice parameter at $f=\frac{2}{3}$.

a/a_0	1.05	1.025	1.0	0.95	0.90
X_4' (1, 0, 0)	0.5623	0.5842	0.6082	0.6628	0.7279
X_1	0.6135	0.6481	0.6835	0.7564	0.8314
L_2' $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	0.4461	0.4598	0.4747	0.5084	0.5484
L_1	0.4378	0.4665	0.4968	0.5639	0.6376
K_3 $(\frac{3}{4}, \frac{3}{4}, 0)$	0.6318	0.6568	0.6839	0.7449	0.8166
K_1	0.6566	0.6844	0.7107	0.7656	0.8259
K_1	0.6869	0.7289	0.7761	0.8800	0.9942
W_3 $(\frac{1}{2}, 1, 0)$	0.7014	0.7294	0.7596	0.8271	0.9055
W_2'	0.7580	0.7827	0.8088	0.8654	0.9274
W_1	0.7603	0.8215	0.8876	1.0359	1.0294
E_F[a]	0.712	0.740	0.782	0.867	0.940
E_F[b]		0.776±0.008	0.894	0.894	0.984

[a] Calculated as part of band-structure calculation.

[b] Calculated by fitting the band near the Fermi energy to a pseudopotential and discussed in text.

TABLE IV. Conduction band energies relative to Γ_1 variation with exchange factor at $a/a_0=1.0$.

f	$\frac{2}{3}$	0.72	0.75	1.0	Segall (Ref. 13)
X_4' (1, 0, 0)	0.6082	0.6078	0.6076	0.6066	0.622
X_1	0.6835	0.6829	0.6825	0.6779	0.698
L_2' $(\frac12,\frac12,\frac12)$	0.4747	0.4751	0.4754	0.4786	0.483
L_1	0.4968	0.4952	0.4943	0.4860	0.512
K_3 $(\frac34,\frac34,0)$	0.6839	0.6836	0.6835	0.6831	0.699
K_1	0.7107	0.7114	0.7118	0.7144	0.723
K_1	0.7761	0.7736	0.7721	0.7598	0.802
W_3 $(\frac12,1,0)$	0.7596	0.7595	0.7594	0.7596	0.776
W_2'	0.8088	0.8108	0.8120	0.8217	0.819
W_1	0.8876	0.8820	0.8788	0.8509	0.923
E_F[a]	0.782	0.781	0.780	0.771	
E_F[b]	0.814±0.008				

[a] Calculated as part of band-structure calculation.

[b] Calculated by fitting the band near the Fermi energy to a pseudopotential and discussed in text.

mined changes in S to obtain changes in E_u and thereby the change in the Ashcroft pseudopotential under pressure. We use the same model for S_u, but calculate this cross section directly from our computed pressures and energy levels. We calculate $d(\Delta S/S_0)/\Delta p=-3.0\times10^{-3}$/kbar. Part of this discrepancy can be accounted for by the theoretical compressibility being 16% high. Using the experimental compressibility, we calculate $d(\Delta S/S_0)/dP=-3.4\times10^{-3}$/kbar which is too low, but in reasonable qualitative agreement. Also, our results are based on taking differences in calculations extending over a much wider pressure range. The results predict E_u will move above the Fermi surface near $a/a_0=0.92$ or about 500 kbar. Note that points K and U are degenerate.

Burton and Jura[16] have measured the Fermi momentum of aluminum from 0 to 100 kbar at room temperature through the use of positron annihilation. They found that over this range which is from $a/a_0=1.0$ to 0.97 (0 to 100 kbar) the Fermi momentum was well described by the free-electron model. Our results as shown in Fig. 3 are in good agreement with these experiments.

ACKNOWLEDGMENTS

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APPENDIX

In this section we discuss the details of our total-energy calculations. We assume the reader is familiar with the work of Slater and DeCicco.[5]

We first discuss the total Coulomb energy $E_{\rm Coul}$ which may be written as

$$E_{\rm Coul}=\tfrac12\int\rho(\mathbf{r})[V_{\rm ne}(\mathbf{r})+V_{\rm ee}(\mathbf{r})]d\mathbf{r}+\tfrac12\int\rho(\mathbf{r})V_{\rm ne}(\mathbf{r})d\mathbf{r}+E_{\rm nn}. \tag{A1}$$

$V(\mathbf{r})$, the Coulomb potential, is

$$V(\mathbf{r})=V_{\rm ne}(\mathbf{r})+V_{\rm ee}(\mathbf{r}). \tag{A2}$$

In the muffin-tin approximation, $\rho(\mathbf{r})$ and $V(\mathbf{r})$ are treated as constants ρ_c and ϕ_c outside of the muffin tin. $\rho_c=$ (charge outside muffin tin)/(volume outside muffin tin). Slater and DeCicco have shown that in an fcc lattice with the muffin-tin potential,

$$\phi_c=-(0.8163482/a)q_c\times2, \tag{A3}$$

where

$$q_c=-\int_\Delta\rho_c d\mathbf{r}. \tag{A4}$$

Δ represents an integration over the unit cell; a is the lattice constant of the unit cell. The factor 2 converts the Gaussian units of Slater and DeCicco into atomic units (Ry) with a in atomic units. Slater and DeCicco have also shown that $V(\mathbf{r})$ must satisfy Poisson's equation with the boundary condition at the muffin-tin radius R_s such that

$$V(R_s)-\phi_c=0.107123(q_c/a)\times2,$$

leading to a discontinuity in the Coulomb potential.

Equation (A1) may be written as

$$E_{\rm Coul}=\tfrac12N\int_\Delta\rho(\mathbf{r})V(\mathbf{r})d\mathbf{r}-\tfrac12\sum_\alpha Z\int[\rho(\mathbf{r})d\mathbf{r}/|\mathbf{r}-\mathbf{R}_\alpha|]+E_{\rm nn}. \tag{A5}$$

N is the number of cells, and the first term on the right-hand side is integrated only over a single cell,

$$V_{\rm ne}(\mathbf{r})=-\sum_\alpha(Z/|\mathbf{r}-\mathbf{R}_\alpha|)$$

and

$$E_{\mathrm{nn}}=\tfrac{1}{2}\sum_{\alpha}\sum_{\beta}{}'(ZZ/R_{\alpha\beta}).$$

Z is the nuclear charge, $R_{\alpha\beta}$ is the distance between nuclei α and β, and the prime indicates $\alpha\neq\beta$. Since all cells are identical, let $R_1=0$, and the Coulomb energy per atom may be written as

$$\frac{E_{\mathrm{Coul}}}{N}=\frac{1}{2}\int_{\Delta}\rho(\mathbf{r})V(\mathbf{r})d\mathbf{r}-\tfrac{1}{2}Z\int_{\Delta}\frac{\rho(\mathbf{r})d\mathbf{r}}{|\mathbf{r}|}-\tfrac{1}{2}Z\int_{0}\frac{\rho(\mathbf{r})d\mathbf{r}}{|\mathbf{r}|}+\frac{1}{2}\sum_{\beta}{}'\frac{ZZ}{|\mathbf{R}_{\beta}|}. \tag{A6}$$

The prime now indicates $\beta\neq1$.

The 0 denotes a volume integration outside the cell $R_1=0$. The last two terms on the right-hand side of Eq. (A6) represent the interaction of the nuclei with the charges on the other atoms. Equation (A6) may be simplified by the following steps:

Let

$$\rho(\mathbf{r})\equiv\rho_s(\mathbf{r})+\rho_c. \tag{A7}$$

Since $\rho(\mathbf{r})=\rho_c$ outside the muffin-tin radius, then $\rho_s(\mathbf{r})=0$ outside the muffin tin.[17]

Then

$$q_s=-\int\rho_s(\mathbf{r})d\mathbf{r},$$

$$Z=\int_{\Delta}\rho(\mathbf{r})d\mathbf{r}=Z_s+Z_c, \tag{A8}$$

where

$$Z_c=-q_c,\qquad Z_s=-q_s.$$

Substitution of Eqs. (A7) and (A8) into (A6) gives

$$\frac{E_{\mathrm{Coul}}}{N}=\frac{1}{2}\int_{\Delta}\rho(\mathbf{r})V(\mathbf{r})d\mathbf{r}-\tfrac{1}{2}Z\int_{\Delta}\frac{\rho(\mathbf{r})d\mathbf{r}}{\mathbf{r}}+\tfrac{1}{2}Z\left[-\int_{0}\frac{\rho_s(\mathbf{r})d\mathbf{r}}{|\mathbf{r}|}+\sum_{\beta}{}'\frac{Z_s}{|\mathbf{R}_{\beta}|}\right]+\tfrac{1}{2}Z\left\{-\int_{0}\frac{\rho_c d\mathbf{r}}{|\mathbf{r}|}+\sum_{\beta}{}'\frac{Z_c}{|\mathbf{R}_{\beta}|}\right\}. \tag{A9}$$

It can be shown that the term in square brackets on the right-hand side of Eq. (A9) is zero. Since $\rho_s(\mathbf{r})=0$ outside the muffin tins, the integral over the space outside the central cell is only over the muffin-tin spheres. By Gauss's law each integral over each muffin tin is cancelled by a corresponding term Z_s/R and the bracketed term becomes zero.

The term in curly brackets on the right-hand side of Eq. (A9) is the potential at the origin due to a constant electron charge distribution ρ_c outside the cell and a lattice of positive ions of charge Z_c. The well-known Ewald potential ϕ^E is related to the term in curly brackets by

$$\phi^E=-\int_{\Delta}\frac{\rho_c d\mathbf{r}}{\mathbf{r}}\int_{0}\frac{\rho_c d\mathbf{r}}{\mathbf{r}}+\sum_{\beta}{}'\frac{Z_c}{|\mathbf{R}_{\beta}|}. \tag{A10}$$

Equation (A9) becomes

$$\frac{E_{\mathrm{Coul}}}{N}=\frac{1}{2}\int_{\Delta}\rho(\mathbf{r})V(\mathbf{r})d\mathbf{r}-\tfrac{1}{2}Z\int_{\Delta}\frac{\rho(\mathbf{r})d\mathbf{r}}{\mathbf{r}}+\tfrac{1}{2}Z\left(\phi^E+\rho_c\int_{\Delta}\frac{d\mathbf{r}}{\mathbf{r}}\right). \tag{A11}$$

For an fcc lattice[5]

$$\phi^E=-4.584850(Z_c/a)$$

and

$$\rho_c\int_{\Delta}\frac{d\mathbf{r}}{\mathbf{r}}=\frac{Z_c}{a}\times3.821656$$

as obtained by numerical integration.

E_{ex}, the total exchange energy, is obtained by direct integration using the muffin charge distribution:

$$\frac{E_{\mathrm{ex}}}{N}=\tfrac{3}{4}f\int_{\Delta}\rho(\mathbf{r})V_{\mathrm{ex}}(\mathbf{r})d\mathbf{r}.$$

E_k may be calculated in the usual manner by rearranging Eq. (A3) and summing over the individual electron kinetic energies. This is written as

$$\frac{E_k}{N}=\sum_i\epsilon_i-\int_{\Delta}\rho(\mathbf{r})[V_{\mathrm{ne}}(\mathbf{r})+V_{\mathrm{ee}}(\mathbf{r})+fV_{\mathrm{ex}}(\mathbf{r})]d\mathbf{r}.$$

The total energy is

$$E=E_k+E_{\mathrm{Coul}}+E_{\mathrm{ex}}.$$

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