

Interionic Potential in Aluminum

M. S. Duesbery and Roger Taylor

National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

(Received 15 September 1972)

It is suggested that, contrary to recent calculations, the interionic potential in aluminum does not have a negative potential well in the vicinity of the first neighbor. Also, it is demonstrated that the calculated Al potential is extremely sensitive to the choice of electron-gas screening and that any screening function which does not satisfy the compressibility theorem accurately gives unreliable results.

The purpose of this paper is to discuss the functional form of the interionic potential in aluminum. It is well known that a calculation of the interionic potential in simple metals is sensitive to the choice of electron-gas screening,¹⁻⁴ and aluminum is no exception to this rule. In Fig. 1 are illustrated three aluminum potentials all calculated with the same electron-ion interaction, a one-orthogonalized-plane-wave (OPW) model in which the non-local terms were retained explicitly. The three potentials were calculated using (i) Geldart and Taylor⁵ (GT) screening, (ii) Singwi *et al.*⁶ (SSTL) screening, and (iii) a modified SSTL screening obtained by adjusting the constant A in Table IV of their paper so that the compressibility theorem⁷ is satisfied exactly. Clearly, the principal differences between these potentials is in the vicinity of the first neighbor. The SSTL screening gives a deep negative well with a minimum just beyond the first-neighbor distance, whereas the other two remain positive until just before the second-neighbor distance, from which point on all three potentials are quite similar. The question is: Which one is the more likely to be correct?

Recently Shyu *et al.*³ and Shaw and Heine,⁴ both using SSTL screening, have calculated Al potentials which contain a deep negative well at the first-neighbor distance. This result is consistent with structural arguments based on interionic forces. However, one must remember that a metal is not held together solely by two-body effective interionic forces, but that a key role is played by the volume-dependent forces arising from the ground-state energy of the conduction electrons. Hence it is not at all necessary that there should be a potential well at the first-neighbor distance, and we shall show that the available experimental evidence suggests that the potential in aluminum should take a form similar to that generated using GT screening.

Consider first the formation of a vacancy. This results in a change in volume v_f , giving rise to an energy shift ΔE_v , due to the volume-dependent forces given by

$$\Delta E_v = \frac{1}{2}[v_f(c_{12} - c_{44})], \quad (1)$$

where c_{12} and c_{44} are elastic constants. By measuring the electrical resistance quenched into a sample of aluminum at different pressures Emrick and McArdle⁸ have deduced a value of $v_f = 0.62v_a$, where v_a is the atomic volume. Using the elastic constants of Kamm and Alers,⁹ Eq. (1) gives $\Delta E_v = 1.0$ eV, which should be compared with the measured value of the formation energy of a vacancy $E_f = 0.65$ eV.¹⁰⁻¹² Admittedly, there is some uncertainty in v_f , but even if we take v_f to be as low as $0.5v_a$ we obtain $\Delta E_v = 0.83$ eV, which is still significantly larger than E_f . Thus the contribution to E_f from the two-body forces ΔE_i must be negative, meaning that the ionic lattice must actually lose energy by the removal of one ion. This will not happen if the potential has a deep

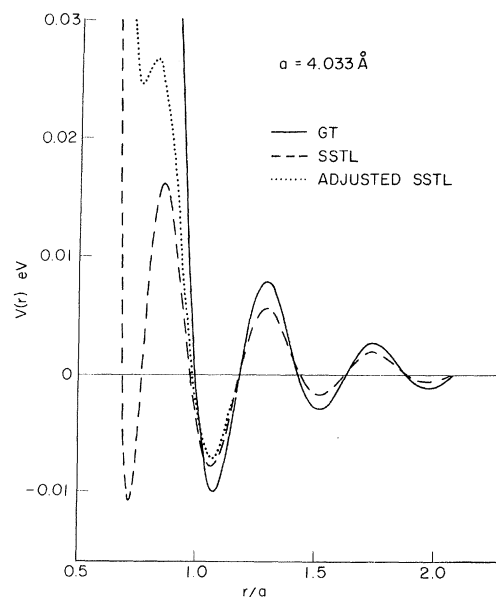


FIG. 1. Aluminum interionic potentials calculated using three different approximations to electron-gas screening.

negative well at the first-neighbor distance. To a zeroth-order approximation the necessary nearest-neighbor interaction can be estimated at about one-sixth of the discrepancy, suggesting a value of order 0.06 eV. Allowing for relaxations which always lower the calculated energy, it seems likely that the first-neighbor interaction should be even higher than this estimate.

Let us now turn to the structure factor $S(q)$ of liquid aluminum measured by Ruppertsberg and Wehr.¹³ These authors attempted to determine the interionic potential from $S(q)$ by using the Percus-Yevick and hypernetted chain theories. They concluded that neither of these theories is applicable to liquid metals, in agreement with North *et al.*,¹⁴ who did similar work on lead. In both cases, though, this conclusion is based solely on the hypothesis that the first neighbor must sit in a negative potential well, an assumption that is not warranted. An examination of the pair potentials calculated by Ruppertsberg and Wehr¹³ from their liquid-aluminum data shows that they are similar to the GT and modified SSTL potentials in Fig. 1 in that they do not go negative until approximately the second-neighbor distance. Hence, subject to the validity of the Percus-Yevick and hypernetted chain theories, the liquid-Al data lend further support to the contention that the Al interionic potential is positive at the first-neighbor distance.

A further piece of circumstantial evidence is furnished by the Gilat-Nicklow¹⁵ force-constant analysis of the experimental phonon dispersion curves. Their first-neighbor tangential force constant $\alpha_3^1 = (1/r) (dV/dr)$, where V is the interionic potential, takes the value $\alpha_3^1 = -1337$ dyn/cm. This indicates a very steep slope in $V(r)$ at the first neighbor, which suggests that a minimum in $V(r)$ is unlikely to occur near that point. It is interesting to note that Shyu *et al.*³ calculate $\alpha_3^1 = -232$ dyn/cm, which is off by a factor of 6. We obtain a similar result with SSTL screening, whereas the other two potentials in Fig. 1 give $\alpha_3^1 \approx -800$ dyn/cm, which is rather more reasonable though still not large enough numerically. Shyu *et al.*³ also quote results obtained using Shaw-Pynn¹⁶ screening parameters giving rise to yet another potential positive at the first neighbor. In this case they obtained $\alpha_3^1 = -925$ dyn/cm. We should mention, however, that Leigh *et al.*¹⁷ have pointed out that some force-constant analyses are not unique. But their arguments apply only to situations where the polarization vectors of the

phonons are not known, which is not the case in aluminum.

At this point it is clear that the experimental evidence favors an Al potential similar to one calculated using GT screening rather than one using SSTL screening. But to complete the argument it is important to understand why it is that these two screening functions give such different results for small r . Let us first make the point that all of the oscillations in a metallic interionic potential, including the first well, are manifestations of the well-known charge-density oscillations in an electron gas. Without any electron screening the interionic potential is purely Coulombic, where no significant overlap between ions occurs. When screening is introduced this Coulombic potential is rapidly canceled out as r is increased, leaving behind only the long-range oscillations. To a rough approximation the Coulombic potential is replaced by a Yukawa potential $e^{-\lambda r}/r$, where λ^2 is proportional to the magnitude of the electron-gas screening function $\pi(q)$ at $q=0$. Thus, the larger the value of $\pi(0)$ the more rapidly is the Coulombic potential canceled out. Now it is well known that $\pi(0)$ is determined by the compressibility of the electron gas,⁷ which fortunately is insensitive to different approximations to the correlation energy. $\pi_{GT}(0)$ has been constructed to satisfy the compressibility theorem. On the other hand, $\pi_{SSTL}(0)$ is somewhat too large at Al density; however, the authors⁶ indicate that they consider this deviation from the compressibility theorem not to be significant. Unfortunately, this is not the case. As we have already stated, we adjusted the SSTL A parameters such that the compressibility theorem was satisfied and thus generated a potential similar to that resulting from the use of $\pi_{GT}(q)$. Quite clearly, the larger value of $\pi_{SSTL}(0)$ has resulted in a more rapid cancellation of the Coulombic potential, giving rise to an earlier onset of the long-range oscillations than should actually occur. Hence we see that any electron-gas screening or dielectric function must at least satisfy the compressibility theorem in order to give reliable results, and deviations from this theorem cannot be tolerated.

In conclusion, the available experimental and theoretical evidence supports the view that the first neighbor in Al does not lie in a deep negative potential well. Also, it is quite clear that the choice of screening is most critical and that the minimum requirement of any screening function is that it must satisfy the compressibility theorem accurately.

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VOLUME 7, NUMBER 6

15 MARCH 1973

Diamagnetic Susceptibility of Lithium*

Sarada P. Mohanty

Department of Physics, Utkal University, Bhubaneswar-4, Orissa, India

Prasanta K. Misra†

Department of Physics, University of Texas, Austin, Texas 78712

(Received 31 July 1972)

We have calculated the diamagnetic susceptibility of lithium using an expression derived by us recently, since no reliable theoretical result is available. We compare our result with available experimental and theoretical results.

The diamagnetic susceptibility of lithium was first calculated by Kjeldaas and Kohn.¹ They used a generalized effective-mass theory and took into account fourth-order terms in the expansion of $\bar{k} - \bar{k}_0$. However, their result is only of limited usefulness, since they considered the very special case of electrons confined to the vicinity of the top or bottom of an energy band. Furthermore, the ratio of the second to the first term in the expansion in powers of k_0 is 0.6 for lithium, so that higher-order terms may also be important in their calculation.

Fletcher and Larson² calculated the diamagnetic susceptibility of lithium by applying the Landau-Peierls³ formula to the equilibrium quasiparticle energy calculated in the Bohm-Pines⁴ theory of electron correlation, and by modifying their Coulomb-gas calculations by using a band effective mass. However, their result is not reliable since there are other contributions to the diamagnetic susceptibility which are of the same order of magnitude as the Landau-Peierls term⁵ and further, as evident from Kjeldaas and Kohn's result,¹ the effective-mass formalism does not yield correct results for lithium. Glasser⁶ calculated the diamagnetic susceptibility of lithium by subtracting from his result for the magnetic susceptibility the

result for the paramagnetic susceptibility calculated from Abe's expression.⁷ However, it has been shown⁵ that the difference between Glasser's expression for magnetic susceptibility and Abe's expression for paramagnetic susceptibility is identically equal to Misra and Roth's⁵ expression for diamagnetic susceptibility obtained by using nondegenerate perturbation theory. Therefore, Glasser's result is not reliable, since, because of the strong pseudopotential, the nondegenerate perturbation theory is not valid for lithium.

Misra and Roth⁵ calculated the diamagnetic susceptibility of the alkali metals from their general expression for diamagnetic susceptibility of simple metals, which was derived through the use of a pseudopotential formalism and degenerate perturbation theory. However, we have recently shown⁸ that there is a difficulty in using Misra and Roth's expression for metals for which either the Fourier components of the pseudopotential are strong, or for which there is a neck in the Fermi surface. From the model-potential form factors calculated by Animalu and Heine and tabulated by Harrison,⁹ we note that the pseudopotential is strong for the (110) and (200) G shells of lithium while the pseudopotential for the other G shells of lithium, as well as the pseudopotentials of all the other alkali met-