Aluminum under high pressure. I. Equation of state*

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A curve of applied pressure P versus lattice constant a is calculated for single-crystal aluminum. It results from an application of the method of structural expansions for deriving the energies of simple metals, a method known to give reasonable results for the elastic constants even at second order in the effective electron-ion interaction. The latter (in the present calculation) is taken from Fermi-surface analysis and it is verified (with this essentially experimental information) that the extant face-centered cubic structure remains the preferred crystalline phase up to the highest pressures considered. Arguments are given to suggest that the P versus a curve should have reasonable *a priori* accuracy, and can admit of possible improvement if experimental data in the intermediate-presssure region can be provided to refine the (in principle) energy-dependent pseudopotential. At three megabars the lattice constant is reduced by only 22%; the ion cores at this pressure are still very well separated.

I. INTRODUCTION

Among the simple metals, aluminum is in many ways one of the simplest, being cubic close packed under normal conditions and possessing ion cores occupied by electrons in levels of s and p symmetry. It is mainly a consequence of the latter that its nearly-free-electron band structure can be interpolated so accurately by a spatially local pseudopotential, a feature which distinguishes it somewhat from the alkali metals. Although the Fermi surfaces of the alkali metals are a good deal simpler than that of aluminum, the apparent complexity of its multiply-connected Fermi surface can be used to advantage in a study of the transport properties at high pressure. This will be the content of a later work; for the present we are concerned with the equation of state of Al, a necessary preliminary in discussing the dependence of transport properties on pressure.[1] Effects of temperature (for normal conditions) are quite small, and our aim here is therefore to express the equation of state in terms of pressure versus lattice constant. Such a relation can only be considered potentially useful if no crystalline phase changes are likely to occur.[2] We show by a series of arguments that the common face-centered cubic phase of Al appears to remain the stable phase for pressures exceeding 3Mbar. In terms of the lattice constant (or equivalently the r_s electron spacing parameter) these colossal pressures represent a rather modest change of around 20%. The electron density is increased, but not greatly. It is not unreasonable to suppose, therefore, that the method based on structural expansions about the uniform interacting electron gas will continue to function as it does for the system taken at more reasonable pressures. The method is summarized in Sec. II, and in the course of discussing the standard second-order theory[3] we comment on the importance of higher-order corrections to the present calculations.

Section III describes the application of the formalism to the problem of deciding which of several possible simple structures (including fcc) will possess the lowest Gibbs energy. For the fcc phase, a curve of pressure versus lattice constant a is presented (Sec. IV); up to and above 3 Mbar, the changes in a are quite monotonic. Up to about 800 kbar, our calcuations, based on the method of structural expansions in a weak pseudopotential, can be compared directly with the results of Ross and Johnson[4] who obtain the equation of state of aluminum from an *a priori* calculation of the band structure by the augmented-plane-wave (APW) method.

We estimate that not until pressures of over 100 Mbar are reached will the ion cores of Al be substantially contiguous. This is a very different situation from the one prevailing in ionic crystals where the pressure scale is founded largely on assumed short-range interactions.[5] Although the atomic number of Al is relatively low, it may compete reasonably well in x-ray scattering power with NaCl and may, therefore, be an alternative candidate for calibration and use as a pressure scale.

II. ENERGY OF SIMPLE METALS

On account of the compactness of its ion core (and the absence of filled d-shell levels) the pseudopotential in Al, although energy dependent to a small degree[6] is remarkably local and provides an excellent interpolation to *a priori* band structures. Invoking an adiabatic approximation,

we shall take it that an ion of the dynamic lattice of Al carries with it a bare pseudopotential, $v(\vec{k})$ known (at the Fermi energy) from Fermi surface analysis.[7] It is a function which as is well-known oscillates in sign as k increases, a fact which reflects the finite size of the Al ion core. Since we shall shortly need to consider the possibility of corrections arising from dynamic lattice effects, it is convenient to set down a Hamiltonian for the *electron* system that is written[8] for instantaneous positions $\vec{r}(\vec{R})$ of the ions near equilibrium sites $\vec{R}$, i.e.,

$$H = H_{eg} + H_M + H_{ei},\tag{1}$$

where for the present H_{eg} can be taken as the standard Hamiltonian for the interacting electron gas (uniform compensating positive background) and the ionic Hamiltonian H_M leads to the Madelung energy NE_M of point ions. In rydbergs it can be written (for ZN electrons)

$$ZNE_M = \sum_{k \neq 0} \frac{8\pi}{k^2}[S(\vec{k}) - 1],\tag{2}$$

where for the ions in a volume V the structure factor for the ionic system is

$$S(\vec{k}) = (1/N)\langle \hat{\rho}_{\vec{k}}\hat{\rho}_{-\vec{k}}\rangle - N\delta_{\vec{k},0},\tag{3}$$

with

$$\rho_{\vec{k}} = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{r}(\vec{R})},$$

and the average in (3) being taken over the states of the crystal. The final term in (1), H_{ei}, is the electron ion interaction in which it is convenient to include the largely compensating zeroth Fourier component of all the long-range interactions; that is, a term E_0 which although independent of structure is always difficult to calculate from first principles. It can, however, be eliminated by exploiting a fragment of experimental information such as, for example, the equilibrium density.[9]

Accordingly we write

$$H_{ei} = E_0 + \sum_{\vec{k} \neq 0} \hat{\rho}_{\vec{k}} v(\vec{k})\hat{\rho}^e_{-\vec{k}},\tag{4}$$

where for the electrons the density operator is written

$$\hat{\rho}^e_{-\vec{k}} = \sum_i e^{-i\vec{k}\cdot\vec{r}_i}.\tag{5}$$

We turn first to the static lattice case for which the contribution of E_M to the thermodynamic function is known, at least for most simple structures. The problem of calculating the energy of a simple metal then reduces to an expansion (relative to the structureless electron gas system) in orders (beginning at the second) of H_{ei}. Since the ionic cor-

relation function [for example, $S(\vec{k})$] are then δ functions on the reciprocal lattice they reduce the resulting summations in the perturbation series to lattice sums. Thus, in addition to the ground-state energy[10] from H_{eg} (and E_M) we have, as the first term of the structural expansion, a second-order band-structure contribution $E^{(2)}_{BS}$ of the form

$$E^{(2)}_{BS} = \frac{1}{2} \sum_{[\vec{K}]}{}' |v(\vec{K})|^2 \chi^{(1)}(\vec{K})/\epsilon(\vec{K});\tag{6}$$

$[\vec{K}]$ reciprocal-lattice set,

where $\epsilon(\vec{K})$ is the dielectric function of the interacting electron gas and $\chi^{(1)}(\vec{K})$ its (static) first-order polarizability. At this level of approximation the internal energy is then

$$E = (E_{eg} + E_M + E_0) + E^{(2)},\tag{7}$$

and it is interesting, before proceeding further, to examine their relative contributions to the pressure at a given volume V, or what is equivalent, a mean electron spacing r_s $[V/NZ = (r_s a_0)^3 \frac{4}{3}\pi]$. Table I shows[11] that as pressure increases the contribution from $E^{(2)}$ becomes progressively a smaller fraction of the total. Since we know[9] the ground-state energy and compressibility of Al to be quite well given near $P = 0$ by (7) and its derivatives, we may conclude that even at high pressures the higher-order band-structure contributions to E are not likely to be an important factor in limiting the accuracy of a calculation of P vs a. The most significant of these corrections is the third-order band-structure energy. If the electron gas is treated, for example, within the random-phase approximation, this term can be written[8,12]

$$\frac{1}{3} \sum_{\vec{K}\vec{K}'} \frac{v(\vec{K})\,v(\vec{K}')\,v(\vec{K}-\vec{K}')}{\epsilon(\vec{K})\,\epsilon(\vec{K}')\,\epsilon(\vec{K}-\vec{K}')} \chi^{(2)}(\vec{K},\vec{K}',\vec{K}-\vec{K}'),\tag{8}$$

where $\chi^{(2)}$ is the second-order polarizability of the

TABLE I. The quantities E_{eg}, E_M, and E_0 are present at any order of the calculation and are convenient to group together in the comparison of the relative pressure contributions. The first column gives an estimate of the pressure (in Mbars) from $E_{eg} + E_M + E_0$ and the second column for $E^{(2)}_{BS}$. Energies are given in rydbergs.

r_s	P $(E_{eg} + E_M + E_0)$	P $(E^{(2)}_{BS})$
2.07	0.48 (−1.29)	−0.48 (−0.097)
1.9	1.39 (−1.24)	−1.07 (−0.138)
1.8	2.38 (−1.189)	−1.62 (−0.176)
1.7	3.95 (−1.110)	−2.37 (−0.227)
1.6	6.47 (−0.993)	−3.35 (−0.292)

electron system. As remarked earlier, $v(\vec{k})$ for Al (and indeed any non-point-ion system) alternates in sign as its argument increases and, as a consequence, there is substantial self cancellation in (8). Furthermore, relative to $\mathscr{E}_F$, the $|v(\vec{K})|$ are considerably less than ~0.1 (for example, $|v_{111}/\mathscr{E}_F|$ = 0.0209, and $|v_{200}/\mathscr{E}_F|$ = 0.0657). It follows that the higher-order band-structure energies are quite small in comparison with $E_{BS}^{(2)}$. This has already been noticed by others,[13] although we must recognize that the derivatives of the higher-order terms (in the elastic constants for example) need not always be unimportant.

As far as a calculation of the pressure is concerned it seems a reasonable approximation to neglect the higher-order band-structure energies. The approximation would appear less justifiable in the calculation of the ground-state energy for various crystal structures. But in fact it remains numerically valid. The concern is that differences in Gibbs energy for different crystal structures are quite small, about 4–6 mRy between hcp and fcc per electron if calculated with a second-order expression. And these can be less than typical third-order energies. However, we need not the *absolute* third-order energies, but their *differences* for different structures; these are in turn smaller by about an order of magnitude. We shall see in a moment that inclusion of dynamic effects are likely to reduce the third-order differ-

ences still further, so that a calculation of the energy at second order is sufficient for the present purposes.

Relaxing the static lattice assumption requires (a) the inclusion of phonon energy term, if indeed the excitations are to be described by phonons, and (b) the reintroduction in (6) and (7) of the corresponding ionic correlation functions, for example, $S(\vec{k})$ [Eq. (3)]. If $\vec{u}(\vec{R})$ is the displacement of an ion from site $\vec{R}$, then

$$S(\vec{k}) = \frac{1}{N} \sum_{\vec{R}\vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} \langle e^{i\vec{k}\cdot\vec{u}(\vec{R})} e^{-i\vec{k}\cdot\vec{u}(\vec{R}')} \rangle, \qquad (9)$$

and if the $\vec{u}(\vec{R})$ may be developed as a linear synthesis of phonon operators, it follows that[14]

$$S(\vec{k}) = \frac{1}{N} \sum_{\vec{R}\vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} \exp\tfrac{1}{2}\{\langle -[\vec{k}\cdot\vec{u}(\vec{R})]^2$$
$$-[\vec{k}\cdot\vec{u}(\vec{R}')]^2$$
$$+[\vec{k}\cdot\vec{u}(\vec{R})][\vec{k}\cdot\vec{u}(\vec{R}')]\rangle\},$$
$$(10)$$

and this replaces the sequence of δ functions which led to the lattice sum in the second-order term (6). The correlation function corresponding to (9) and appearing in the third-order expression is easily seen to be of the form

$$\sum_{\vec{R}\vec{R}'\vec{R}''} e^{i\vec{k}\cdot\vec{R}} e^{i\vec{q}\cdot\vec{R}'} e^{-i(\vec{q}+\vec{k})\cdot\vec{R}''} \exp\{-\tfrac{1}{2}\langle [\vec{k}\cdot\vec{u}(\vec{R})]^2 + [\vec{q}\cdot\vec{u}(\vec{R}')]^2 + [(\vec{q}+\vec{k})\cdot\vec{u}(\vec{R}'')]^2$$

$$+ 2[\vec{k}\cdot\vec{u}(\vec{R})\vec{q}\cdot\vec{u}(\vec{R}')] - 2[\vec{q}\cdot\vec{u}(\vec{R}')(\vec{k}+\vec{q})\cdot\vec{u}(\vec{R}'')]$$
$$- 2[\vec{k}\cdot\vec{u}(\vec{R})(\vec{k}+\vec{q})\cdot\vec{u}(\vec{R}'')]\rangle\}, \qquad (11)$$

which is straightforward to generalize to higher orders.

For metals with substantial Debye temperatures (in which category we may place Al) one method of handling (10) and (11) is to proceed by a multiphonon expansion. The zero-phonon term leads immediately back to (6) and (8). The one-phonon term leads, when combined with the kinetic energy of the phonon system,[15] to the internal energy of the phonons. The remaining multiphonon terms, as is known from the analysis of thermal diffuse x-ray scattering are quite small. Thus we may, with a sufficient accuracy, treat the phonons independently of the electron system and calculate the Gibbs energy of the latter assuming a rigid lattice. The internal energy can then be written

$$E = (E_{eg} + E_0 + E_M) + E_{BS}^{(2)} + E^{ph}, \qquad (12)$$

where E^{ph} is the internal energy of the phonon system.

III. STRUCTURAL CONSIDERATIONS

From the known Fermi surface of Al (and the assumption of a static lattice) the values of $v(K)$, $\vec{K}$ ≡(1, 1, 1,),(2, 0, 0) can be extracted and these can be interpolated and extended by an empty-core pseudopotential $[v(k) = (-8\pi Z/k^2)\cos kr_c]$. The range of validity (in k) of such a simple form is quite sufficient to assure convergence of the sums in (6), and hence of the band-structure energy. Since $v(k)$ is a property of the ion we may repeat the procedure at any chosen volume or density. Assuming for the moment that this is fixed we must examine the structure-dependent terms in (12) as the ions are rearranged in a variety of possible

crystal structures.

To begin with we consider the electronic terms (and Madelung energy) and allow ourselves at this point the freedom of a structure with a two atom basis. The task is to ascertain which of the structures (at least, which of the simple structures) is preferred for Al: to this end we will select carefully a system of primitive and basis vectors which will allow us continually to deform between different structures by means of a smooth variation of parameters.[16] Refer now to Fig. 1(a). We take $\vec{a}$, $\vec{b}$, and $\vec{c}$ as primitive vectors which are written in the form

$$\vec{a} = a(s, 0, 0), \quad \vec{b} = a(v', \xi, 0), \quad \vec{c} = a(0, 0, \eta). \quad (13)$$

Direct lattice vectors are then written

$$\vec{R} = n\vec{a} + p\vec{b} + q\vec{c}.$$

We take the basis vectors

(a)

(b)
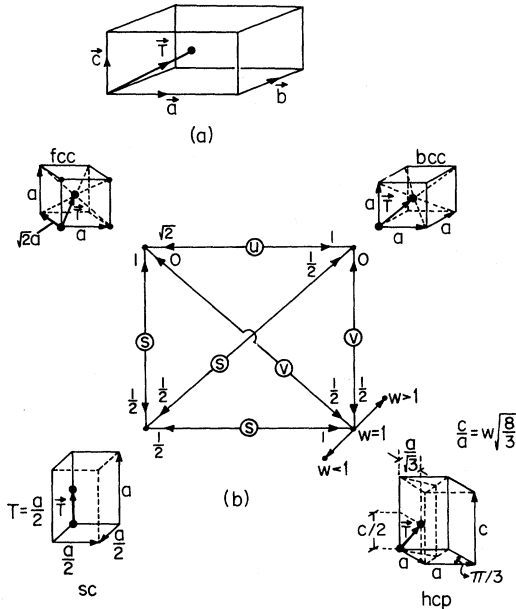
	s	u	v	w
sc	$\frac{1}{2}$	arbitrary	arbitrary	arbitrary
bcc	1	1	0	1
fcc	1	$\sqrt{2}$	0	1
ideal hcp	1	arbitrary	$\frac{1}{2}$	1
hcp	1	arbitrary	1/2	≠1

(c)

FIG. 1. (a) General structure defined. (b) Some particular cases and representations of continuous one-parameter transformations of them into each other. (c) Values of the parameters for these particular cases. The parameters are defined by Eqs. (13)-(15).

$$\vec{b}_1 = 0, \quad \vec{b}_2 = \vec{T} = \tfrac{1}{2}a(2s - 1, (2s - 1)\zeta, \eta). \quad (14)$$

In (13) and (14) the parameters v', ζ, η, and ξ are chosen in the following way:

$$v' = (2s - 1)v,$$
$$\xi = u - v(2u - \sqrt{3}) + (1 - s)[1 - 2u + 2v(2u - \sqrt{3})],$$
$$\eta = w + 2vw(\sqrt{\tfrac{8}{3}} - 1) + 2(1 - s)[1 - w - 2vw(\sqrt{\tfrac{8}{3}} - 1)],$$
$$\zeta = u - 2v(u - 1/\sqrt{3}), \quad (15)$$

with s, u, v, w taken as independent parameters. Transformation (15) is only one of many ways of continually deforming the standard simple crystal structures. We have selected it because it permits us to examine single-cubic (sc), face-centered cubic (fcc), body-centered cubic (bcc), and hexagonal closed packed (hcp) with variable (c/a) ratio. As an example, note that when $s = \frac{1}{2}$ we have (whatever finite values u, v, w may assume) a simple-cubic structure. On the other hand, if $s = 1$, $v = 0$, and $w = 1$, the structure is fcc for $u = \sqrt{2}$, and bcc with $u = 1$. Further, if $s = 1$, $v = \frac{1}{2}$, and $w = 1$, we have hcp with ideal ratio. These are summarized on Figs. 1(b) and 1(c). Although it cannot be deduced simply from the results we shall give, it is interesting to note that the transformation we have chosen moves the atoms in a very natural way, keeping them well apart, and proceeding as directly as possible from one structure to another. In a sense we are moving the atoms along valleys in the energy-structure space.

The lattice reciprocal to (13) is spanned by primitive vectors

$$\vec{A} = (2\pi/a)(1/s, -v'/s\xi, 0),$$
$$\vec{B} = (2\pi/a)(0, 1/\xi, 0), \quad (16)$$
$$\vec{C} = (2\pi/a)(0, 0, 1/\eta),$$

and the reciprocal-lattice vectors are

$$\vec{K} = h\vec{A} + l\vec{B} + m\vec{C},$$

which we use to define in Al $(Z = 3)$

$$\vec{x} = (2k_F)^{-1}\vec{K},$$
$$x = \left(\frac{\pi}{6Z}s\xi\eta\right)^{1/3}\left[\frac{h^2}{s^2} + \left(\frac{l - hv'/s}{\xi}\right)^2 + \frac{m^2}{\eta^2}\right]^{1/2}. \quad (17)$$

With the choice of basis given in (13) the structure factor, per ion, is

$$\tfrac{1}{2}(1 + e^{-i\beta}),$$

where

$$\beta = \vec{K} \cdot \vec{T} = \pi[h(2s - 1)/s$$
$$+ (l - hv'/s)(2s - 1)\zeta/\xi + m]. \quad (18)$$

Accordingly, the band-structure energy (in Ry/elec-

tron) becomes

$$E_{BS}^{(2)} = \sum_{\vec{x} \neq 0} \left(\frac{1}{\epsilon(\vec{x})} - 1 \right) \frac{k_F^2 x^2}{8\pi Z^2} |v(x)|^2 n(1 + \cos\beta). \quad (19)$$

In (19), $\epsilon(\vec{x})$ (the dielectric function of the inter-
acting electron gas) can be written

$$\epsilon(x) = 1 + (\lambda^2/x^2) f(x) g(x); \quad \lambda^2 = 1/(\pi a_0 k_F),$$

with

$$f(x) = \frac{1}{2} + \frac{1 - x^2}{4x} \ln \left| \frac{1 + x}{1 - x} \right|,$$

and $g(x, r_s)$ a correction for exchange and corre-
lation. We have not found the latter to make any
important correction in the matter of deciding
between relative structures at second order.

Using Ewald's method we can determine the
Madelung energy in the standard form (again in
Ry/electron)

$$E_M = C_M Z^{2/3}/r_s. \quad (20)$$

To find C_M, we normalize the direct lattice vectors
by the Wigner-Seitz radius

$$r_{WS} = (3s\xi\eta/8\pi)^{1/3} a,$$

i.e., we define

$$\vec{p} = \vec{R}/r_{WS},$$

where

$$\rho = (8\pi/3s\xi\eta)^{1/3} [(ns + pv')^2 + p^2\xi^2 + q^2\eta^2]^{1/2}.$$

Similarly, put

$$\vec{t} = \vec{T}/r_{WS},$$

where

$$|\vec{p} + \vec{t}| = (8\pi/3s\xi\eta)^{1/3} \{[ns + pv' + \frac{1}{2}(2s - 1)]^2$$

$$+ [p\xi + \frac{1}{2}(2s - 1)\eta)]^2 + (q + \frac{1}{2})^2\eta^2\}^{1/2}.$$

Finally, put

$$\vec{G} = r_{WS}\vec{K},$$

with

$$G = 2(9\pi Z/4)^{1/3}\vec{x},$$

then

$$C_M = -\frac{3}{P^2} + \frac{3}{2P^2} \sum_{K \neq 0} (1 + \cos\beta) \frac{e^{-K^2/P^2}}{K^2/P^2} - \frac{P}{\sqrt{\pi}} + \frac{\text{erfc}(\frac{1}{2}Pt)}{t} + \sum_{\rho \neq 0} \left(\frac{\text{erfc}(\frac{1}{2}P\rho)}{\rho} + \frac{\text{erfc}(\frac{1}{2}P|\vec{p} + \vec{t}|)}{|\vec{p} + \vec{t}|} \right), \quad (21)$$

where $P(>0)$ is Ewald's dimensionless parameter
and erfc denotes the complementary error func-
tion. Then at second order, we evaluate (12) by
using (6) for $E_{BS}^{(2)}$ [with $v(K)$ there replaced by
$\frac{1}{2}(1 + e^{-i\beta})v(K)$] and (20) and (21) for the Madelung
energy. For a given structural choice (corre-
sponding to a particular selection of s, u, v, w) we
determine E_0 by the zero-pressure condition
$(\partial E/\partial r_s)_{r_{s0}} = 0$. Expressed as an energy per elec-
tron, E_0 always has the form

$$\alpha/(\frac{4}{3}\pi r_s^3),$$

where α is a property of the ion alone and is as-
sumed not to alter under reasonable variations of
density. Since the total energy near zero pressure
contains small contributions from the omitted
higher-order band-structure terms, the imposi-
tion of the zero-pressure condition forces their
inclusion in a crude way through the choice of α.
To the extent that these terms are not seriously
density dependent the subsequent use of this α
will therefore continue to incorporate such terms.
If one takes the Noziéres-Pines form for the cor-
relation energy,[17] it is easy to see that

$$\alpha = \frac{4\pi}{9} \left\{ r_{s0}^2 \left[0.916 + Z^{2/3}C_M + 0.031r_{s0} \right. \right.$$

$$\left. \left. + r_{s0}^2 \left(\frac{\partial E_{BS}^{(2)}}{\partial r_s} \right)_{r_{s0}} \right] - 4.42r_{s0} \right\}, \quad (22)$$

where for the fcc structure observed for Al in its
ground state[18] $r_{s0} = 2.0647$. What is required in
(22) is $E_{BS}^{(2)}(r_s)$, and this can be calculated by a
combination of a direct numerical summation
(out to a chosen reciprocal-lattice shell) augmented
by integration for the remainder. This remainder,
designated by $S(x_1, r_s)$ (where x_1 is the radius of
the shell) is independent of structure and depends[19]
very weakly on r_s. Its contribution is in any event,
quite small. At $r_s = r_{s0}$ and for $x_1 = 2.5$ we find
$S = 0.005$ Ry/electron, which amounts to 5% of $E_{BS}^{(2)}$
and 0.4% of E.

IV. ENERGIES AND PHASES: RESULTS AND DISCUSSIONS

In Fig. 2 we show a selection of the results we
obtain for the Helmoltz free energy E as the crys-
tal structure is continuously deformed from fcc to
hcp $(c/a = \sqrt{\frac{8}{3}})$. In this example fcc is lower in
energy at all densities considered. This result
remains true for other structures, the two that
are always closest in energy (at least of the simple
structures we consider) being fcc and hcp. It is a
straightforward matter to compute the PV term
and, hence, in the ground state the Gibbs energy
for different phases. We find fcc Al (with an as-
sumed static lattice) to have the lowest Gibbs
energy and to be the preferred structure, even up
to theoretical pressures in excess of 3 Mbar.

Contributions to the thermodynamic functions
from the ionic degrees of freedom can be estimated
from the Debye model; in particular, the zero-
point energy is of order $\frac{3}{8} k_B \Theta_D$ per *electron* (about
0.001 Ry) and for temperatures less than the Debye
temperature will remain of this order. *Changes* in
this energy accompanying changes in crystal struc-
ture will be much less than 0.001 Ry. The contri-
bution of the phonons to the pressure is readily
shown to be $(\frac{9}{8}\gamma)nk_B\Theta_D$, where $n =N/V$ is the ionic
density and γ is the Grüneisen constant. Even for
changes of 50% in the equilibrium value of n, the
phonons change the pressure calculation above by
at most a few kilobars. Figures 3 and 4 give the
Gibbs energy as a function of pressure for fcc and
hcp, and (for comparative purposes) as a function
of r_s for sc, fcc, bcc, and hcp. In Fig. 5 we plot
the pressure on a single crystal of Al (under pure
hydrostatic strain) as a function of its lattice con-
stant a (rather than r_s) at a nominal temperature
of 300 °K. The equation of state given there may
also be appropriate to polycrystalline samples
under less than pure hydrostatic conditions. It is
worth remarking that at 3 Mbar, where $a = 3.14$ Å,
and the nearest-neighbor separation is $(1/\sqrt{2})a$
$= 2.22$Å, the distance between ion cores (taking them
to have a radius of 0.59 Å) is still 1.04 Å. For the
pressure range in Fig. 5 the energy (and the corre-
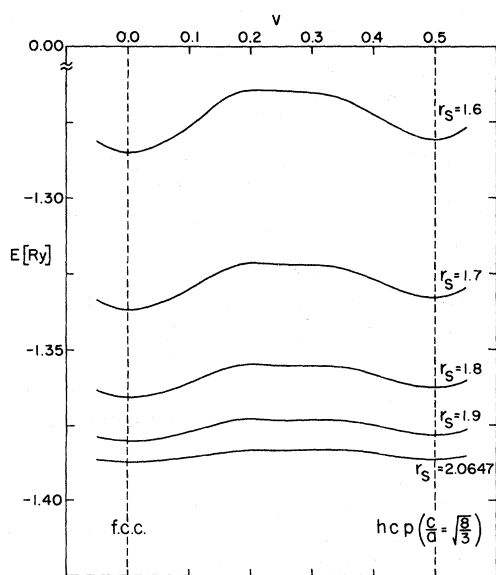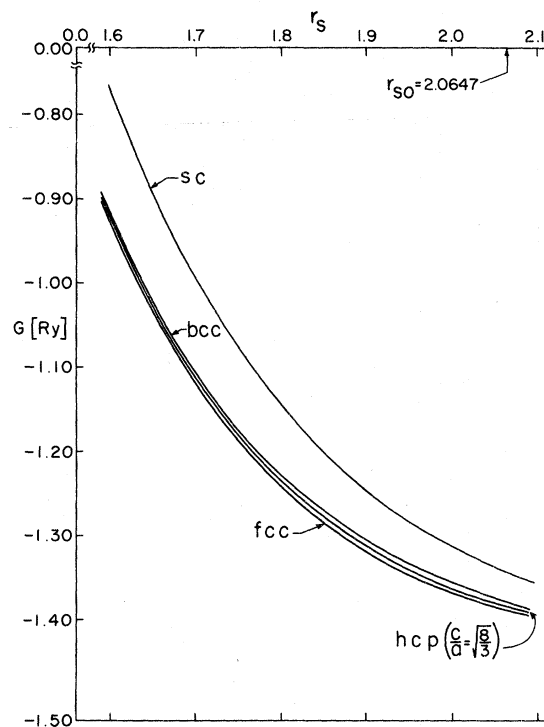sponding pressure) is dominated by the terms aris-

FIG. 3. Gibbs free energy as a function of r_s for
several common structures. Compare with Fig. 4
where G is plotted against the natural variable pressure.

FIG. 2. Helmholtz free energy as a function of r_s
and v; the other parameters fixed at their fcc values;
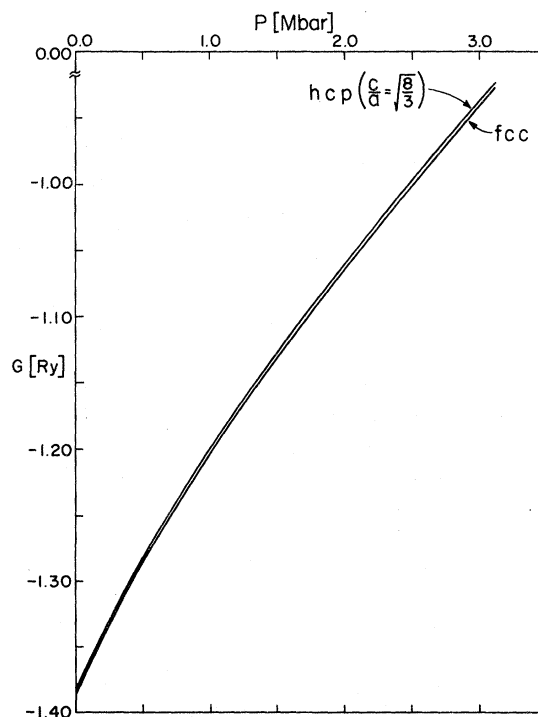varying v here takes the structure from fcc to hcp.

FIG. 4. Gibbs free energy as a function of pressure
for the fcc and hcp structures; these have the lowest
Gibbs free energy for any fixed pressure P.

ing from electron gas, Madelung energy, and to a much lesser extent, band structure. Energies arising from the direct overlap of ion cores (so called core-core exchange, or Born-Mayer terms) are evidently not important, although it is conceivable that at very much higher pressures (we estimate they will be in excess of 100 Mbar) they could be. This kind of term is difficult to calculate with confidence from first principles, and is normally parameterized in an exponential form (or even as a power law) in expressions giving its contribution to the internal energy. In pressure scales based on these forms, the concern (aside from the implicit pair force approximation) is that the low-pressure determined parameters may not remain valid in a region of substantial ion-core wave-function overlap. At 3 Mbar we have only a 22% reduction in lattice constant, and core-core overlap is still a small effect; its neglect leads to errors which will be far less important than those arising from the neglect of, for example, the higher-order band-structure contributions to the
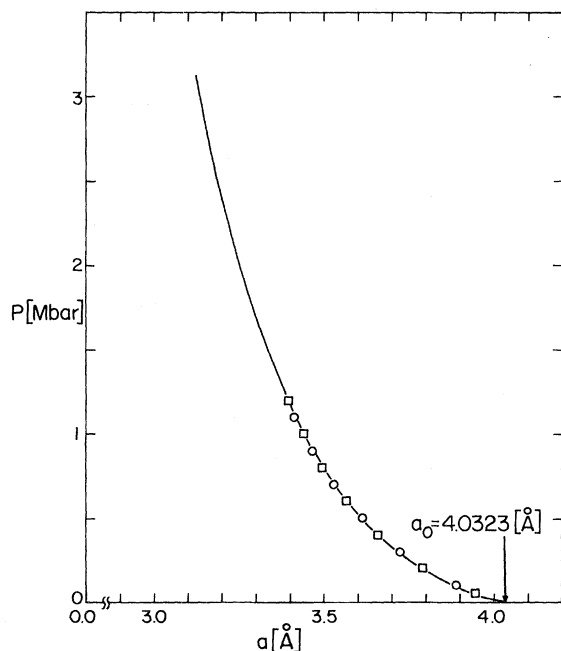

FIG. 5. Pressure as a function of lattice constant for the fcc structure, and experimental points obtained from reduced shock-wave data for two dilute alloys (○ 2024 Al, □ 921-T Al; see Ref. 22) assuming their zero-pressure lattice constant is equal to that of pure Al.

energy.

As far as the use of Al in high-pressure devices is concerned it suffers from the disadvantage that its atomic number is quite low. It should, however, be visible to x rays in a diamond cell, and the curve presented in Fig. 5 is therefore amenable to experimental test, provided, of course, that sufficiently hydrostatic conditions can be arranged.

If a test of this kind were found to establish as numerically sound the basic curve up to, say, 0.5 Mbar (corresponding to $a = 3.61$ Å), then according to the arguments we have given about it would then appear reasonable to accept the balance of the curve leading to the ultra-pressure region.[20] An independent determination of the pressure can also be used to refine, for example, the form of the pseudopotential used in the high-density regime. It is worthwhile mentioning that the equation of state obtained here agrees within experimental error with the results in the range from 0 to 0.2 Mbar obtained by Roy and Steward.[21] It also agrees very well with shock-wave results for 2024 aluminum and 921-T aluminum up to 1.2 Mbar.[22] Assuming these dilute alloys behave as pure aluminum (with the same lattice constant at zero pressure), we get from the reduced shock data the points plotted in Fig. 5. Small changes in the actual lattice constant are to be expected, and in addition we must expect minor effects from the different pseudopotentials and valences of the impurities. But in homogeneous *dilute* alloys these can only displace the experimental points slightly from those plotted in Fig. 5. Finally, our curve is almost parallel to the corresponding one extracted from Ross and Johnson's paper,[4] but is shifted to the left by $\Delta(V/V_0)$ about -0.06. Although some of this difference may be due to numerical inaccuracy (e.g., the APW calculations take only a few points in the fundamental symmetry element of the Brillouin zone) and some due to questions surrounding the correct choice of local exchange potential, probably the bulk of the discrepancy can be traced to the different methods of handling of the zero-pressure condition. In the method of structural expansions,[8] the contribution to the total energy of the zeroth Fourier component of all the interactions is eliminated with the zero-pressure condition at the corresponding experimentally *known* r_s: the *a priori* calculations (such as those in Ref. 4) seek to obtain every term in the ground-state energy from first principles.

The reasons for choosing Al (the paradigm of small-core, close-packed-cubic nearly-free-electron metals) do not exclude other metals displaying similar features, and it may well be that the principles leading to the choice of a metal rather than an ionic crystal for the measurement

of pressure, can be applied to metals such as In, or Pb, providing, of course, that closer attention is paid to problems arising from spin-orbit coupling, nonlocal effects, and the nature of neighboring levels above the Fermi energy.

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[1] These are most naturally calculated as functions of volume (for a given temperature) which is eliminated in favor of the pressure only if the equation of state is known.

[2] This does not preclude changes in electron structure such as might occur when a Fermi surface changes its topology.

[3] For a review of the techniques, see V. Heine and D. Weaire, Solid State Phys. 24, 249 (1970).

[4] M. Ross and K. W. Johnson, Phys. Rev. B 2, 4709 (1970).

[5] D. L. Decker, J. Appl. Phys. 36, 157 (1965); W. A. Bassett, T. Takahashi, T. W. Stook, Rev. Sci. Instrum. 38, 37 (1967).

[6] See, for example, K. Sturm and N. W. Ashcroft, Phys. Rev. B 10, 1343 (1974).

[7] N. W. Ashcroft, Philos. Mag. 8, 2055 (1963). The Fourier components so determined are *folded* in the sense that they are extracted from experiment with the aid of a low-order secular equation (see Ref. 6). In addition they incorporate small Debye-Waller type corrections (see Sec. IV).

[8] C. J. Pethick, Phys. Rev. B 2, 1789 (1970); J. Hammerberg and N. W. Ashcroft, *ibid.* 9, 409 (1974).

[9] N. W. Ashcroft and D. C. Langreth, Phys. Rev. 155, 682 (1967). Any other contributions to the energy from bound charge (fluctuations in the ion cores, for example) will be subsumed in this E_0.

[10] We will take up the (small) effects of temperature in Sec. IV.

[11] For the purposes of this comparison it is sufficient to choose any of the common structures. Here we have given the figures appropriate to fcc.

[12] P. Lloyd and C. Sholl, J. Phys. C 1, 1620 (1968); E. G. Brovman, and Yu Kagan, Zh. Eksp. Teor. Fiz. 57, 1329 (1969) [Sov. Phys.—JETP 30, 721 (1970)].

[13] For example, E. G. Brovman and G. Solt, Solid State Commun. 8, 903 (1970).

[14] See, for example, N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart, and Winston, New York, 1975).

[15] D. Stroud and N. W. Ashcroft, Phys. Rev. B 5, 371 (1972).

[16] We are therefore performing a partial scan of Bravais lattice space using a technique not unlike that of E. G. Brovman, Yu Kagan, and A. Kholas, Zh. Eksp. Toer. Fiz. 61, 2429 (1971) [Sov. Phys.—JETP 34, 1300 (1972)].

[17] P. Nozières and D. Pines, *Quantum Liquids* (Benjamin, New York, 1966).

[18] This is determined, for $T = 0$ from data on thermal expansion recorded in *Properties of Materials at Low Temperature* (Pergamon, New York, 1961); NBS part II; 2.132; and combined with the lattice constant measured by A. S. Cooper, Acta. Crystallogr. 15, 578 (1962).

[19] For large enough x, $S(x_1, r_s)$ can be calculated by integration (rather than summation) where the asymptotic result can be written $S(x_1, r_s) \sim -(2Z/9\pi^2 x_1^3)$ $\times (1 - 3 \sin y/y + \cdots)$, where $y = 4(9\pi/4)^{1/3}(r_c/r_s)x_1$.

[20] In this respect it is worth noting that the energy dependence of the pseudopotential is a subtlety that, although expected to give small corrections (see Ref. 5) for small over-all energy changes, might well require proper inclusion for large changes in density.

[21] N. N. Roy and E. G. Steward, Nature (Lond.) 224, 905 (1969). The agreement of their results with the predictions of the Murnaghan equation of state is also within experimental error.

[22] R. G. McQueen, S. P. Marsh, J. N. Fritz, and W. J. Carter, *High-Velocity Impact Phenomena*, edited by R. Kinslow (Academic, New York, 1970), pp. 530, 531.