Core polarization and the equation of state of potassium

J. Cheung* and N. W. Ashcroft

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853

(Received 13 April 1981)

We calculate the zero-temperature equation of state of potassium with a model Hamiltonian that includes core-polarization effects. Density fluctuations in the ion cores lead to van der Waals interactions that are dynamically screened by the valence electrons. They also lead to screening of other static interactions, effects that are incorporated through the use of a background dielectric function $\epsilon_c(q)$. Inclusion of core-polarization effects yields significant improvement between the theoretical and experimental equations of state, particularly at high pressures.

I. INTRODUCTION

In calculations of the thermodynamic functions of the simple metals it is common to assume that core-polarization effects can be neglected, an assumption that is normally justified on the grounds that the electrons in the corresponding ions are tightly bound and in consequence not significantly polarizable. It then follows that the dispersion forces and the effects of any background dielectric shielding associated with the internal structure of the ions should be small, at least in comparison with the much stronger Coulomb interactions and electron-gas properties. Under normal conditions these assumptions are usually valid: The screened van der Waals interactions, for example, produce only a slight softening of the replusive part of the pseudopotential-derived ion-ion potential.[1] At high pressures, however, where interionic separations are much reduced, the softening of such potentials can have noticeable effects, as we shall see here. In addition, the likely importance of the background screening can be gauged by examining the quantity $\epsilon_c(0) \simeq 1 + 4\pi n_i \alpha$, where α is an ionic polarizability and n_i is the ionic number density. In the alkali metal series this does not depart appreciably from unity (the range is about $1.01-1.27$); nevertheless, such departures can lead to quite significant corrections to the various terms comprising the total energy of a metal,[2] particularly at high pressure where n_i has been increased.

In a previous paper[3] (referred to as I) we derived a model Hamiltonian to treat the problem of a system of interacting dipoles and electrons for use in the calculation of thermodynamic and structural properties of simple metals. It was shown there

that the collective core-core excitations give rise to screened polarization waves, and the lowest-order dispersion forces associated with these waves are the screened van der Waals interactions. It was also shown that in addition to participating in physical processes involving collective excitation and dynamic screening, the polarizable ions screen all the *static* interactions. At the microscopic level the system of ions constitutes an inhomogeneous dielectric which for long-ranged interactions in situations of high symmetry may be reasonably well approximated by a dielectric continuum with dielectric function $\epsilon_c(q)$. In this paper we shall apply the principal results of I to be the case of potassium which has a rather substantial ionic polarizability (see Table II of Ref. 1). It also has a high compressibility which makes it well suited to the present calculation.

The paper is orgainized as follows: In Sec. II, the key results for the total energy of a simple metal with polarizable ions are restated. In Sec. III we intorduce the additional approximation needed to evaluate the zero-temperature isotherm. This requires us to address the form of the static background dielectric function $\epsilon_c(q)$ for a dielectric continuum representing the ions, as well as the atomic polarizabilities themselves. The results are discussed in Sec. IV.

At high compression the effects we are discussing are quite significant, as will be seen. It should be noted here that by ignoring core-polarization effects entirely it is still quite possible to obtain a detailed quantitative description of the elastic properties of the alkali metals[4,5] using pseudopotential methods. We shall see below that the explanation for this minor paradox is simply the observation that for modest compressions the correction terms arising

© 1981 The American Physical Society

from core polarization effects can be almost entirely absorbed into the standard zero pressure fitting procedure in which the aggregate of all long-wavelength terms is adjusted to an experimental datum. The volume dependence of the core-polarization terms is, however, sufficiently different that under more extreme circumstances, such as the treatment of shock Hugoniots and the determination of Grüneisen parameters, this procedure may require reexamination.

II. GROUND-STATE ENERGY OF A SIMPLE METAL

We shall neglect the energy associated with the nuclear degrees of freedom[5]: The Hamiltonian for a simple metal of valence Z and of volume Ω whose ions are polarizable can then be written[1,3]

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{\vec{q} \neq 0} \frac{v_c(q)}{\Omega \epsilon_c(q)} \hat{\rho}^v(\vec{q}) \hat{\rho}^v(-\vec{q}) \tag{1a}$$

$$+ \sum_{\vec{q} \neq 0} \frac{v_{ps}(q)}{\Omega \epsilon_c(q)} \hat{\rho}^i(\vec{q}) \hat{\rho}^v(-\vec{q}) \tag{1b}$$

$$+ \frac{1}{2} \sum_{\vec{q} \neq 0} \frac{Z^2 v_c(q)}{\Omega \epsilon_c(q)} [\hat{\rho}^i(q) \hat{\rho}^i(-q) - N] \tag{1c}$$

$$+ NZE_0 + \frac{1}{2} \sum_{\vec{R}, \vec{R}'} {}' \phi_L^{sc}(\vec{R} - \vec{R}') . \tag{1d}$$

As described in I the terms here have the following meaning: Term (1a) is the Hamiltonian of an interacting electron gas in a neutralizing dielectric continuum with dielectric constant $\epsilon_c(q)$. The valence-electron density operator is $\rho^v(\vec{q}) = \sum_i e^{i\vec{q} \cdot \vec{r}_i}$; the Coulomb interaction is $v_c(q) = 4\pi e^2/q^2$. Term (1b) is a characteristic pseudopotential form for the interaction between the valence electrons and the ions, but modified here to incorporate the effects of the dielectric continuum. The pseudopotential $v_{ps}(q)$ used in (1b) is assumed local; note that the ion density operator is $\hat{\rho}^i(\vec{q}) = \sum_{\vec{R}} e^{i\vec{q} \cdot \vec{R}}$. Term (1c) is the Coulomb energy of point charges, also in the dielectric continuum. The terms in (1d) are, respectively, the sum of all $q = 0$ terms and the screened van der Waals interactions. As is well known, E_0 has an inverse volume dependence[6]: If n_v is the mean valence electron density, it can be written as

$$E_0 = \frac{\alpha}{4\pi r_s^3/3} \left[\frac{e^2}{2a_0} \right] , \tag{2}$$

where

$$r_s a_0 = (3/4\pi n_v)^{1/3} .$$

The screened fluctuating dipole interaction between ions is[1,7]

$$\phi_L^{sc}(r) = \int_{-\infty}^{\infty} \frac{du}{2\pi} \alpha_0^2(iu) \left[\left[\frac{\partial^2 v(r,iu)}{\partial r^2} \right]^2 + \frac{2}{r^2} \left[\frac{\partial v(r,iu)}{\partial r} \right]^2 \right] , \tag{3}$$

where

$$v(r,iu) = \int \frac{d\vec{q}}{(2\pi)^3} \left[\frac{v_{ps}(q)}{\epsilon_{eg}(q,iu)} \right] e^{i\vec{q} \cdot \vec{r}} ,$$

the quantity $\epsilon_{eg}(q,\omega)$ being the wave-number- and frequency-dependent dielectric function of the interacting electron gas.

Perturbation theory can be applied in a straightforward manner to (1). The contributions to the ground-state energy are then: (a) the corrected energy of the interacting electron gas, which in Ry per electron, is[8]

$$E'_{eg} = E_{eg} + E'_{vv} , \tag{4a}$$

where

$$E_{eg} = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + E_{corr} , \tag{4b}$$

and

$$E'_{vv} = \frac{1}{2\Omega} \sum_{\vec{q} \neq 0} S_{eg}(q) \frac{v_{ps}^2(q)}{v_c(q)} [\epsilon_c^{-1}(q) - 1] , \tag{4c}$$

and where $S_{eg}(q)$ is the static structure factor of the interacting electron gas; (b) the corrected Madelung energy[9]

$$E'_M = E_M + E_{Mc} , \tag{5a}$$

where

$$E_M = - \frac{\alpha_M Z^{1/3}}{r_s} , \tag{5b}$$

$$E_{Mc} = \frac{1}{2\Omega} \sum_{\vec{q} \neq 0} Z v_c(q) S_{ion}(q) [\epsilon_c^{-1}(q) - 1] , \tag{5c}$$

and S_{ion} is the ensemble averaged ionic structure

factor; (c) the corrected band-structure energy

$$E_{BS}^{(2)} = \frac{1}{2}\frac{NZ}{\Omega}\sum_{\vec{q}\neq0}\left[\frac{v_{ps}(q)}{\epsilon_c(q)}\right]^2\chi^v(q)S_{ion}(q) \ ,$$

(6)

where $\chi^v(q)$ is the first-order polarizability of the interacting electron gas; and (d) the aggregate of all $q = 0$ terms, as given by (2). If these terms are augmented by the screened fluctuating dipole interactions, the total static lattice ground-state energy can be written

$$E(r_s) = NZ(E'_{eg} + E'_M + E_{BS}^{(2)} + E_0)$$

$$+ \frac{1}{2}\sum_{\vec{R},\vec{R}'}\phi_L^{sc}(\vec{R} - \vec{R}') \ .$$

(7)

Here the band-structure energy has been calculated to second order in the electron-ion pseudopotential. For monovalent metals (such as potassium) this neglect of higher-order band-structure energy terms is satisfactory.[10] The corrections associated with $\epsilon_c(q)$ are also calculated within a linear response framework, again a reasonable approximation since the effects we are incorporating here are, in any event, fairly small.

III. ZERO-TEMPERATURE ISOTHERM

If F is the Helmholtz free energy of a system of N particles at temperature T, then the pressure is $p = -(\partial F/\partial\Omega)_{T,N}$. At $T = 0$, $F = E$, which is given by (7). The various contributions to E require the averaged core-dielectric function $\epsilon_c(q)$, the frequency-dependent valence-electron dielectric function $\epsilon(q,\omega)$, the frequency-dependent ionic polarizability $\alpha(\omega)$, and the valence-electron static response functions.

Provided the background dielectric constant $\epsilon_c(q = 0)$ is reasonably close to unity, as is the case here, we may neglect local-field corrections and write, as earlier

$$\epsilon_c(q) = 1 + 4\pi n_i\alpha(0) \quad (q \to 0) \ .$$

(8)

In the opposite limit $(q > 2\pi/d$, where d is an ionic diameter) we make a local-density approximation, taking the large wave-vector limit of the Lindhard result[10]

$$\epsilon_c(q) = 1 + \frac{1}{3\pi k_F^c a_0}\left[\frac{2k_F^c}{q}\right]^4 \ .$$

(9)

Here k_F^c is a characteristic Fermi wave vector corresponding to a *locally uniform* core-electron density n_c. Let $x = (q/2k_F)$; then for $Z = 1$, a simple interpolation between (8) and (9) is

$$\epsilon_c(q) = 1 + 4\pi n_i\alpha(0)\left[1 + 4\left[\frac{n_v}{n_c}\right]\left[\frac{\alpha(0)}{a_0^3}\right](k_F a_0)^4 x^4\right]^{-1} \ ,$$

(10)

where $\alpha(0) = \alpha(\omega = 0)$ and $k_f^3 = 3\pi^2 n_v$ (v refers to the valence electrons). This form for $\epsilon_c(q)$ is similar to the wave-vector-dependent dielectric functions used in semiconductors and other narrow-gap insulators.[11] It is plotted in Fig. 1 for the choice[12] $\alpha(0) = 0.9$ Å^3 and[13] $n_c = 8n_v$.

To evaluate the correction to the standard electron-gas energy, we note that the second term of (4) can be identified as one-body and two-body contributions, that is ,

$$E'_{vv} = \frac{1}{2\Omega}\sum_{\vec{q}\neq0}v_{ps}^2(q)\frac{1}{v_c(q)}\left[\frac{1}{\epsilon_c(q)} - 1\right]$$

(11)

$$+ \frac{1}{2\Omega}\sum_{\vec{q}\neq0}[S_{eg}(q) - 1]v_{ps}^2(q)\frac{1}{v_c(q)}\left[\frac{1}{\epsilon_c(q)} - 1\right] \ .$$

(12)

For an empty-core pseudopotential[14] with core radius r_c and the interpolation form (10), the first of these can be evaluated in closed form and the result is (in rydbergs)

$$- (k_F a_0)(G/2a^3)[1 + e^{-\sqrt{2}as}(\cos\sqrt{2}as + \sin\sqrt{2}as)] \ ,$$

(13)

with

$$G = (n_c/n_v)(3k_F a_0)^{-1} \ ,$$

$$a^4 = G[1 + 4n_i\alpha(0)]/4\pi n_i\alpha(0) \ ,$$

and

$$s = 2k_F r_c \ .$$
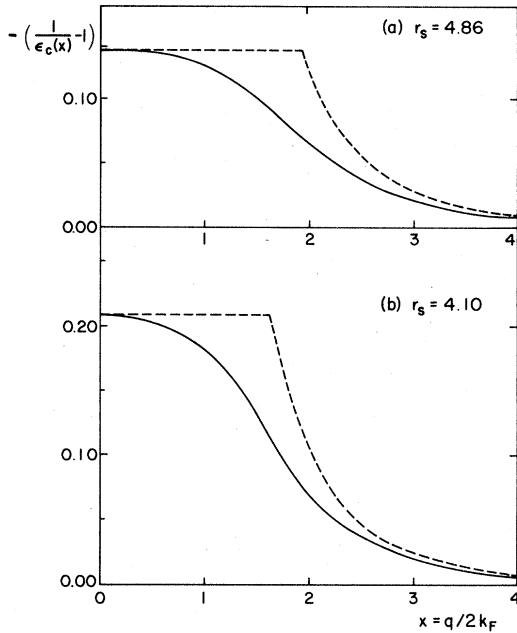
To determine (12) it is sufficiently accurate to take

FIG. 1. Interpolated form for $\epsilon_c(q)$ for potassium. The dotted curves show the high- and low-q limits of $\epsilon_c(q)$. The solid curve is from Eq. (10). (a) $r_s = 4.86$ ($\Omega/\Omega_0 = 1.0$); (b) $r_s = 4.10$ ($\Omega/\Omega_0 = 0.6$).

the Hartree-Fock result[15] for the electron-gas structure factor $S_{eg}(q)$, i.e.,

$$S_{eg}(q) = \tfrac{3}{2}x - \tfrac{1}{2}x^3 \quad (x < 1) \ ,$$

$$(14)$$

$$S_{eg}(q) = 1 \quad (x < 1) \ ,$$

where

$$x = q/2k_F \ .$$

Since $\epsilon_c(x)$ is already close to unity, it is reasonable to ignore further corrections to the correlation energy arising form the modification of the effective electron-electron interaction because of core-polarization effects.

We turn now to the energy of the screened van der Waals interactions: Its determination requires the frequency-dependent atomic and electron-gas polarizabilities. Again, since this contribution is not a major one, we may make reasonable approximations in both quantities. For the atomic polarizability we take the usual Lorentz form

$$\alpha(\omega) = \alpha(0)[1 - (\omega/\omega_0)^2]^{-1} \ , \qquad (15)$$

where ω_0 is a characteristic frequency (estimated to be the equivalent of 47 eV for potassium[16]). The wave-vector- and frequency-dependent dielectric function for the valence electrons is taken to have the simple form[17]

$$\epsilon(q,\omega) = 1 + k_{TF}^2/(q^2 - k_{TF}^2\omega^2/\omega_p^2) \ , \qquad (16)$$

where k_{TF} is the Thomas-Fermi wave vector. Notice that this leads to the familiar $q \to 0$ (for $\omega = 0$) and $\omega \to 0$ (for $q = 0$) limits. The point is that the use of (15) and (16) in conjunction with (3) gives

$$NZE_{vdW} = \tfrac{1}{2} \sum_{R \neq 0} \phi_L^s(\vec{R}) \ ,$$

where

$$\phi_L^s(R) = - \frac{e^2}{2a_0} \frac{3\hbar\omega_0}{4(e^2/2a_0)} \frac{1}{[1 + (\omega_p/\omega_0)^3]} \left[\frac{\alpha_0}{a_0^3}\right]^2 \left[\frac{a_0}{R}\right]^6$$

$$+ \frac{\hbar\omega_p}{(e^2/2a_0)} \frac{1}{2\pi} \int dy \left[\frac{\alpha^2(iu)}{a_0^6}\right] f_1(\vec{R},iu) \quad \left[y = \frac{u}{\omega_p}\right] \ , \qquad (17)$$

with

$$F_1(R,iu) = [1 + (u/\omega_p)^2]^{-1}\cosh^4 Qr_c e^{-2QR}$$

$$\times \left[6\left[\frac{a_0}{R}\right]^6 + 12Qa_0\left[\frac{a_0}{R}\right]^5 + 10(Qa_0)^2\left[\frac{a_0}{R}\right]^4 + 4(Qa_0)^3\left[\frac{a_0}{R}\right]^3 + (Qa_0)^4\left[\frac{a_0}{R}\right]^2\right] \ .$$

Here the quantity Q is defined by

$$Q^2 = k_{TF}^2[1 + (u/\omega_p)^2] \ .$$

The sum in (17) can be evaluated with relatively little computational effort. Finally, we determine the parameter α in E_0 by the zero-pressure condition[6]

which leads to

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

$$\left. - r_{s0}^2 \left[\frac{\partial E'}{\partial r_s}\right]_{r_{s0}} - 4.42\,r_{s0} \right] \ , \qquad (18)$$

where E' refers to the sum of the energy contributions other than those having their origin in electron-gas and electrostatic terms. In the case of potassium the zero-pressure electron spacing parameter[18] is $r_{s0} = 4.860$.

The total energy of bcc potassium can now be obtained by adding the contributions given by Eqs. (4)–(6) and (17) with α chosen to give the correct zero-pressure density, and subsequently held fixed. The various contributions to the energy and pressure are listed in Table I for a sequence of volume compressions. The $T = 0$ equation of state is shown in Fig. 2 and compared there with the low-temperature experimental results of Monfort and Swenson.[19] Above 20 kbar the comparison is made to an extrapolation achieved using[19]

$$P_{T=0}(\Omega) = 37.0[(\Omega_0/\Omega)^{3.85} - 1]/3.85 \qquad (19)$$

in units of kbar. It is clear from Fig. 2 that the agreement between theory and experiment is satisfactory.

The importance of core-polarization contributions can be judged by comparing these results with core effects neglected altogether. In practice this is (unintentionally) carried out by the fitting procedure in which all $q = 0$ terms are assumed incorporated in the aggregate E_0. Since the actual zero pressure density is determined by *all* contributions to the energy, the explicit neglect of core polarization is equivalent to assuming their implicit incorporation in E_0 (and assigning them thereby an inverse

volume dependence). Figure 3 and Table II summarize the results of such a procedure. A direct comparison of these two sets of results show that though there is a qualitative similarity (and quantitative to within 30%) the effects of core polarization are not small in potassium. The comparison also shows that to the extent that the difference in energies computed by the two different methods can be assumed inversely volume dependent, much of the difference can be absorbed in E_0.

IV. DISCUSSION

As might have been anticipated from the fact that the potassium ion is quite polarizable, we find that core-polarization effects in postassium metal contribute noticeably to its thermodynamic functions, particularly at high pressures. We now examine the degree to which this conclusion may depend on the approximations and numerical procedures adopted. First, the interpolation form used for $\epsilon_c(q)$ is plausible on physical grounds, is convenient for numerical reasons, but is nevertheless still approximate. On the other hand, much of the contribution from these terms originates with the small-q contribution where the background dielectric constant is best known. In the same long-wavelength limit the dipole approximation used throughout is expected to be valid and so is the standard procedure for evaluating local-field effects.[20] When wavelengths become comparable to the spatial extent of the core-electron

TABLE I. Computed energy and pressure for potassium as a function of volume with core-polarization effects taken into account. The various quantities are defined in the text. Ω_0 is the zero-pressure volume.

Ω/Ω_0	Energy (Ry/electron)							
	E_{eg}	E_M	E_0	E_{Mc}	E_{BS}	E'_{vv}	E_{vdW}	E_{tot}
1.0	−0.1610	−0.3687	0.2793	−0.1003	−0.0149	−0.0557	−0.0012	−0.4225
0.9	−0.1620	−0.3819	0.3104	−0.1085	−0.0171	−0.0609	−0.0015	−0.4215
0.8	−0.1628	−0.3972	0.3492	−0.1184	−0.0199	−0.0673	−0.0019	−0.4183
0.7	−0.1633	−0.4152	0.3991	−0.1302	−0.0237	−0.0751	−0.0024	−0.4108
0.6	−0.1633	−0.4371	0.4656	−1448	−0.0287	−0.0852	−0.0032	−0.3967

Ω/Ω_0	Pressure (kbar)						
	$P(E_{eg} + E_M + E_0)$	$P(E_{vdW})$	$P(E_{Mc})$	$P(E_{BS})$	$P(E'_{vv})$	P_{tot}	P_{expt}[a]
1.0	44.6	−0.7	−23.3	−6.0	−14.5	0.0	0.0
0.9	59.3	−1.0	−27.5	−7.6	−17.5	5.7	4.8
0.8	80.7	−1.3	−32.8	−9.9	−21.5	15.3	13.1
0.7	113.0	−2.0	−40.0	−13.1	−27.0	30.9	(28.3)
0.6	164.5	−3.0	−49.8	−18.1	−35.2	58.5	(59.1)

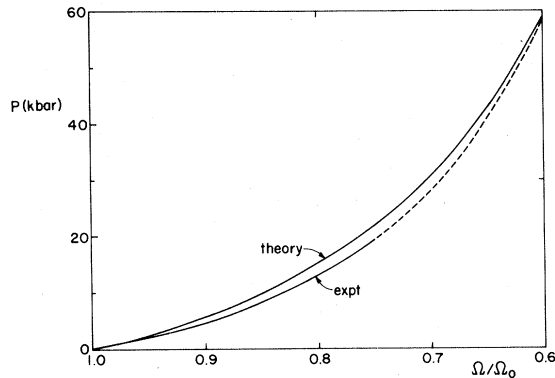[a]Reference 19. Numbers in parentheses are obtained by extrapolation.

FIG. 2. Comparison of computed equation of state of potassium (core-polarization effects included) with the experimentally determined function. The dotted portion of the experimental curve is obtained by extrapolation of Eq. (32) (Ref. 19).

charge distribution, however, the description in terms of translationally invariant core-electron response functions is not strictly justified. For such wavelengths it *is* the case that the dielectric function approaches unity quite closely so that though the interpolation form we use [Eq. (10)] lacks the expected symmetry, the error thereby introduced is certainly small.

It is also worth noting that the parameters $\alpha(0)$ and

ω_0 can be expected to be weak functions of density.[21] Furthermore, it is well known that a nonlocal pseudopotential is required for a correct decription of band structure of potassium (there are empty d-symmetry bands lying above the Fermi energy[22,23]). Of the terms most affected by such considerations, the band-structure energy is foremost. Nevertheless, once such nonlocal contributions are *averaged,* as in the construction of the *total* energy, the resulting uncertainties in the equation of state are not great. The reason is that the contributions to the equation of state from E_{BS} are -6 kbar at $\Omega/\Omega_0 = 1$, and -18 kbar at $\Omega/\Omega_0 = -0.6$. If E_{BS} were completely omitted, then at $p = 0$, E_0 would acquire (by virtue of the fitting procedure) an additional term to cancel the -6 kbar. Since E_0 is assigned an inverse volume dependence, it would yield -17 kbar at $\Omega/\Omega_0 = 0.6$, thus leading to a total error of only 1 kbar. At *very* high pressures, the d bands which are the major source of this nonlocality, might actually intersect the Fermi surface, a phenomenon observed[24] in Cs at around 42.5 kbar. The nearly-free-electron approach, on which our calculations have been based, will then be invalidated. We note that in the experimentally determined equation of state (at room temperature) no such transition of this nature has so far been observed for pressure up to 50 kbar.[19,25] All of these effects may need ulti-

TABLE II. Computed energy and pressure for potassium as a function of volume (core polarization effects neglected).

Ω/Ω_0	Energy (Ry/electron)		
	$E_{eg} + E_M + E_0$	$E_{BS}^{(2)}$	E_{tot}
1.0	-0.3702	-0.0166	-0.3868
0.9	-0.3667	-0.0195	-0.3862
0.8	-0.3607	-0.0233	-0.3840
0.7	-0.3507	-0.0283	-0.3790
0.6	-0.3346	-0.0348	-0.3694

Ω/Ω_0	Pressure (kbar)			
	$P(E_{eg} + E_M + E_0)$	$P(E_{BS}^{(2)})$	P_{tot}	P_{expt}[a]
1.0	7.9	-7.9	0.0	0.0
0.9	14.1	-10.2	3.9	4.8
0.8	23.4	-13.3	10.2	13.1
0.7	38.2	-17.4	20.8	(28.3)
0.6	62.7	-22.8	39.9	(59.1)

[a]Reference 19. Numbers in parentheses are obtained by extrapolation.
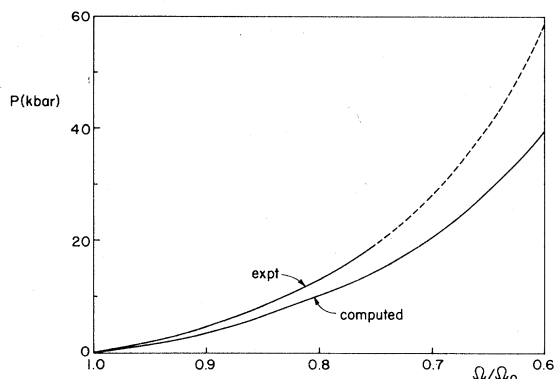
FIG. 3. The computed equation of state shown in this figure neglects core effects.

mately further consideration, but within a few kbar will not alter the principal conclusion, namely that at high pressure core-polarization effects in potassium appreciably modify its equation of state.

ACKNOWLEDGMENTS

*Present address: Bell Laboratories, Holmdel, New Jersey.

[1]K. K. Mon, N. W. Ashcroft, and G. V. Chester, Phys. Rev. B 19, 5103 (1979).

[2]C. A. Kukkonen and J. W. Wilkins, Phys. Rev. B 19, 6075 (1979); C. A. Kukkonen, Ph.D. thesis, Cornell University, 1975 (unpublished).

[3]J. Cheung and N. W. Ashcroft, Phys. Rev. B 23, 2484 (1981).

[4]T. Soma, J. Phys. F 10, 1401 (1980).

[5]Such *thermal contributions* to the equation of state can be estimated from the Mie-Grüneisen equation of state. In the alkali metals these can be a few kbar (see Ref. 4).

[6]N. W. Ashcroft and D. C. Langreth, Phys. Rev. 155, 682 (1967).

[7]J. J. Rehr, E. Zaremba, and W. Kohn, Phys. Rev. B 12, 2062 (1975); J. Mahanty and R. Taylor, *ibid.* 17, 554 (1978).

[8]In (4b), E_{corr} is the correlation energy of the interacting electron gas for which we take the Noziéres-Pines form [D. Pines and P. Noziéres, *The Theory of Quantum Liquids* (Benjamin, N.Y., 1966)]. Other forms lead to very similar results; see, for example, P. Vashista and K. S. Singwi, Phys. Rev. B 6, 875 (1972). In (4c), $v_{ps}(q)$ is a pseudopotential approximating the coupling of valence electrons to fluctuating dipoles, as discussed in Refs. 1 and 3.

[9]In (5b), α_M is the standard Madelung constant; see D. C. Wallace, *Thermodynamics of Crystals* (Wiley, N.Y., 1972); C. Friedli and N. W. Ashcroft, Phys. Rev. B 12, 5552 (1975).

[10]See, for example, Ref. 4 and M. L. Cohen and V. Heine, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 38.

[11]D. R. Penn, Phys. Rev. 128, 2093 (1962); W. Brandt and J. Reinheimer, Can. J. Phys. 46, 607 (1968); G. Srinivasan, Phys. Rev. 178, 1244 (1969).

[12]A. Dalgarno, Adv Phys. 11, 281 (1962).

[13]Here we are estimating the local density appropriate to the $3s^2 3p^6$ shell of the potassium ion, ignoring contributions from the far less polarizable inner shell.

[14]N. W. Ashcroft, Phys. Lett. 23, 48 (1966); N. W. Ashcroft, J. Phys. C 1, 232 (1968).

[15]The use of (14) in $(1/2\Omega) \sum_{\vec{q} \neq 0} v_c(q) [S_{eg}(q) - 1]$ gives only the exchange energy.

[16]N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).

[17]As noted by Rehr et al. (Ref. 7), this form, though approximate, nevertheless yields approximately 90% of the energy bound up in the screened fluctuating dipole interactions. In (16), $\omega_p = (4\pi n_e e^2/m)^{1/2}$ is the plasma frequency and k_{TF} is the Thomas-Fermi wave vector, $k_{TF}^2/k_F^2 = (16/3^2)^{2/3} r^s$.

[18]C. S. Barrett, Acta Cryst. 9, 671 (1956); D. R. Schouten and C. A. Swenson, Phys. Rev. B 10, 2175 (1974).

[19]C. E. Monfort, III, and C. A. Swenson, J. Phys. Chem. Solids 26, 291 (1965).

[20]S. L. Adler, Phys. Rev. 126, 413 (1962); S. R. Nagel and T. A. Witten, Jr., Phys. Rev. B 11, 1623 (1975).

[21]They are also related by a sum rule: See J. M. Ziman, *Principles of the Theory of Solids,* 2nd ed. (Cambridge University Press, London, 1972).

[22]M. J. G. Lee and L. M. Falicov, Proc. R. Soc. London, Sect. A 304, 319 (1968).

[23]J. Moriarty, Phys. Rev. B 5, 2006 (1972); 6, 4445 (1972); 10, 3075 (1974).

[24]A. Jayaraman, R. C. Newton, and J. M. McDonough, Phys. Rev. 159, 527 (1967); D. B. McWhan, G. Parisot, and D. Bloch, J. Phys. F 4, L69 (1974).

[25]S. N. Vaidya, I. C. Getting, and G. C. Kennedy, J. Phys. Chem. Solids 32, 2545 (1971); F. P. Bundy and H. M. Strong, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1962), Vol. 13, p. 81.