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# Crystal and electronic structure of metallic lithium at low temperatures

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With the use of traditional Hartree-Fock small-atomic-cluster techniques to simulate perfect infinite Li crystals, *ab initio* total-energy calculations have been performed for several competing Li crystal structures. Despite the inherent limitations and approximations of the method, the results of the calculations are in accord with Overhauser's prediction about a low-temperature complex $9R$ phase. Furthermore, using clusters of varying size and complexity, several key physical quantities of the $9R$, bcc, fcc, and hcp phases have been calculated with good accuracy for the experimentally known quantities. The predictions for the yet unmeasured quantities suggest simple alternative experimental tests of the calculation.

Recently[1] Overhauser has suggested that the ground-state crystal structure of metallic lithium is of the $9R$ complex close-packed type, similar to the structure of samarium. Contrary to earlier suggestions[2] about the new phase resulting by a structural phase transformation on cooling at low temperatures, a recent study[3] has shown that the ground-state crystal structure is neither hexagonal close packed (hcp) nor face-centered cubic (fcc). The $9R$ complex close-packed structure, suggested by Overhauser fits all crystallographic requirements of the observed polycrystalline diffraction pattern at low temperatures (4.2 K). This work was strongly motivated by Overhauser's proposal and the intriguing possibility of testing this and also of examining the electronic features of the low-temperature structure in the most computationally economical way.

After considering most of the possible advantages and disadvantages, the *ab initio* unrestricted Hartree-Fock (UHF) cluster method was adopted for this work (for lack of anything better under the circumstances). Both, the choice of the UHF to perform the extensive total energy calculations together with the finite-cluster-size representation of the infinite metal can be criticized, not quite unjustifiably, as rather poor. On the other hand, besides the legitimate but trivial argument of judging the suitability of a method of calculation from the results it can produce, there is some further evidence for the plausibility of this choice. Marshall *et al.*[4] have concluded by comparing results for small Li clusters that the UHF method is the most accurate available simple Hartree-Fock type of method which also produces results in fair agreement with the often accepted as more accurate $X\alpha$ method. These conclusions have been also verified by more recent calculations,[5] which, although pointed out the need for inclusion of the configuration interaction (CI), confirmed that considering a balance of reliability and computational cost, the UHF is the most appropriate method in comparison to other simple approaches to study metal clusters. With reference to the finite size of the cluster, available evidence from Be clusters tends to suggest that several experimental quantities, such as the work-function approach the bulk value by the time the cluster size is about 10—15 Å.[4] This "criterion" for the size of the clusters is more or less satisfied in the present calculation. However, binding energies of metallic systems are expected to depend stronger on the cluster size and, more important, on correlation effects. Kunz and Klein[6] have examined, in more detail, the general problem associated with the finite cluster size. The problem of correlation should be addressed within the framework of the CI cluster method,[5] or within second- (and higher-) order perturbation theory.[7] Both methods appear to require an enormous computer time and space often at the expense of cluster size and number of basis functions. Note however that sometimes proper correlation corrections for the infinite system,[8] when included for finite clusters often are counterbalanced by short-range correlations due to the relaxation of the orbitals.[4] In any case, most of these effects are expected to depend only weakly on to the cluster geometry for given nearest-neighbor distance, cluster size, and basis set, and for not large variation of the coordination number.[9] Therefore, since this is mainly a comparative study of total binding energies to search for the geometrical structure with the highest binding energy among the best candidates, most of the drawbacks mentioned above could be assumed to be less serious. Other secondary approximations usually made in such types of calculations[10] do not seem to have any significant effect here.

Four different geometrical structures bcc, fcc, hcp, and $9R$ have been mainly examined here. The basis functions and the cluster size are approximately the same in all four cases, in order to reduce spurious effects resulting from a difference of basis sets or number of atoms in the cluster. To this end, as will be explained in this section, parallel sets of calculations have been run with rich basis but small clusters on one hand (not smaller than 13 atoms), and poor basis and larger clusters on the other. The small set of basis functions (set 1) is comprised of five Gaussian-type orbitals (GTO) for each Li atom, contracted out of twelve primitive Gaussians. The larger set (set 2) consists of nine GTO's contracted out of the same twelve primitive Gaussians but without any *s* contrac-

TABLE I. GTO—basis set used for Li. Note: Set 2 of basis functions is the same as set 1 but without any *s* contractions.

| Orbital type | Exponents | Set 1 Contraction coefficients |
|---|---|---|
| *s* | 266.274 69 | 0.006 38 |
| | 40.048 14 | 0.047 00 |
| | 9.028 71 | 0.200 00 |
| | 2.433 00 | 0.479 13 |
| | 0.710 63 | 0.420 24 |
| | 0.047 79 | 1.000 00 |
| *p* | 0.080 00 | 0.738 88 |
| | 0.020 00 | 0.673 84 |

tions, giving more flexibility to the *s*-type orbitals. The contraction coefficients and exponents of both sets are shown in Table I.

The clusters used to approximate the four crystal structures under study fall roughly into two categories. The clusters in the first category, utilize the large basis set (nine GTO's) and include at least first and second near atomic neighbors, thus stressing the importance of the right coordination and rich basis set to get better binding. In the second class of clusters, the smaller set of basis set is used, but a larger number of atoms is contained emphasizing the packing of layers along the $c$ axis of the hexagonal unit cell. Let us loosely call, for brevity, the former class of clusters the "binding clusters" and the second category the "packing clusters." The binding cluster for the fcc structure contains, in a cubic set of axis with cube edge $a$, the atom at (0,0,0) and its twelve nearest neighbors obtained from the "prototype" atom at $(\pm a/2, \pm a/2, 0)$ by interchanging signs and position of the 0. In the same cubic set of axis the bcc binding cluster includes, besides the atom at the origin, the eight first and six second nearest neighbors, obtained, as before, from the atoms at $(\pm a/2, \pm a/2, \mp a/2)$ and $(\pm a, 0, 0)$, respectively, by changing signs and position of 0. The coordinates of the thirteen atoms of the hcp binding cluster are shown in Table II under the columns of layers $A$ and $B$ (seven atoms from the column of layer $A$ with $z=0$ and six atoms from the column of layer $B$ with $z=\pm\frac{1}{2}$). Similarly to the hcp, the reference binding cluster for the $9R$ phase can be constructed from Table II by taking the seven $A$ atoms with $z=0$, the three $B$-type atoms with $z=+\frac{1}{2}$, and the three $C$-type atoms with $z=-\frac{1}{2}$. This cluster as is, without the use of additional packing clusters, cannot be uniquely associated with the $9R$ phase since the sequence $BAC$ of packing layers also appears, for instance, in the $4H$ structure $AB\,AC\,AB\,AC\ldots$. The need for the so-named "packing clusters" now becomes evident. In Table II, as has been already mentioned, the coordinates (lattice and cartesian) of the cluster atoms in the three packing types $A$, $B$, and $C$ are given in standard notation. The vertical coordinate of the layers, $z$, is expressed in units of $c \equiv \sqrt{8/3}a$, and takes the values $\pm 2, \pm\frac{3}{2}, \pm 1, \pm\frac{1}{2}, 0$. Thus, the longest $9R$ cluster has length $\frac{9}{2}\sqrt{8/3}a$, which is also the length of the $c$ axis of the $9R$ hexagonal unit cell. The largest $9R$ packing cluster should include the sequence of layers:

$$B(+2)\,C(+\tfrac{3}{2})\,B(+1)\,C(+\tfrac{1}{2})\,A(0)\,C(-\tfrac{1}{2})\,A(-1)\,B(-\tfrac{3}{2})\,A(-2)\;,$$

where the numbers in the parenthesis, after the packing symbol denote the value of $z$ in units of $c$. However, for the purpose of uniquely distinguishing between the two $9R$ and the $6R$ sequences, which possess the two largest periodicities, the two extreme layers $B(+2)$ and $A(-2)$ are not needed and have been eliminated from the above sequence. Thus, the $9R$ packing cluster consists of the sequence:

TABLE II. Coordinates of the layers $A,B,C$ in units of the hcp lattice lengths $(a,a,c)$. $c=\sqrt{8/3}a$. For the fcc lattice $c=\sqrt{6}a$.

| Layer $A$ | | Layer $B$ | | Layer $C$ | |
|---|---|---|---|---|---|
| Lattice $(a,a,c)$ | Cartesian $(a,a,c)$ | Lattice $(a,a,c)$ | Cartesian $(a,a,c)$ | Lattice $(a,a,c)$ | Cartesian $(a,a,c)$ |
| $0,0,z$ | $0,0,z$ | $\frac{2}{3},\frac{1}{3},z$ | $\frac{1}{2},\sqrt{3}/6,z$ | $\frac{1}{3},\frac{2}{3},z$ | $\frac{1}{2},-\sqrt{3}/6,z$ |
| $1,1z$ | $\frac{1}{2},\sqrt{3}/2,z$ | $-\frac{1}{3},\frac{1}{3},z$ | $-\frac{1}{2},\sqrt{3}/6,z$ | $\frac{1}{3},-\frac{1}{3},z$ | $-\frac{1}{2},-\sqrt{3}/6,z$ |
| $0,1,z$ | $-\frac{1}{2},\sqrt{3}/2,z$ | $-\frac{1}{3},-\frac{2}{3},z$ | $0,-\sqrt{3}/3,z$ | $-\frac{2}{3},-\frac{1}{3},z$ | $0,\sqrt{3}/3,z$ |
| $-1,0,z$ | $-1,0,z$ | | | | |
| $-1,-1,z$ | $-\frac{1}{2},-\sqrt{3}/2,z$ | | | | |
| $0,-1,z$ | $\frac{1}{2},-\sqrt{3}/2,z$ | | | | |
| $1,0,z$ | $1,0,z$ | | | | |

$$C(+\tfrac{3}{2})B(+1)C(+\tfrac{1}{2})A(0)C(-\tfrac{1}{2})A(-1)B(-\tfrac{3}{2})\,,$$

which includes 25 atoms [three atoms for each layer above or below the reference layer $A(0)$ which includes seven atoms as in Table II] and a total of 125 basis functions (set 1 in Table I). This number of basis functions and atoms almost exhausts the practical limitations of computer time and space, especially in view of the repeated number of calculations required, for several packing sequences and distances. The corresponding packing cluster for the $6R$ structure is

$$A(+\tfrac{3}{2})B(+1)C(+\tfrac{1}{2})A(0)C(-\tfrac{1}{2})B(-1)A(-\tfrac{3}{2})\,,$$

with similar construction for the hcp ($AB\,AB\ldots$) and the $4H$ packing clusters. It should be mentioned here that although these packing clusters can by no means describe correctly the binding process of the corresponding bulk crystals, nevertheless it is believed (after testing a few distinct cases) that they should be able to provide relative energy differences with estimated errors smaller than the magnitude of these energy differences. In addition to these large clusters, smaller size clusters were also used, where necessary, for comparisons with the corresponding binding clusters. The common reference cluster between the binding and the packing clusters was primarily the hcp thirteen-atom cluster and to a smaller degree the thirteen-atom fcc cluster. The thirteen-atom fcc packing cluster is obtained from Table II [seven $A(0)$ atoms, three $B(-\frac{1}{2})$ atoms, and three $C(+\frac{1}{2})$ atoms] by setting $c=\sqrt{6a}$.

The procedure used in this calculation was first, to establish that the $9R$ structure has the lower possible total energy compared to the other structures considered, and second, to include corrections into the $9R$ binding energy by considering the differences in energy between the binding and packing clusters. Within the expressed limitations of the method of calculation and well within the expected errors the first part was confirmed by both type of clusters. The corrections of the second part were incorporated by scaling down the difference in total energy per atom between the hcp and $9R$ packing and binding clusters for given values of the lattice constant $a$. These "rationalized" differences were then algebraically added to the $9R$ binding energy given by the small binding cluster. The magnitude of this correction was also checked by comparing the $9R$ and hcp total energies with the fcc values. This procedure, was repeated for each value of $a$, giving the total binding energy as a function of nearest-neighbor distance. The final total binding energy curves for all four structures are shown in Fig. 1.

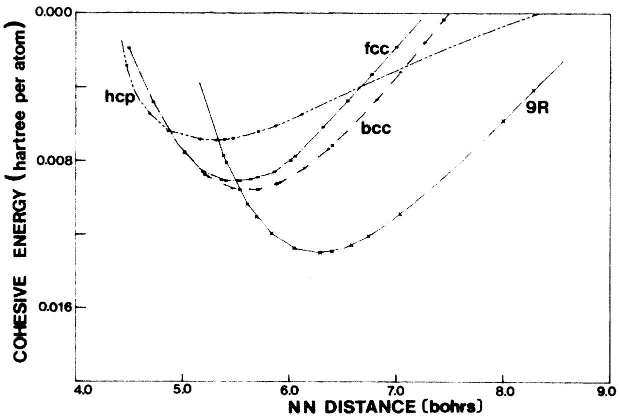

FIG. 1. Total binding energy per atom versus nearest-neighbor distance. Solid line represents the $9R$ structure. Long-dashed line stands for the bcc structure, dashed-dotted line represents the fcc structure, and short-dashed line the hcp structure.

It can be seen clearly from Fig. 1, as was already stated, that the $9R$ phase has the lowest energy with a difference of 0.08 eV from the bcc phase. This energy difference seems to be unrealistically large because in an order of magnitude estimate it appears to imply a much larger transition temperature than the 70 K found experimentally. This exaggerated energy difference besides the main approximations (adiabatic, UHF, etc.) should in a substantial part be traced to spurious effects due to the "renormalization process" of the energy differences described earlier and to the small size of the clusters, which could create unrealistic "surface effects." Wherever possible these effects have been checked and their magnitude was estimated to be quite smaller than the energy differences themselves. The same comments should apply also to the nearest-neighbor distance which shows some unrealistically large fluctuations for the different phases. Contrary to the differences in the binding energies, the absolute values of the binding energies are greatly underestimated as was expected from earlier calculations of metallic clusters[4] and from the discussion about the drawbacks of the method above. Simple remedies[9] to correct the absolute values of the binding energies were not attempted since this is a comparative study and only the differences in binding energies are important. On the other hand, the shape of the binding-energy curves around the minimum seems to be extremely well described. The force constant ($CF$), directly related to some type of averaged phonon frequency, $CF=m\langle\omega^2\rangle$, calculated out of the bcc binding curve is in extremely good agreement (well within the uncertainty) with the experimental value quoted in the literature.[11] Similarly, the value for the bulk modules $B$ obtained here $B=0.099\times10^{12}$ dyn/cm$^2$ is in fair agreement with the experimental value of $0.11\times10^{12}$ dyn/cm$^2$. These results are very important, since they have been obtained by such a simple method and with this type of success. Good values of $B$ for the bcc phase have been also obtained earlier in a similar type of calculation.[12] Several important results of this calculation, besides the binding energy and the force constants, have been summarized in Table III. With the exception of the binding energies all other quantities are in reasonable to very good agreement with experiment for the bcc phase. For the other phases, not known experimental data exist at this time to test the predictions of this work. The column marked "estimated" cohesive energy is simply obtained from column 2 by adjusting the bcc binding energy to have the correct value, for the purpose of predictions. The work functions in the fourth column are simple Koopman's values. If the relaxation of

TABLE III. Results of this calculation for the four structures of Li examined here, together with the corresponding experimental data for the bcc phase. NN denotes nearest neighbor.

| Structure | Equillibrium NN distance (bohrs) | Calculated binding energy per atom (mhartree/atom) | Force const. $m\langle\omega^2\rangle$ (eV/Å$^2$) | Work function $W$ (eV) | Fermi energy $\varepsilon_F$ (eV) | "Estimated" cohesive energy (eV/atom) | Li 1*s* binding energies/(eV) |
|---|---|---|---|---|---|---|---|
| bcc | 5.57 | 10.12 | 0.81 | 3.3 | 4.1 | 1.50 | −59.50 |
| 9*R* | 6.25 | 13.01 | 0.86 | 4.1 | 5.0 | 1.58 | −60.86 |
| fcc | 5.70 | 9.67 | 0.87 | 3.8 | 5.1 | 1.49 | −61.40 |
| hcp | 5.50 | 7.60 | 1.35 | 4.0 | 3.6 | 1.43 | −60.44 |
| exp (bcc) | 5.65[a] | 55.15[a] | 0.73[b] | 2.38[a] | 3.95[c] | 1.50[a] | −59.48[d] |

[a] Values quoted in Ref. 4.

[b] This value estimated in Ref. 11 from the Debye temperature $\Theta_D$, carries an error of up to 25%.

[c] Augmented plane wave value quoted in Ref. 11.

[d] From Ref. 14.

the orbitals is taken into account by performing ΔSCF (SCF, self-consistent field) calculations the bcc value becomes 2.5 eV in much closer agreement with experiment. Finally and most important, the last column gives the 1*s*-core binding energies obtained by ΔSCF-UHF calculation without the need for any additional atomic-like corrections.[13] For the bcc phase the agreement with experiment[14] is excellent, meaning perhaps an extremely small atomic-like contribution besides relaxation, in the spirit of Ref. 13. This good agreement, allows more confidence of the predictions for the other phases (9*R*), which in any case are open to experimental test.

Two of the predictions about 9*R* phase deserve special attention. First, the averaged phonon frequency of the new phase although slightly larger (in the correct direction for explaining the lack of superconductivity) is essentially the same as in the bcc phase. This seems to be in accordance with the results obtained by Overhauser and his co-workers[15] and indicates that, the lack of superconductivity in Li should be mainly due to the electronic contribution. Second, the 1*s*-core binding energies estimated here with very good accuracy should be among the best candidates for an excellent experimental test of the validity of the present predictions.

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