m. If they had set the scattering by the two general sites n and m to zero,

$$T^{(2)}_{nm} = \langle \tau_n + \tau_n \langle G \rangle \tau_m + \tau_n \langle G \rangle \tau_m \langle G \rangle + \cdots \rangle = 0 \; , \qquad (17)$$

formula (12) above would have been obtained. This could, perhaps, be done by modifying their technique only slightly. The generalization of Freed and Cohen[4] also is improper because they also did not set the average scattering by a pair of defects in the medium to zero. In this case they do not even get the proper limit at low concentrations. The generalizations to larger n clusters than two now also seems to be that clearly the average t matrix for scattering each particular n cluster must be set to zero as suggested also in Ref. 2.

The way to perform the formal calculation of scattering by pairs and larger clusters of defects now seems clear, at least within this model containing only diagonal randomness. It would be very useful to see numerical calculations to check the properties of these formulas with regard to the physically expected qualitative features.

Finally, the effect of the disorder at high concentration is becoming quite well understood now, within the model of only diagonal randomness. This model can, however, only be of limited use in real systems,[5] so that more sophisticated physical models, including off-diagonal disorder, should be considered within the spirit of the configuration-averaging techniques now developed for the diagonal model. Some attempts have recently been made along these lines[6] which are useful in certain circumstances.

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Comment on Effective Ion-Ion Interactions in Metals

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It is found that the contributions of both nonlocality in the pseudopotential and exchange correlation in the screening reduce the cutoff radius of the strong screened Coulomb repulsion between ions in metals, thus revealing extra oscillations at short range in the effective interionic interaction. This analysis of the situation resolves some previous puzzles, and lends support to arguments about structural stability based on rearrangements of near neighbors.

Though the interatomic spacing in simple metallic systems is determined primarily by the volume-dependent contributions to the total energy,[1-3] it is the small structure-dependent contributions which govern many of the physically interesting properties of metals and their alloys, including phonon frequencies, elastic constants, and the relative energies of different crystal structures.[3,4] The structure-dependent part of the energy, U_s, can be expressed as a sum over reciprocal lattice vectors g involving the "energy-wave-number characteristic" $\Phi_{bs}(g)$, or alternatively, as a sum of effective screened interionic potentials $\Phi(r)$ in real space. While numerical calculations have almost invariably been done in terms of reciprocal space because the convergence is better, they have often been interpreted with semiquantitative arguments involving the real-space picture of the interaction potential $\Phi(r)$. The latter was found in early work to have a sharp minimum in the region of the nearest-neighbor position.[4] Naturally, this was an appealing result because it suggested correlations between crystal structure and the position of the minimum. Several such interpretations and arguments in terms of $\Phi(r)$ may be found in the recent review article by Heine and Weaire.[3]

Structural arguments based on real-space interatomic potentials are attractive because of their

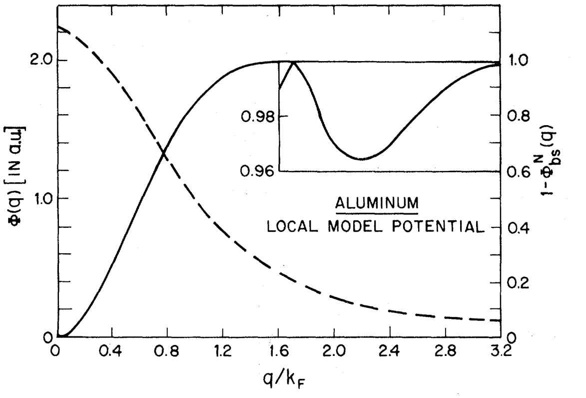

FIG. 1. Functions $1-\Phi^N_{bs}(q)$ (full line) and $\Phi(q)$ (broken line) for aluminum, computed using a local optimized model potential. Note that the sharp cusp in $\Phi^N_{bs}(q)$ at $q \approx 1.6\, k_F$ is smoothed when nonlocality is introduced.

elegant simplicity and physical appeal. Further they seem to have been reasonably successful in explaining distorted structures and the structures of solid solutions.[3,5,6] However, there has been concern about their validity because various authors employing slightly different approximations have obtained rather different $\Phi(r)$ in the region of interest.[7] In fact, sometimes the first few minima, around the nearest-neighbor positions, are completely missing. However, while the $\Phi(r)$ are sensitive to the approximations which are made in constructing the model or pseudopotential, the total structural energy itself does not change very much.[7]

The purpose of this paper is to examine systematically the changes produced in $\Phi(r)$ by two improvements in a simple local-pseudopotential picture of a metal: (a) the introduction of a nonlocal potential and (b) the inclusion of many-electron effects in the screening. This analysis has enabled us to resolve some of the earlier uncertainty about the interpretation of $\Phi(r)$ at short range.

We begin by reviewing a few points very briefly. Recall first that the structure-dependent part of the total energy of a metal can be written in terms of the energy-wave-number characteristic $\Phi_{bs}(q)$ as

$$U_s = U_E + {\sum_q}' |S(q)|^2 \Phi_{bs}(q) , \tag{1}$$

where U_E is the Ewald energy of point ions in a uniform negatively charged background, and $S(q) = N^{-1}\sum_i e^{-i\vec{q}\cdot\vec{r}_i}$ is the usual structure factor for the crystal. Aside from a constant term independent of structure, Eq. (1) can be expressed as a sum over pairwise, screened, effective ionic interactions

$$\Phi(r) = [2(Z^*)^2/\pi] \int_0^\infty [1-\Phi^N_{bs}(q)] j_0(qr)\, dq . \tag{2}$$

We have introduced an effective valence Z^* to account for the possibility of a depletion hole contribution.[8] The function $\Phi^N_{bs}(q)$ is the energy-wave-number characteristic normalized such that $\Phi^N_{bs}(0) = 1$. Equation (2) can easily be rewritten as the Fourier transform of an effective interaction potential in momentum space

$$\Phi(q) = [4\pi(Z^*)^2/\Omega q^2][1-\Phi^N_{bs}(q)] , \tag{3}$$

with Ω the atomic volume.

We start with the pseudopotential theory in its most simplified form, i.e., in a local approximation without exchange. Then $\Phi^N_{bs}(q)$, and hence $\Phi(q)$, is a simple function of the bare (that is unscreened) ion pseudopotential $v^{\text{ion}}(q)$ and the Hartree dielectric function $\epsilon(q)$:

$$\Phi^N_{bs}(q) = \left(\frac{4\pi Z^*}{\Omega q^2}\right)^{-2} [v^{\text{ion}}(q)]^2 \left[1 - \frac{1}{\epsilon(q)}\right] . \tag{4}$$

To illustrate the results obtained, we have plotted in Fig. 1 the functions $[1-\Phi^N_{bs}(q)]$ and $\Phi(q)$ computed from the local form of the optimized model potential[9]

$$V^{\text{ion}}(q) = -(4\pi Z/\Omega q^2) j_0(qR_M) \tag{5}$$

with the model radius R_M as well as Z and Ω appropriate for aluminum. [Note $Z^* = Z$ for an energy-independent potential.] The corresponding $\Phi(r)$, shown as curve 1 in Fig. 2, is typical for all nontransition metals. $\Phi(r)$ rises very steeply at small r ($r < 8$ a.u. in the present case): This is the outer edge of the screened Coulomb repulsion

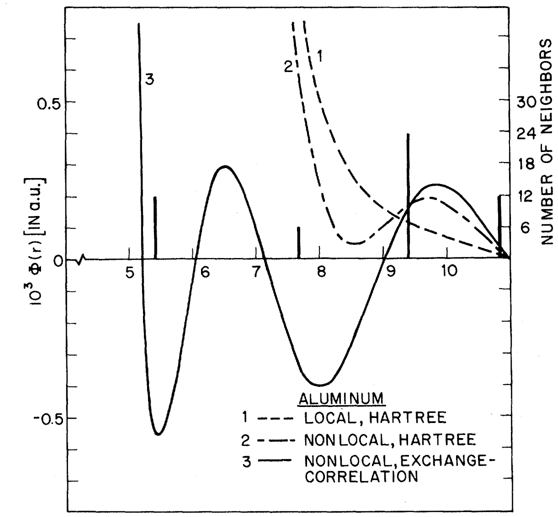

FIG. 2. Interionic potential for aluminum obtained using (1) local-Hartree (2) nonlocal-Hartree and (3) nonlocal-model-potential theory screened with the STLS dielectric function including exchange and correlation (Ref. 14). Neighbor positions for fcc aluminum are indicated.

between the ions, which is very strong on the energy scale of 10^{-3} a.u. of our figure. Then at larger r come oscillations determined primarily by where $\Phi_{bs}^{N}(q)$ drops first to zero. This zero is related to the first node in the pseudopotential form factor at wave-number q_0. When nonlocality is included in the calculation, the zero in $\Phi_{bs}^{N}(q)$ disappears but a pronounced minimum remains, and the oscillations at intermediate r can be attributed to this minimum. Finally, at still larger r, come the Friedel oscillations, which arise entirely from the logarithmic singularity in $\epsilon(q)$ at $q = 2k_F$.

We now relax the first of our approximations and treat properly the nonlocal nature of the ionic pseudopotential while retaining the Hartree approximation for screening.[9] The algebra involved in the calculation of $\Phi_{bs}^{N}(q)$ becomes rather complex and the simple expression (4) is no longer valid. However, numerical results are available for several metals,[7] and we can make use of them in (2) to compute the effective interionic potential. We shall regard the difference between the nonlocal and local calculations as a "correction for nonlocality," $\Delta\Phi_{bs}^{N}(q)$, plotted in Fig. 3. We note that it is quite small around the first few reciprocal-lattice vectors g of the fcc structure, or indeed any other closely packed structure such as hcp or bcc. It therefore does not influence strongly the relative energies of these structures. On the other hand, phonon spectra involve sampling and differencing $\Phi_{bs}^{N}(q)$ over the whole range of q, and in calculations for Na, Al, and Mg it was found that the correct treatment of nonlocality contributed on the order of 10% to the phonon frequencies and improved considerably the agreement with experiment.[10,11] This is the approximate magnitude of correction we would expect from comparing the scales of Figs. 1 and 3.

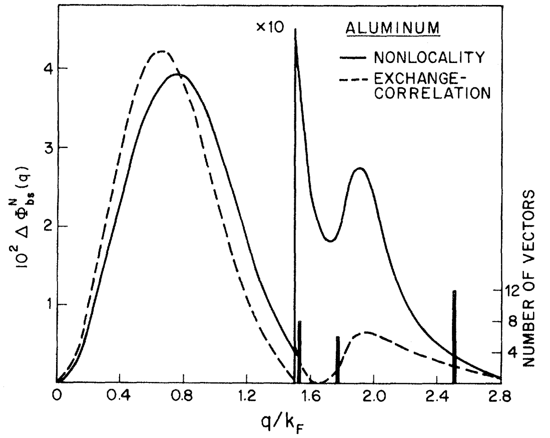

FIG. 3. Corrections to the energy-wave-number characteristic, $\Phi_{bs}^{N}(q)$, for aluminum: (1) when nonlocality is added to the theory but screening remains Hartree; (2) when the nonlocal potential is screened with the STLS (Ref. 14) dielectric function which includes exchange and correlation. Reciprocal lattice vectors are shown.

However the effect of nonlocality on $\Phi(r)$ in Fig. 2 appears at first sight much more drastic: It has produced an extra minimum. What we wish to show is that such a description of the situation is too superficial. We have already noted that the oscillations of $\Phi(r)$ derive from the way $\Phi_{bs}^{N}(q)$ drops to zero (or in the nonlocal calculation has a sharp minimum) at $q_0 \approx 1.6 k_F$ (Fig. 1). These oscillations extend quite far in toward $r = 0$ on the scale of Fig. 2, but are overlaid by the enormously larger screened Coulomb repulsion. At $r = 5$ a.u. we have $q_0 r \approx \frac{5}{2}\pi$ so there may be another oscillation even to the left of the region plotted in Fig. 2. These all appear on the total $\Phi(r)$ as tiny ripples and we can see this for the outermost oscillation on curve 1 of Fig. 2. At $r = 8.5$–9 a.u., $\Phi(r)$ has strong positive curvature like a kink, and at $r \approx 10$ a.u. almost zero curvature. We can therefore regard $\Phi(r)$ in this region as a smoothly decreasing function with a ripple on it.

Now the main part of $\Delta\Phi_{bs}^{N}(q)$ lies in the range $q/k_F \approx 0$–1.6. Since it is positive, its effect is to broaden the central hump of $\Phi_{bs}^{N}(q)$, and hence reduce the screening length of the Coulomb interaction which, as we remarked earlier, is described by this range of q. The strongly repulsive part of $\Phi(r)$ in Fig. 2 is therefore pulled in to lower r, thus exposing the oscillation in the range $r = 8$–11 a.u. which we previously only saw as a ripple on the outer edge of the repulsive interaction.

That the large changes in $\Phi(r)$ arise from the peak in $\Delta\Phi_{bs}^{N}(q)$ around $q/k_F = 0.8$ becomes clear if we write

$$\Delta\Phi(r) = [-2(Z^*)^2/\pi] \int_0^\infty \Delta\Phi_{bs}^{N}(q) j_0(qr)\, dq \,, \qquad (6)$$

and observe that the value of the integral is large only when r is in the range $0 \leq r \lesssim 4\pi$, that is, when the first node in $j_0(qr)$ occurs for $q/k_F \gtrsim 0.25$. It is precisely in this range of r where we observe the greatest changes in $\Phi(r)$ due to the improvements in $\Phi_{bs}^{N}(q)$. Although we have no particular physical arguments to offer, it seems from several calculations that the sign of the contribution is always such as to reduce the range of the strong repulsive interaction and therefore to expose one more oscillation of $\Phi(r)$.

Exchange and correlation can be added very easily to a local calculation by replacing $\epsilon(q)$ in (4) by the "proton" dielectric constant $\epsilon_p(q)$ (refer to Sec. 10 of Ref. 3 and to Ref. 12). The formulation is a little more involved in the nonlocal theory, but it has been shown that the correction term $\Delta\Phi_{bs}^{N}(q)$ can be expressed as a simple function of the "electron" dielectric function $\epsilon_e(q)$ and the form factor $w(q)$ computed in Hartree approximation.[12] In our present example the contribution $\Delta\Phi_{bs}^{N}(q)$ from exchange and correlation is shown in Fig. 3, based on the calcu-

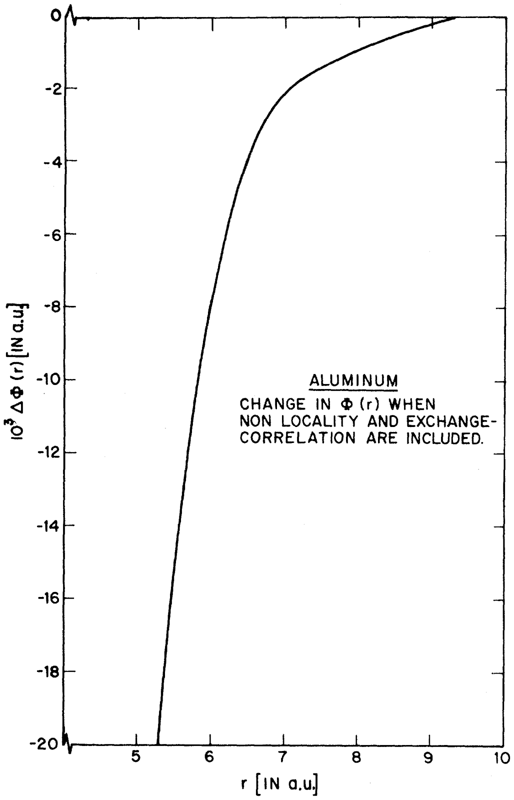

FIG. 4. Difference $\Delta\Phi(r)$ between the interionic potentials 3 and 1 plotted in Fig. 2. This curve illustrates that there are no oscillations present in the difference potential in the range $r=5-9$ a.u. Hence, the oscillations exposed in curve 3 of Fig. 2 were in fact present in the $\Phi(r)$ computed in the local Hartree approximation but were masked by the strong short-range repulsive part of the potential.

lations of Shyu *et al.*[13] using the Singwi-Tosi-Land-Sjölander (STLS)[14] form of the exchange and correlation. Similar results are obtained from the Toigo-Woodruff[15] calculation of exchange and correlation.

The corresponding $\Phi(r)$ is shown as the third curve in Fig. 2. Similar results for a number of simple metals have been obtained by Shyu *et al.*[13] Our purpose here is not so much to describe the calculation of $\Phi(r)$ as to provide some interpretation of the resulting interaction potential. As expected from Fig. 3, the effect of adding exchange correlation is similar to that of nonlocality, in the sense that the repulsive part of $\Phi(r)$ is drawn in to still lower r, thus revealing one further oscillation. This is further evidence that the corrections $\Delta\Phi_{bs}^{N}(q)$ do not themselves originate the oscillations, because the $\Delta\Phi_{bs}^{N}(q)$ for nonlocality and exchange correlation are remarkably similar, whereas the former first produces one oscillation and the other then one more oscillation *in a different place*. The only way to make sense of these results is in terms of rolling back the strong repulsion to reveal the oscillations.

To document this even further, we plot in Fig. 4 the $\Delta\Phi(r)$ from nonlocality and exchange correlation combined, i.e., the difference between curves 1 and 3 from Fig. 2. Even after allowing for the difference in scale, we see $\Delta\Phi(r)$ has no oscillations in the range $r=5.0-9.0$ a.u. of the magnitude of those in curve 3 of Fig. 2. Thus, the oscillations in the final $\Phi(r)$ (curve 3) must be present already in the nonlocal Hartree approximation, curve 1 of Fig. 2.

In the case of exchange correlation we can provide a general argument about the sign and magnitude of its effect on $\Phi(r)$ by calculating $\Phi(q=0)$, the integral of $\Phi(r)$ over all space. To simplify the argument we shall consider the local-model potential [Eqs. (4) and (5)] with the Hartree dielectric function replaced by $\epsilon_p(q)$. The $\lim_{q\to 0}\Phi(q)$ can now be evaluated directly and we obtain

$$\Phi(q=0)=\tfrac{2}{3}E_F^0 Z\,[1+\tfrac{1}{3}(k_{TF}R_M)^2-\gamma(k_{TF}/k_F)^2] \quad (7)$$

with k_{TF} the usual Thomas-Fermi screening parameter, k_F the Fermi wave-number, and E_F^0 the free-electron Fermi energy. The first two terms in this equation derive from the local model potential screened in Hartree approximation. The last term represents the effect of exchange correlation and the parameter γ is determined by the compressibility sum rule. [For a more detailed discussion of $\epsilon_p(q)$ and the origin of the parameter γ refer to Refs. 3, 12, 14, and 15. γ is identical to the parameter a in Eq. (10.59) of Ref. 3. For exchange alone, $\gamma=\frac{1}{4}$.] We find that the reduction in $\Phi(q=0)$ is typically about 10% and this is in agreement with typical improvements in phonon frequencies.[10,11]

The reduction occurs because exchange and correlation, by keeping electrons automatically out of one another's way, allow the screening electron cloud to shrink around the positive ion. Since at short distances the interionic potential is just the bare Coulomb potential, we must interpret the reduction in the integral of the potential as a reduction in the screening range, as seen in Fig. 2 for $\Phi(r)$. Clearly, it is a general and substantial effect.

We have seen, therefore, that both nonlocality and exchange-correlation tend to reduce noticeably the range of the strong screened Coulomb repulsion between ions. Thus, they tend to reveal some further oscillations in the effective ionic interaction $\Phi(r)$ which are otherwise present only as small ripples on the much stronger repulsion.

How does all this affect the discussions about crystal structures in terms of the real-space interaction $\Phi(r)$? A typical argument concerns the stability of the fcc structure in aluminum to a tetragonal shear, as found in indium. Since a small shear involves only small atomic displacements while keeping the volume of the cell constant, the calculation of the energy from (1) involves the first and particularly the second differential coefficient of $\Phi_{bs}(q)$. We see these are not strongly affected by the corrections $\Delta\Phi_{bs}^{N}(q)$ in Fig. 3, certainly not by the main hump at $q/k_F = 0.8$, because all the reciprocal-lattice vectors lie beyond it. Similarly, calculating the energy of the shear in terms of the real-space interaction $\Phi(r)$ would involve differentiating it at the atomic positions.[16] A large contribution comes from the oscillations, irrespective of whether they are exposed as in curve 3 of Fig. 2 or whether they are a ripple on a strong repulsion as in curve 1. The change in the repulsive part brought about by the low-q hump in $\Delta\Phi_{bs}^{N}(q)$ (Fig. 3) is a smooth function which does not affect the result, in agreement with the description in reciprocal space.

A different type of situation involves much larger atomic rearrangements, e.g., a comparison of fcc with the diamond structure. The latter has reciprocal-lattice vectors at $q/k_F \sim 1$. Therefore, the main hump of $\Delta\Phi_{bs}^{N}(q)$ (Fig. 3) does contribute to the total energy. Correspondingly in real space the two structures have a 25% difference in nearest-neighbor distances d (at the same volume) and, consequently, it is crucial where the sharp rise in $\Phi(r)$ comes relative to them. For the case of aluminum which we have been considering, we might argue on the basis of curve 3 in Fig. 2 that the fcc structure with $d = 5.4$ a.u. is likely to be much more stable than the diamond structure with $d \cong 4.2$ a.u. Detailed calculations confirm this qualitative reasoning.

The results we have presented tend to increase confidence in structural arguments based on the real-space interaction $\Phi(r)$, which in any case are only a physical interpretation of difficult calculations which are usually done in reciprocal space, for reasons of convergence. We have found that both nonlocality and exchange-correlation reduce the range of the screened Coulomb repulsion, and it appears, from the calculations we have presented, that there is indeed a minimum in $\Phi(r)$ around the nearest-neighbor position. This lends some support to earlier structural arguments based on qualitative interpretation of interionic interactions in which such a minimum has usually been assumed. However, further calculations taking careful account of exchange-correlation and nonlocality are clearly needed to confirm in general the results we have presented here.[13,17] It is known that inclusion of these improvements in the theory leads to markedly better agreement with experiment for the phonon spectra of several metals,[10,11] and apparently they are equally important for a discussion of the real-space interaction $\Phi(r)$.

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