PHYSICAL REVIEW B VOLUME 18, NUMBER 2 15 JULY 1978

Resistivity of liquid metals under elevated pressure

J. Cheung and N. W. Ashcroft
Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853

(Received 17 March 1978)

The variations of scaled resistivities of a representative set of simple liquid metals are evaluated as a function of pressure. The resistivities are determined within the framework of the nearly-free-electron model while the pressures are obtained from variational calculations of the free energy. Structural information is provided by the hard-sphere approximation to the actual liquid structure. In general, the scaled resistivities show a dependence on pressure that is quite sensitive to the detailed form of the electron-ion interaction, or pseudopotential. For the case of potassium, where experimental results are available, the agreement between the calculated and experimental results is quite satisfactory.

I. INTRODUCTION

Since the early work of Bridgman,[1] much information has been accumulated on the variation of the transport properties of metals with pressure. To date, the theoretical description of these variations is somewhat limited. Calculations that have been made are quite approximate, and the models employed have been generally crude. Although it is believed that the pressure variation of physical properties of matter can be accounted for within our present level of understanding of the condensed state, it is recognized that various effects (e.g., the variation of the Fermi surface with volume or the change in phonon spectra) must enter in an exceedingly complex way.

In the course of a series of calculations on the resistivity of crystalline metals at high pressure,[2] we have found that corresponding studies on liquid metals provide considerable physical insight into the orders of magnitudes expected for the pressure-induced changes. As with many calculations on liquid metals the numerical work, when compared with that for the crystalline counterpart, is relatively straightforward. Although the physics of liquid and solid states is very different, the effects we see in the liquid can often provide a useful guide to the behavior of corresponding effects in the solid state. This is particularly true of disorder scattering of electrons, i.e., liquid-structure versus phonon disorder. We shall be concerned here with the former, i.e., resistivity of liquid metals as functions of pressure. Apart from their bearing on the resistivity of crystalline metals under similar conditions, such calculations are very much of interest in their own right.

In Secs. II and III we briefly describe the procedure by which both resistivity (ρ) and pressure (p) are calculated as a function of r_s, the dimensionless electron-spacing parameter given for a system with mean electron density n by

$$r_s a_0 = (3/4\pi n)^{1/3},$$

where a_0 is the Bohr radius. The purpose of these two sections is to obtain both the equation of state of the liquid metal and the logarithmic derivative of resistivity with respect to pressure, $(r_s/\rho)(\partial\rho/\partial r_s)$. The subsequent intent is the elimination of r_s between the two functions, thus gaining a relation of the type $\rho = \rho(p)$, or more precisely $\gamma = \gamma(p)$, where $\gamma = \rho/\rho(0)$.

To this end Sec. IV describes how the numerical calculations are carried out. The ionic structure factor $S(q)$ which enters the standard low-order expression for the resistivity, is evaluated with the Percus-Yevick hard-sphere solution which is known to fit the low-pressure structural data quite well. It is a function of a single parameter η (the packing fraction), which, for a given density, is evaluated variationally. In Sec. V we present the results for a representative set of simple metals. Little experimental (or indeed theoretical) work has appeared in the area of *solidification pressures* at temperatures much higher than the melting temperatures. This information is needed in order to determine the region of the p-T plane in which our results really do apply to liquid metallic phases. Since we expect higher temperatures generally to correspond to higher pressures, we have used, where possible, starting ($p = 0$) resistivities corresponding to the *highest* temperature values as quoted in the literature. It should be noted that some of the results we obtain may be inapplicable (in the sense of an assumed liquid phase) at the high-pressure end of our curves.

II. EVALUATION OF RESISTIVITY

The point of view taken here is that the reduced resistivity of a simple liquid metal $[\gamma = \rho/\rho(0)]$ will scale, as a function of volume, in the same way as the function γ calculated from the standard weak coupling expression for ρ, namely,[3,4]

$$\rho = \frac{a_0\hbar}{e^2}\,\frac{4\pi^3 Z}{a_0 k_F}\int d\omega \int_0^1 dx\, x^3 v^2(x) \times \frac{\beta\hbar\omega}{1-e^{-\beta\hbar\omega}}\,S(x,\omega)\,, \quad \left(x=\frac{q}{2k_F}\right). \tag{1}$$

Here $a_0\hbar/e^2$ is the atomic unit of resistivity (its value is 21.77 $\mu\Omega$ cm), Z is the valence of the metal, and k_F is the Fermi wave vector. The quantity $v(x)$ is related to the matrix element for scattering between plane-wave levels $\vec{k}$ and $\vec{k}'$ at the Fermi surface ($\vec{q}=\vec{k}'-\vec{k}$) and is defined by the Fourier transform of the electron-ion pseudopotential, assumed local, and normalized to its long wavelength limit. The structural information on the ions in the liquid metal is contained in the dynamic structure factor $S(q,\omega)$. At high temperatures we may rewrite (1) as

$$\rho = \frac{a_0\hbar}{e^2}\,\frac{4\pi^3 Z}{a_0 k_F}\int_0^1 dx\, x^3 v^2(x)\int d\omega\left[1+\frac{\beta\hbar\omega}{2}-\frac{1}{3}\left(\frac{\beta\hbar\omega}{2}\right)^2+\frac{1}{45}\left(\frac{\beta\hbar\omega}{2}\right)^4+\cdots\right]S(x,\omega) \tag{2}$$

$$= \frac{a_0\hbar}{e^2}\,\frac{4\pi^3 Z}{a_0 k_F}\left(\int_0^1 dx\, x^3 v^2(x) S(x) + \frac{2m}{M}\,\frac{T_F}{T}\int_0^1 dx\, x^5 v^2(x) + O(T^{-3})\right), \tag{3}$$

where M is the mass of an ion, and T_F the Fermi temperature. In arriving at (3) we have used the definition of the static structure factor in terms of $S(q,\omega)$ and the first-moment sum rule.[5] The second term in (2) is of order 1% of the first term and can usually be neglected. Higher moments of $S(q,\omega)$ involve details of the effective interionic potentials,[6] but these moments are extremely small.

The result obtained by keeping only the first term in (3), namely,

$$\rho = \frac{a_0\hbar}{e^2}\,\frac{4\pi^3 Z}{a_0 k_F}\int_0^1 dx\, x^3 v^2(x) S(x)\,, \tag{4}$$

has been the center of some controversy[7,8] since its appearance. It is the lowest-order result possible, and much of the argument has had to do with the likely importance of corrections going beyond what is essentially an application of the Born approximation. Equation (4) can also be derived[9] by starting with the Kubo-Peierls-Greenwood expression for the *conductivity*, and performing an expansion (and subsequent inversion) in the imaginary part of the electron self energy, assuming this to be small when scaled to the Fermi energy. (Such an assumption is equivalent, of course, to the assertion that there is a long mean free path.) This procedure reproduces (4) as the leading term in ρ and also permits, in principle, a systematic attack on the higher order terms. These, however, require structural information on liquid metals beyond pair distribution functions, and these in turn lead to further approximations. One such approximation to the n-body correlation function, the geometric approximation,[8] permits the resummation of a large class of higher-order terms, and results in an expression for the resistivity identical in *form* to (4) but with v replaced by an effective structure-dependent potential. As shown by Ashcroft and Schaich,[8] this effective potential differs little from typical pseudopotentials, so that within the geometric approximation (or for *model* fluids whose physical structure is given precisely by the stipulated form of the higher correlation functions) there is some indication that such higher-order corrections tend to cancel among themselves. The geometric approximation permits us correctly to describe scattering from pairs of ions, while treating the effects of larger clusters only in an average sense. It therefore still neglects certain sets of terms whose importance is hard to assess. On the other hand, given that the structure of (4) can be preserved within approximations that do include many of the higher order terms, and given that (4) itself has had remarkable qualitative success in accounting for the resistivities of pure metals *and* alloys over a *wide range of electron densities*, it is a reasonable first step to assume that the resistivities of liquid metals will scale (against density) according to the predictions of Eq. (4).

III. EVALUATION OF PRESSURE

We begin with

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}\,, \tag{5}$$

where F is the Helmholtz free energy of a metal with volume V. To calculate F we consider the Hamiltonian H for a system of N ions of charge Ze and mass M, to which electrons (mass m) are coupled by the weak unscreened pseudopotential v_b. Then if $\vec{r}_i$, $\vec{R}_j$ and $\vec{p}_i$, $\vec{P}_j$ are electron and ion coordinates and momenta, H may be written

$$H=\sum_i \frac{p_i^2}{2m}+\frac{1}{2}\sum_{i,j}{}' \frac{e^2}{|\vec{r}_i-\vec{r}_j|}+\sum_j \frac{P_j^2}{2M} + \frac{1}{2}\sum_{i,j}{}' \frac{Z^2e^2}{|\vec{R}_i-\vec{R}_j|}+\sum_{i,j} v_b(\vec{r}_i-\vec{R}_j)\,,$$

provided the conditions on density are such that the ions see each other as point charges (no core-core overlap or screened fluctuating dipole interactions). Introducing Fourier transforms and grouping all $k=0$ terms together, we have $H=H_{ee}+H_{ii}+H_{ei}$, where

$$H_{ee}=\sum_i \frac{p_i^2}{2m}+\frac{1}{2V}\sum_{\vec{k}\neq 0}\frac{4\pi e^2}{k^2}(\rho_{\vec{k}}^e\rho_{-\vec{k}}^e-NZ) \qquad (6)$$

is the Hamiltonian of NZ interacting electrons in a uniform compensating background,

$$H_{ii}=\sum_i \frac{P_i^2}{2m}+\frac{1}{2V}\sum_{\vec{k}\neq 0}\frac{4\pi e^2Z^2}{k^2}(\rho_{\vec{k}}^i\rho_{-\vec{k}}^i-N) \qquad (7)$$

is the Hamiltonian of N-point ions in a uniform background, and[10]

$$H_{ei}=+\frac{1}{V}\sum_{\vec{k}\neq 0}v_b(k)\rho_{\vec{k}}^i\rho_{-\vec{k}}^e+E_0\,. \qquad (8)$$

Here

$$\rho_{\vec{k}}^e=\sum_i e^{i\vec{k}\cdot\vec{r}_i}\,,$$

$$\rho_{\vec{k}}^i=\sum_i e^{i\vec{k}\cdot\vec{R}_i}\,,$$

and $v_b(k)$ is the Fourier transform of the pseudopotential. For an empty core potential, this takes the form

$$v_b(k)=(-4\pi Ze^2/k^2)\cos kr_c\,, \qquad (9)$$

with r_c the core radius. In (8), E_0 is the limit of the $k=0$ terms and, for states of fixed N, becomes

$$E_0=NZ\frac{N}{V}\lim_{\vec{k}\to 0}\left(v_b(k)+\frac{4\pi Ze^2}{k^2}\right)$$
$$=NZ3\frac{(r_c/a_0)^2}{r_s^3}\left(\frac{e^2}{2a_0}\right) \qquad (10)$$

for a potential $v_b(k)$ of the form given by (9). More generally it has the structure $E_0=NZ(\alpha/r_s^3)e^2/2a_0$.

To derive the thermodynamics of the system, we require $\mathrm{Tr}\,e^{-\beta H}$. By making the standard adiabatic approximation, and taking the electron system to be in a ground state appropriate to each ionic configuration, the thermodynamics then follows from $\mathrm{Tr}_i e^{-\beta H_i}$, where H_i is an effective Hamiltonian for the ions and is defined by

$$H_i=E_e(V)+E_0+H_{ii}'. \qquad (11)$$

In (11), $E_e(V)$ is the ground-state energy of the interacting electron gas, and H_{ii}' represents, for a given volume, the Hamiltonian of a system of ions interacting via n-body forces ($n\geq 1$) whose origin is the direct Coulomb interaction augmented by *indirect* interactions arising from the electron response[11] to v_b. At the level of linear response (to which we restrict attention here) H_{ii}' can be written

$$H_{ii}'=\sum\frac{P^2}{2M}+\frac{1}{2V}\sum_{\vec{k}\neq 0}\frac{4\pi Z^2e^2}{k^2}(\rho_{\vec{k}}^i\rho_{-\vec{k}}^i-N)$$
$$+\frac{1}{2V}\sum_{\vec{k}\neq 0}|v_b(k)|^2(\rho_{\vec{k}}^i\rho_{-\vec{k}}^i)\frac{k^2}{4\pi e^2}\left(\frac{1}{\epsilon}-1\right), \qquad (12)$$

where ϵ_k is the dielectric constant, and is taken to have the form

$$\epsilon_x=1+(\lambda^2/x^2)F(x),\quad [\lambda^2=(\pi a_0k_F)^{-1}],$$

with $F(x)=f(x)/[1-\lambda^2f(x)(2x^2+g)^{-1}]$. The function $f(x)$ is the Lindhard function[12]

$$f(x)=\tfrac{1}{2}+[(1-x^2)/4x]\ln|(1+x)/(1-x)|\,,$$

and g is a correction for correlation and exchange which is determined by the compressibility sum rule for the interacting electron gas, $g=(1+0.158\lambda^2)^{-1}$.

Since we are interested in relatively high temperatures, we may treat the massive ions classically. In a canonical ensemble with $\langle T_i\rangle=E_{\mathrm{kin}}$ (the total ionic kinetic energy), we have

$$\langle H_i\rangle=U=E_e(V)+E_0+E_{\mathrm{kin}}+\frac{N}{2V}\sum_{\vec{k}\neq 0}\frac{4\pi Z^2e^2}{k^2}[S(k)-1]+\frac{N}{2V}\sum_{\vec{k}\neq 0}|v_b(k)|^2S(k)\frac{k^2}{4\pi e^2}\left(\frac{1}{\epsilon_k}-1\right) \qquad (13)$$
$$=E_e(V)+E_0+\frac{N}{2V}\sum_{\vec{k}\neq 0}\frac{[v_b(k)]^2}{4\pi e^2/k^2}\left(\frac{1}{\epsilon_k}-1\right)+\langle T_i\rangle+\frac{N}{2V}\sum_{\vec{k}\neq 0}\left\{\frac{4\pi Z^2e^2}{k^2}\left[1+\left(\frac{v_b(k)}{4\pi Ze^2/k^2}\right)^2\left(\frac{1}{\epsilon_k}-1\right)\right]\right\}[S(k)-1]\,, \qquad (14)$$

where the third term in (14), a one-body term, is the self-energy of the (linear response) electron distribution around the ions. The last term has the structure $(N/2V)\sum_{\vec{k}\neq 0}\phi(k)[S(k)-1]$, where $\phi(k)$ ($k\neq 0$) is the Fourier transform of an effective-pair interaction between ions. It is in this form that we may now apply the variational principle: given a system at the same volume and (ionic) density with pair interactions $\bar{\phi}$ (taken here as a hard-sphere system), we have[13]

$$F\leq E_e(V)+E_0(V)+\frac{N}{2V}\sum_{\vec{k}\neq 0}\frac{[v_b(k)]^2}{4\pi e^2/k^2}\left(\frac{1}{\epsilon_k}-1\right)$$
$$+F_{\bar{\phi}}+\frac{N}{2V}\sum\phi(k)[S_{\bar{\phi}}(k)-1]$$

or

$$F\leq E_e(V)+E_0(V)+E_{\mathrm{kin}}-Ts_\sigma$$
$$+\frac{N}{2V}\sum_{\vec{k}\neq 0}\frac{4\pi Z^2e^2}{k^2}[S_\sigma(k)-1]$$
$$+\frac{N}{2V}\sum_{\vec{k}\neq 0}\frac{[v_b(k)]^2}{4\pi e^2/k^2}S_\sigma(k)\left(\frac{1}{\epsilon_k}-1\right), \qquad (15)$$

where σ denotes the diameter of the hard spheres in the chosen reference system. For a specified volume, this is determined by $(\partial F/\partial\sigma)_{T,V}=0$. Finally, the coefficient α in $E_0=NZ(\alpha/r_s^3)(e^2/2a_0)$ is a property of *atomic* structure of the ions and is difficult to calculate from first principles. It may be fixed once and for all, however, by using the condition $(\partial F/\partial V)_T=0$ at the observed (1-atm) density. This requires only a knowledge of s_σ, the hard-sphere entropy.

IV. CALCULATIONAL PROCEDURE

The application of the procedure just described is most easily accomplished by taking for $S_\sigma(k)$ the known solution for hard spheres of the Percus-Yevick equation.[14] In this approximation the fifth term in (15), the Madelung energy, can be given in closed form[15]

$$E_M=-NZ\alpha Z^{5/3}/r_s,$$

where

$$\alpha=6\eta^{2/3}[(1-\tfrac{1}{5}\eta+\tfrac{1}{10}\eta^2)/(1+2\eta)],$$

with

$$\eta=\tfrac{1}{6}\pi(N/V)\sigma^3,$$

the packing fraction. The entropy is taken from the Carnahan-Starling equation of state.[16] Given a form for $v_b(k)$, the local unscreened pseudopotential, the last term in (15) can be determined by numerical integration. For the pseudopotential we choose the empty core form described above; it is a function of a single parameter r_c. Since the main purpose here is to examine the scaling of ρ with r_s, it is sufficient to use values of r_c adjusted to give the observed zero-pressure resistivities according to Eq. (4). For consistency, the $S(x)$ used in (4) is also the Percus-Yevick hard-sphere factor [with, as noted, a packing fraction chosen to minimize (15)]. The values of r_c so determined deviate but a few percent from typical values quoted in the literature[7] (some of which are, in the first place, extracted from resistivity data in liquid metals).

As pressure p is applied to the liquid metal, its density and resistivity change. Assuming that the temperature is always chosen to be such that for the range of p considered the system remains liquid, our formalism permits us to calculate (i) ρ as a function of r_s and (ii) $\gamma=\rho/\rho_0$ as a function of r_s, where ρ_0 is the zero pressure resistivity. We can therefore numerically eliminate r_s between these two sets of results and arrive at

$$\gamma=\gamma(p), \tag{16}$$

the scaled resistivity as a function of pressure. The final result is easily checked for its sensitivity to the choice of pseudopotential (see below).

V. RESULTS

We consider representative mono-, di-, tri-, and tetravalent metals and the variation of their scaled resistivities with pressure. In Figs. 1(a)–1(d) we present the results of ρ vs r_s for K, Mg, Al, and Sn. As noted above, the higher pressures indicated in the figures may well be greater than solidification pressures. The determination of this solidification pressure (as a function of temperature) has not been carried out. Where not measured directly it can be estimated in principle by theoretical means.[17]

As it turns out, it is possible to choose more than one value of r_c to fit the experimental resistivity data (and at the same time satisfying the variational condition $\partial F/\partial\eta=0$ with different values of η). Typically, only one of these r_c's is close to the value used with considerable success to fit other experimental data (i.e., r_c's quoted in the literature[18]), and this r_c is used in subsequent calculations. For purposes of comparison, we note that in potassium, the "accepted" value of r_c is 1.12 Å, while we obtain values of 1.03 and 1.46 Å, corresponding to deviations of 8% and 30%, respectively. Table I lists the values of r_c used throughout.

Questions should certainly be raised as to whether the results we obtain are mere consequences of the specific r_c's we use. In response, we have repeated the sequence of calculations with the exception that the r_c's we use are precisely the same as those quoted in the literature. In consequence, we only need to determine η from Eq. (15) and subsequently calculate ρ with Eq. (4). We note that the structure factor in the Percus-Yevick approximation approximates experimental results very well with these values of η. Figures 1(a)–1(d) also display the results obtained in this manner.

Another concern is the validity of the assumption that the ion core radius r_c stays constant as the electronic density is varied. This is a legitimate question since pseudopotentials are certainly energy dependent, and in the one parameter pseudopotential used here this dependence resides in r_c. On the other hand, it should also be recognized that the ion core radius is a parameter under which an exceedingly complicated electron-ion interaction is subsumed. One can investigate how r_c varies in different environments. Experience, however, shows that the variations are small, at least for small changes in r_s. Indeed we would expect the results to be altered somewhat if we use the "ex-

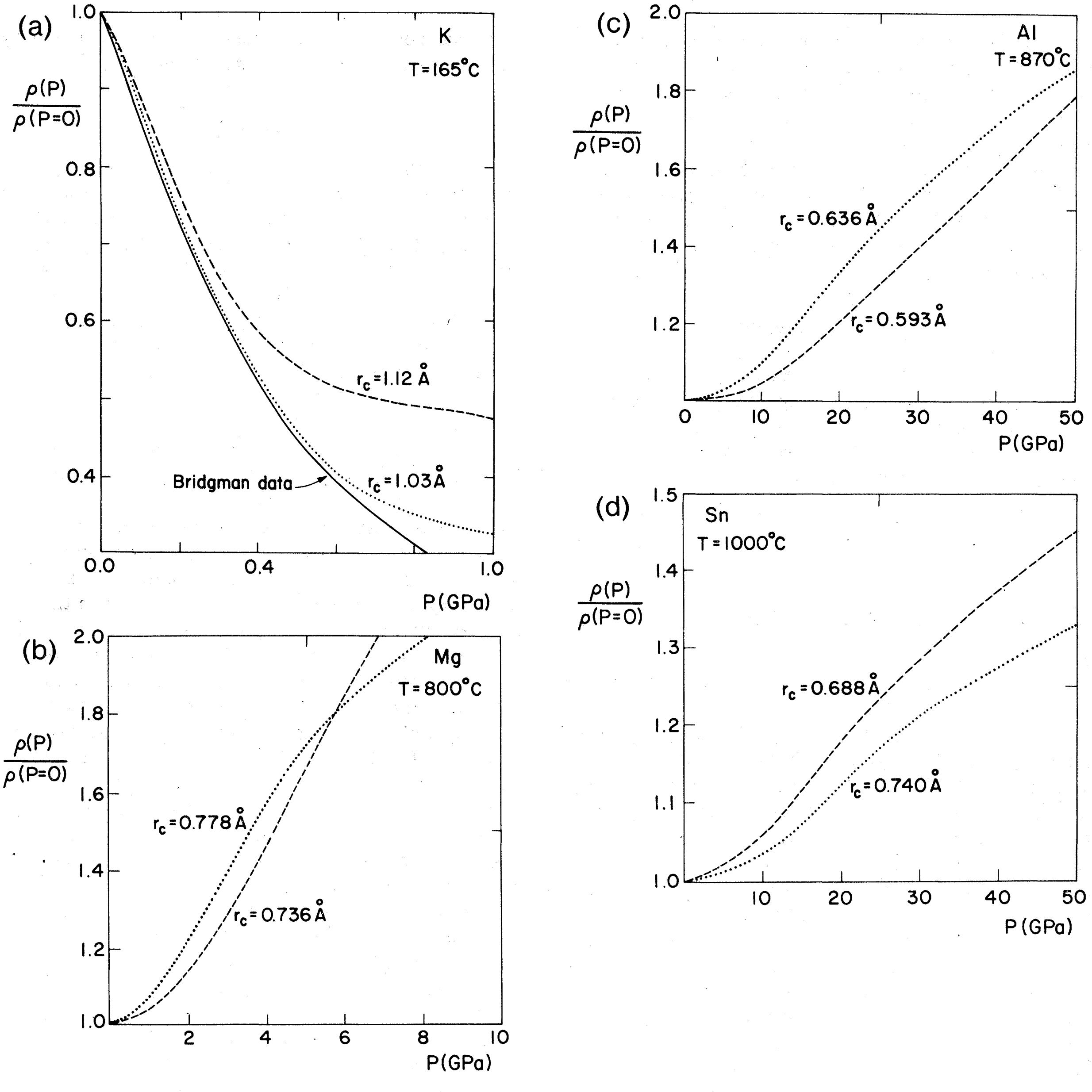

FIG. 1. Variation of resistivity as a function of pressure for (a) K, (b) Mg, (c) Al, and (d) Sn for elevated temperatures. The results obtained for two different values of r_c for each metal are shown. The dashed curves are obtained with the "literature" values of r_c, while the dotted curves are from the adjusted r_c's (see text). In (a) the experimental data of Bridgman are also shown (solid curve). As noted in the text, the actual melting curve may occur at places which would make the assumption of a liquid state invalid.

TABLE I. Empty core radii r_c. The first row are values of r_c determined via Eqs. (4) and (15); the second row are values of r_c quoted in the literature.

	K	Mg	Al	Sn
r_c (Å)	1.03	0.778	0.636	0.740
	1.12	0.736	0.593	0.688

act form" of r_c, nevertheless our results give a reasonable guide to expected pressure coefficients since these involve scaled quantities (logarithmic derivative). Measurements of resistivities of liquid metals at higher pressures would be welcome to see how good these approximations are and provide information as to what adjustments should be made in the ion core radius.

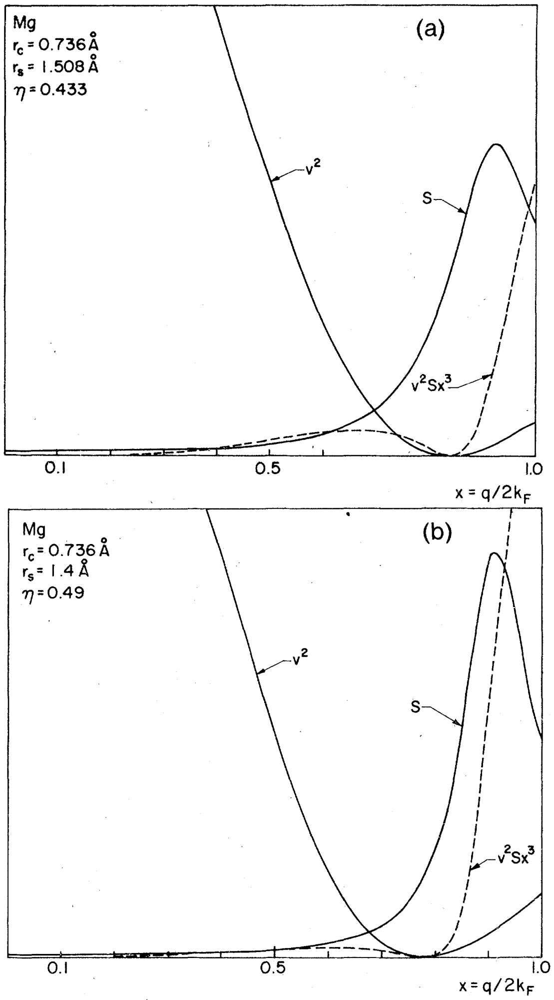

FIG. 2. Functions $S(x)$, $v^2(x)$, and $x^3S(x)v^2(x)$ for Mg at two different values of r_s. It is seen that, for a decrease in r_s, v^2 and S change in such a way that the integrand x^3Sv^2 appearing in Eq. (4) increases. This explains the increase in resistivity for a decrease in r_s for the liquid metal.

One striking result is that the pressure coefficients of the resistivity can be both positive and negative. At first sight one might find this surprising, though on closer examination it is what would be expected. As we see in Eq. (4), the resistivity depends on both the screened electron-ion interaction $v(q)$ and the structure factor $S(q)$ which describes the arrangement of the ions. As the resistivity integrand is weighted by a factor of $(q/2k_F)^3$, the contribution near the region $x = q/2k_F = 1$ usually dominates. In Fig. 2 we have plotted $S(x)$, $v^2(x)$, and v^2Sx^3 for Mg (with $r_c = 0.736$ Å) for two values of r_s (and corresponding values of η). It is readily seen that v^2 and S change in such a way that the integrand $v^2(x)S(x)x^3$ increases near the region $x=1$ upon a decrease in r_s.

While in these calculations we assume that the electron-ion interaction is described by a fixed empty core radius, the variational calculations show that the ion-ion interaction, described by the hard-sphere diameter σ,[19] varies as a function of the volume. Calculations by various authors[20] have indeed shown that the effective ion-ion interaction does change shape as a function of volume. The corresponding variation of σ, the hard-sphere diameter, as a function of the electron density is listed in Table II.

For completeness we also include in Figs. 3(a)–3(d) the equation of state for K, Mg, Al, and Sn. It should be noted that these curves are obtained by considering the volume dependent energies. Equations of state have been obtained via other methods[21] in the same general framework as used here (such as integrating up the compressibility relation), however, it is doubtful that these can give very reliable information, although they do yield the qualitative features.

The variations of the resistivity as a function of r_s are shown in Figs. 4(a)–4(d). The values of $\partial(\ln\rho)/\partial(\ln r_s)$ are listed in Table III.

TABLE II. Variation of hard-sphere diameter σ (in Å) and packing fraction η as a function of r_s (in Å), the electron density, for various liquid metals. The numbers in parentheses are from the second series of calculations. The highest values of r_s correspond to zero pressure.

	K	Mg	Al	Sn
r_s	2.682	1.508	1.153	1.20
σ	3.72(3.88)	2.95(2.87)	2.61(2.55)	2.89(2.82)
η	0.334(0.380)	0.466(0.433)	0.481(0.450)	0.435(0.404)
r_s	2.60	1.45	1.10	1.15
σ	3.69(3.83)	2 .89(2.83)	2.54(2.49)	2.83(2.77)
η	0.358(0.401)	0.496(0.464)	0.508(0.483)	0.467(0.435)
r_s	2.50	1.40	1.05	1.10
σ	3.64(3.76)	2.84(2.78)	2.48(2.42)	2.77(2.71)
η	0.387(0.426)	0.520(0.490)	0.546(0.515)	0.501(0.467)

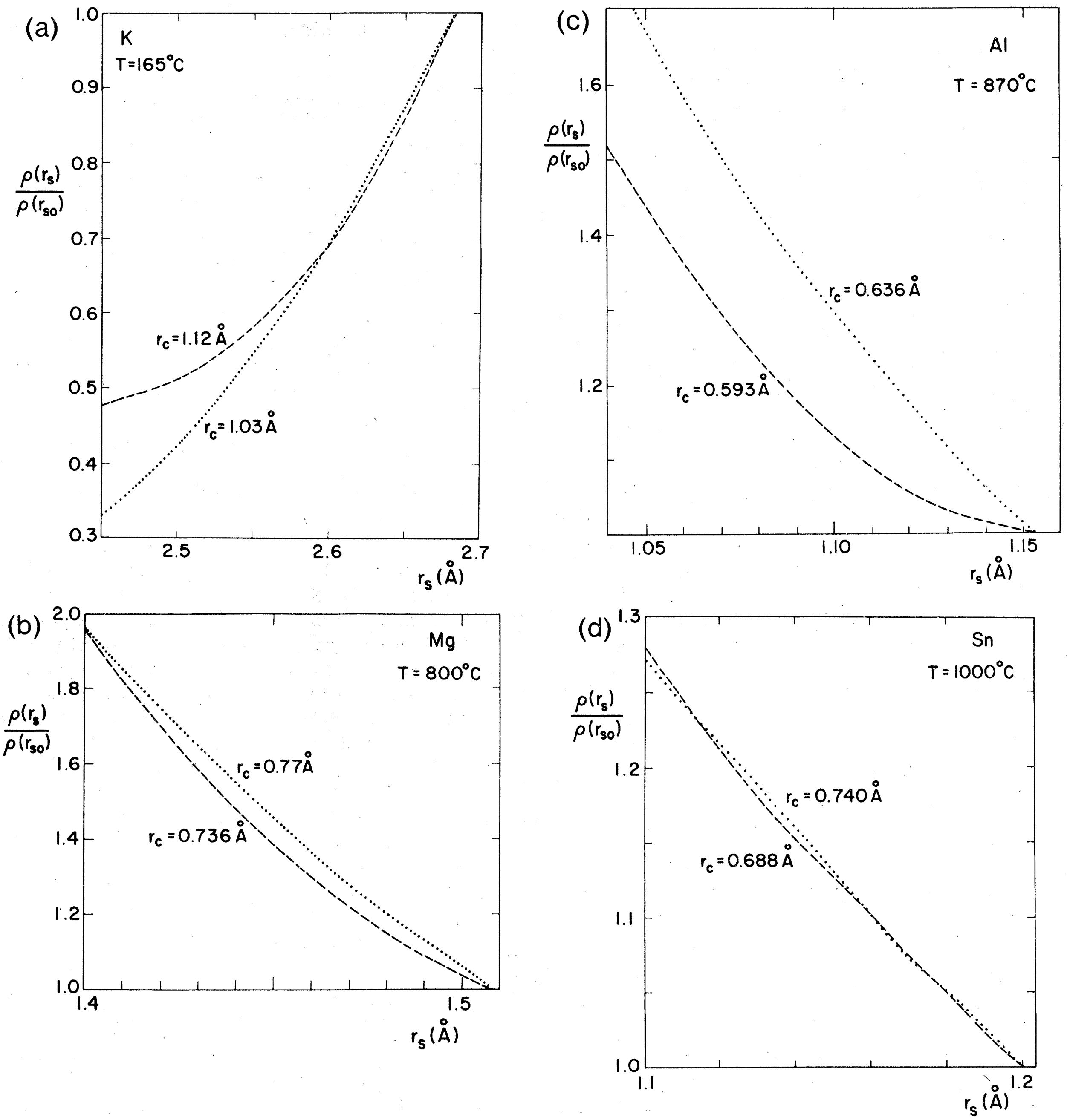

FIG. 3. Variation of the resistivity ρ as a function of r_s for (a) K, (b) Mg, (c) Al, and (d) Sn.

VI. DISCUSSION AND CONCLUSION

Comparison of the results from the two series of calculations shows that although the details differ, the qualitative aspects are similar. We believe they are reasonable guides to the kind of behavior we can expect the liquid metals to have upon the application of pressure. The calculations for potassium show very encouraging agreement with experimental data.[22] To our knowledge, there are no experimental data on liquid Mg, Al, and Sn under compression, thus we have not been able to make a comparison with experiments for these liquid metals. The reason for the similarities between the two different series of calculations is not entirely apparent. As a glance at Table II will show, the different r_c's tend to lead to somewhat different η's. However, we observe that the changes in

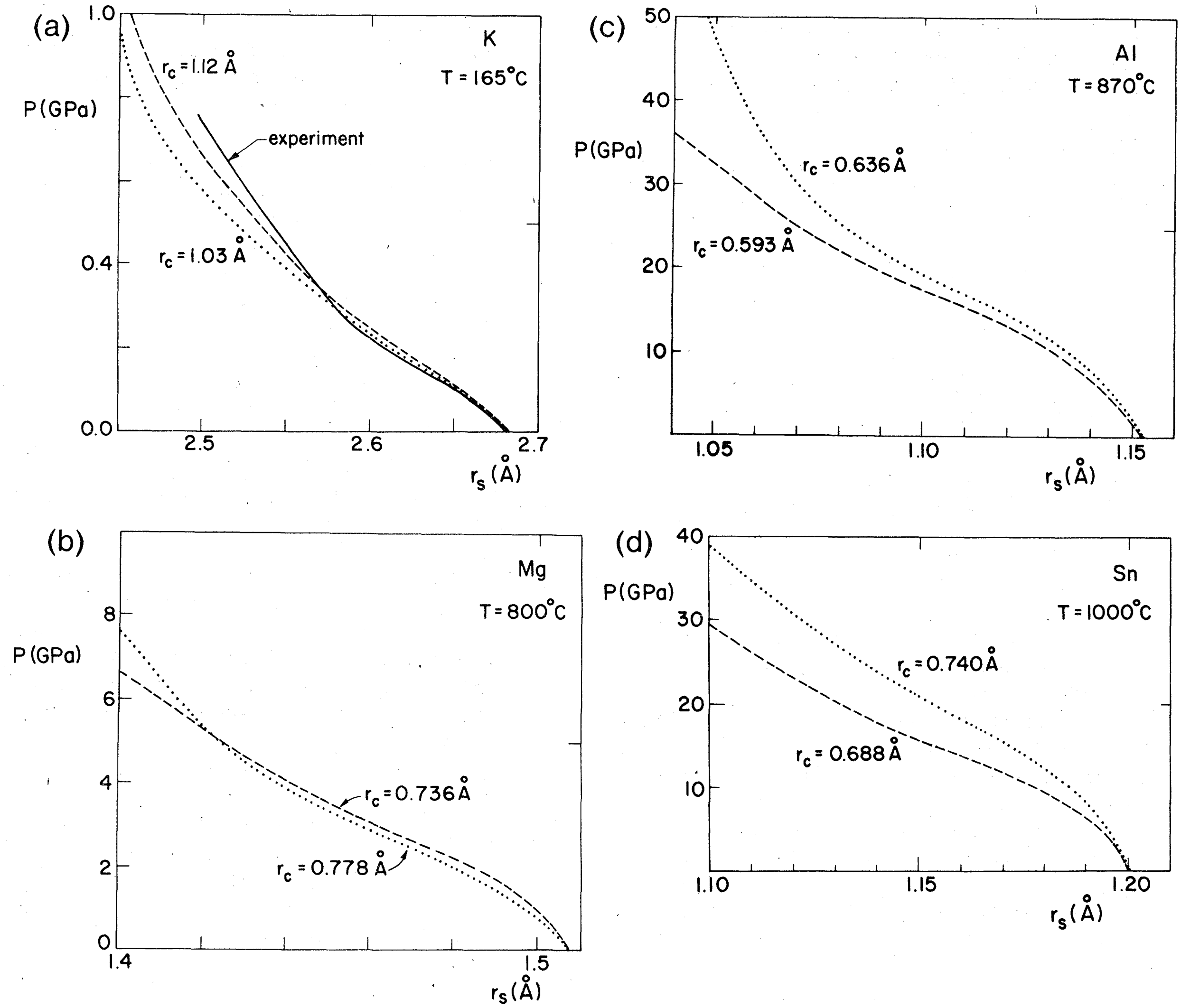

FIG. 4. Equation of state for (a) K, (b) Mg, (c) Al, and (d) Sn at the indicated temperatures. The experimental data for K shown in (a) are interpolated from those reported by Makarenko *et al*. (Ref. 22).

η are about the same for corresponding cases; this probably accounts for the trend we see from metal to metal.

As noted in Sec. V, the variation of the resistivity as a function of pressure is not necessarily of the "expected" form. For the four metals we consider, only potassium shows such "expected" behavior, i.e., resistivity decreases as pressure increases, while the others have resistivities that increase with pressure. With the exception of a few metals (notably lithium), resistivity in the solid decreases as pressure is applied.[23] This indicates that caution must be exercised in drawing conclusions about the sign of changes expected in solid metals, though the magnitude of such changes may be correct.

As noted earlier, the resistivity in both the solid and the liquid state can be thought of as arising from disorder scattering. In the liquid state it is due to the disorder of the ions as reflected by the structure factor $S(q,\omega)$, while in the solid the disorder is in the form of phonons, again described by the structure factor $S(q,\omega)$, usually the one-phonon structure factor. In this regard the results we have give the size of the variations in the resistivity, due to the application of pressure, that

TABLE III. Computed values of $\partial(\ln\rho)/\partial(\ln r_s)$ at zero pressure. Numbers in parentheses are from the second series of calculations.

K	Mg	Al	Sn
−11(−12)	9.6(7.5)	5.1(1.4)	2.9(2.7)

can be expected from disordering scattering.

Quantitative changes in the resistivity in the solid cannot be explained as straightforwardly as in the case of the liquid. To gain insight into the problem, we consider the familiar expression for the resistivity[24] (believed to be applicable for the alkali metals)

$$\frac{a_0\hbar}{e^2}\,8\pi^2 Z\beta\left(\frac{e^2}{2a_0}\right)(a_0k_F)\frac{m}{M}$$

$$\times\sum_{\lambda}\int_{x<1} d^3x\,\frac{x|\hat{\epsilon}(\vec{x},\lambda)\cdot\vec{x}|^2|v(\vec{x})|^2}{(1-e^{-\beta\hbar\omega(\vec{x},\lambda)})(e^{\beta\hbar\omega(\vec{x},\lambda)}-1)},$$

where $\omega(\vec{x},\lambda)$ and $\epsilon(\vec{x},\lambda)$ are the frequency and polarization vector at the reduced wave vector $\vec{x}=\vec{q}/2k_F$. The quantity

$$8\beta\left(\frac{\hbar^2k_F^2}{2m}\right)\frac{m}{M}\sum_{\lambda}\frac{|\vec{x}\cdot\hat{\epsilon}(\vec{x},\lambda)|^2}{(1-e^{-\beta\hbar\omega(\vec{x},\lambda)})(e^{\beta\hbar\omega(\vec{x},\lambda)}-1)},$$

identified as the one-phonon structure factor, can easily be shown to decrease as r_s decreases (i.e., for an increase in pressure) in the high temperature regime. However, to compute its variations with volume correctly, one would need a detailed evaluation of phonon frequencies for volumes at nonzero pressures. We note that the above formula is good only for a metal with a spherical Fermi surface; in the case of polyvalent metals, the changes in the Fermi surface geometry as r_s changes will further complicate the issue as they may introduce new possibilities for electron-phonon scattering events (or eliminate some of them, for that matter). We also expect the effective mass of the electron to change because of changes in the band structure.

Finally, pressure induced changes in the liquid state are of intrinsic interest. Our systematic calculations show that the interionic potential, as reflected in the hard-sphere diameter, *does* change with the environment. Within the framework of the hard-sphere approximation, we believe that these results are to be expected. Certainly the adjustment of the empty core radius r_c together with η to fit the experimental data, leads to values of r_c that differ from those calculations of other properties. Part of this adjustment is probably due to the rescreening of the electrons at a different density, although it is difficult to calculate the exact magnitudes involved. On the other hand, Eq. (4) is a first order result and forcing it to reproduce experimental data may introduce unphysical assumptions while the discrepancies can only be taken into account by an extensive evaluation of higher order contributions. We saw earlier that with the "literature" values of r_c, the structure factors are reproduced quite well. Together with the physically reasonable assumption that the resistivity ratio scales the same way as Eq. (4), it is our contention that the second series of calculations gives a more realistic guide as far as fractional changes in the resistivities are concerned.

ACKNOWLEDGMENT

Work supported by the NSF through the facilities of the Materials Science Center (Grant No. DMR76-81083) MSC Report No. 2971.

---

[1] P. W. Bridgman, *The Physics of High Pressure* (Bell, London, 1949).

[2] J. Cheung and N. W. Ashcroft (unpublished).

[3] J. M. Ziman, Philos. Mag. 6, 1013 (1961).

[4] I. Mannari, Proc. Theor. Phys. 26, 51 (1961).

[5] D. Pines and P. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1966).

[6] R. D. Puff, Phys. Rev. 137, A406 (1965).

[7] B. Springer, Phys. Rev. 154, 621 (1967); D. A. Greenwood, Proc. Phys. Soc. Lond. 87, 775 (1966).

[8] N. W. Ashcroft and W. Schaich, Phys. Rev. B 1, 1370 (1970).

[9] J. S. Langer, Phys. Rev. 120, 714 (1960).

[10] N. W. Ashcroft and D. C. Langreth, Phys. Rev. B 1, 1370 (1967). The Hamiltonian considered in this reference, and also here, refers to electron and ion charges placed in a medium which is unpolarizable. The ion cores are, of course, polarizable, though weakly. We assume that any term in the energy associated specifically with core polarization can be incorporated in the $k=0$ aggregate E_0.

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

[12] J. Lindhard, K. Dan. Vidensk. Selsk. Mat.-Fys. Medd. 28, 8 (1954).

[13] G. A. Mansoori and F. B. Canfield, J. Chem. Phys. 51, 4958 (1969); 51, 4967 (1969); J. Rasaiah and G. Stell, Mol. Phys. 18, 249 (1970).

[14] J. K. Percus and G. J. Yevick, Phys. Rev. 110, 1 (1958).

[15] H. J. Jones, J. Chem. Phys. 55, 2640 (1971); D. Stroud and N. W. Ashcroft, Phys. Rev. B 13, 1660 (1976). Note the relationship between the electronic radius and the Wigner-Seitz cell radius $r_s = r_{\mathrm{WS}}/Z^{1/3}$.

[16] N. F. Carnahan and K. E. Starling, J. Chem. Phys. 51, 635 (1969); 53, 600 (1970). This form of the entropy is obtained by integration of the appropriate Maxwell relation.

[17] See, for example, D. Stroud and N. W. Ashcroft, Phys. Rev. B 5, 371 (1972); H. D. Jones, Phys. Rev. A 8, 3215 (1973).

[18] N. W. Ashcroft and D. C. Langreth, Phys. Rev. 155, 682 (1967); 159, 500 (1967); N. W. Ashcroft, J. Phys. C 1, 232 (1968).

[19] For a more detailed explanation of the physical meaning of σ, see, e.g., N. W. Ashcroft and D. C. Langreth, Phys. Rev. 159, 500 (1967).

[20] See, e.g., R. Taylor and H. R. Glyde, J. Phys. C 6, 1915 (1976) for calculations pertaining to the solid state.

[21] R. G. Ross, Philos. Mag. 22, 573 (1970); M. Hasegawa, Solid State Commun. 11, 531 (1972); S. Tamaki and Y. Waseda, J. Phys. F 6, L89 (1976).

[22] The resistivity data are taken from P. W. Bridgman, Proc. Am. Acad. Arts Sci. 56, 61 (1920); the equation of state data are obtained by interpolation from I. N. Makarenko, A. M. Nikolaenko, and S. M. Stishov, Liquid Metals, 1976 (The Institute of Physics, London, 1977), p. 79.

[23] F. P. Bundy and H. M. Strong, Solid State Phys. 13, 81 (1962).

[24] J. M. Ziman, *Electrons and Phonons* (Oxford University, England, 1960).