Crystals from metallic clusters: A first-principles calculation

A. P. Seitsonen, M. J. Puska, M. Alatalo, and R. M. Nieminen
Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland

V. Milman and M. C. Payne
Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, United Kingdom
(Received 16 February 1993)

The interactions of the "magic" $Al_{12}Si$ clusters are studied by first-principles electron-structure calculations. It is shown that clusters arranged into the fcc lattice do not conserve their separated-cluster icosahedral structure but coalesce to form a close-packed metal.

Recently, Khanna and Jena[1] suggested that new kinds of materials could be constructed out of the most stable metallic clusters. One such cluster is $Al_{12}Si$, in which the Si atom is at the center and forms with the surrounding 12 Al atoms a regular icosahedron. In addition to its compact geometry, the cluster also has a "closed-shell" electron structure for the 40 valence electrons, and is thus expected to have an unusually high stability among the metallic clusters. Indeed, Khanna and Jena[1] found that the binding energy of $Al_{12}Si$ exceeds that of the similar-structure Al_{13} by several eV.

Khanna and Jena[1] were not, however, able to make total energy calculations for a solid composed of $Al_{12}Si$ clusters. Manninen *et al.*[2] calculated the band structure of a fcc lattice composed of spherical potential wells mimicking the potential felt by the valence electrons. The lattice constant was left as a parameter in the calculation. Manninen *et al.*[2] found that there is a band gap between the occupied and unoccupied electron energy levels already when the distance between neighboring wells is about $1a_0$. This calculation shows that the fcc-$Al_{12}Si$ solid could be a system bound together by van der Waals interactions, resembling the solid fullerene. In this paper we report on first-principles total energy electron-structure calculations showing that this kind of solid *cannot* be achieved with $Al_{12}Si$ clusters.

Our calculations for the fcc-$Al_{12}Si$ are performed using a method[3] derived from the one suggested by Car and Parrinello.[4] In short, the electron exchange and correlation are treated in the local-density approximation (LDA).[5] The ion cores are described by pseudopotentials[6] and a plane-wave expansion with a cutoff energy of 180 eV is used for the valence electron wave functions. The expansion coefficients are found by the conjugate gradient method.[7] The calculations for the isolated cluster were carried out with only the Γ point to sample the irreducible Brillouin zone, but for the final calculations for the fcc solid two special **k** points[8] were used. We found this sufficient by testing the convergence with up to 12 **k** points at a few values of the fcc lattice constant. The occupation numbers of the one-electron energy levels were found by the Gaussian-smearing method[9] with the final smearing width of the order of 10 meV.

First we recalculated the properties of free $Al_{12}Si$ and Al_{13} clusters. A simple cubic supercell with lattice constant of 17 Å was used. The optimized central-atom–surface-atom distances are 2.59 and 2.62 Å, respectively. The corresponding binding energies are 44.9 and 41.7 eV, respectively. The results by Khanna and Jena[1] differ slightly from these in the sense that the binding energy difference is 7.7 eV and the bond length decreases from 2.75 to 2.70 Å when the Si atom is replaced by an Al atom. However, we are quite confident in our results because we have obtained nearly the same binding energy and bond length differences between $Al_{12}Si$ and Al_{13} using a totally different type of method, the density-functional all-electron program DMol.[10] This program uses atomic-type basis functions and the discrete variational method to perform the numerical integrals. The method used by Khanna and Jena is more approximative because it uses atomic wave functions corresponding to norm-conserving nonlocal pseudopotentials and these wave functions are fitted to a set of Gaussians.

The total energy of the fcc $Al_{12}Si$ per cluster relative to that of the free cluster is shown in Fig. 1 as a function of the lattice constant. In this calculation the atoms inside the clusters are not allowed to relax. From the
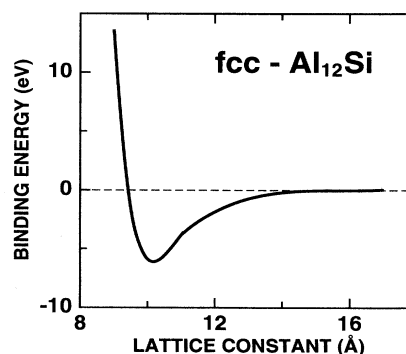

FIG. 1. Total energy of the fcc-$Al_{12}Si$ lattice per $Al_{12}Si$ cluster as a function of the lattice constant. The energy of the free cluster is subtracted. The optimized structure of the free $Al_{12}Si$ cluster is not allowed to relax when the lattice constant decreases.

minimum of the curve the cohesive energy of the fcc solid is about 6.1 eV per cluster, i.e., ~ 1 eV per additional Al-Al bond formed. This energy per bond is roughly half of the binding energy of an Al dimer, but 0.3 eV more than the energy per bond in the Al metal. Thus the bonds formed are metallic in character. This is very clear from the intercluster Al-Al bonds corresponding to the minimum of the total energy curve. The bond length is only 2.61 Å, whereas the intracluster Al-Al bonds are 2.72 Å. Moreover, at this intercluster separation the highest occupied energy bands are broad and there is no energy gap.

The fcc lattice formed by the unrelaxed clusters at the volume corresponding to the minimum energy in Fig. 1 is far from the true ground state of the atomic system in question. We have demonstrated this by allowing the 13 basis atoms of the fcc lattice to move according to the Hellmann-Feynman forces in the constant volume. The energy lowering in the relaxation is 2.2 eV per cluster. The structural relaxation is illustrated in Fig. 2 showing the average pair correlation functions around Al atoms in the unrelaxed and relaxed cluster lattices and in an ideal (atomic) Al fcc lattice. The pair correlation functions have been obtained by representing each atom by a Gaussian function with a finite width and then calculating the total atom density. The pair correlation function corresponding to the unrelaxed cluster lattice (the top panel in Fig. 2) consists of more or less evenly spaced peaks with similar intensities. When equilibrium is achieved the atoms have moved so that the shortest Al-Al bonds have increased to 2.71 Å and the open regions of the unrelaxed cluster lattice have become more filled. As a result, the relaxed pair correlation function (the middle panel in Fig. 2) resembles at short distances that of an ideal close-packed fcc structure (the bottom panel in Fig. 2). This is true for the distances as well as for the integrals (total number of atoms) of the first three peaks or nearest-neighbor shells. However, the ideal fcc lattice cannot be constructed using 13-atom supercells and therefore the long-range ordering differs from the ideal one. We have further determined that the volume of the system will shrink by keeping the atomic positions in the basis fixed but optimizing the lattice constant. However, the resulting volume per atom is due to the mismatch still $\sim 20\%$ larger than that for the ideal fcc Al lattice.

The idea by Khanna and Jena[1] that the $Al_{12}Si$ clusters could be the building blocks of a novel material, which could have exciting properties, was inspired by the research on solid C_{60} (Ref. 11) and on
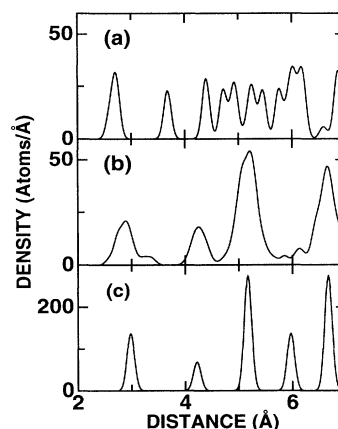

FIG. 2. Average pair correlation functions around Al atoms. (a) Unrelaxed fcc-$Al_{12}Si$ lattice, lattice constant 10.4 Å. (b) Relaxed fcc-$Al_{12}Si$ lattice, lattice constant 10.4 Å. (c) Ideal fcc-Al lattice, lattice constant 4.22 Å.

the metallocarbohedrenes.[12] Solid C_{60} is really a van der Waals bonded system as the first-principles LDA calculations[13] show. In the C_{60} molecule there is a graphitelike bonding mechanism with the σ and π bonds between the carbon atoms. There are no dangling bonds pointing out of the C_{60} molecule and therefore the molecules cannot bind strongly together. In the case of $Al_{12}Si$ cluster the binding mechanism is metallic, and the valence electron gas can bind the clusters strongly together. The situation is analogous to the formation of Mg metal. The Mg atom has a closed-shell structure, but when the solid is formed the uppermost filled s band and the first empty p band overlap resulting in a metal.

In conclusion, we have performed first-principles calculations for a solid composed of $Al_{12}Si$ clusters. The total energy minimization of a fcc structure of rigid $Al_{12}Si$ clusters leads to such a small lattice constant that the smallest intercluster Al-Al distances are shorter than the intracluster Al-Al bond length. When the clusters are then allowed to relax the Al atoms tend to move towards a close-packed arrangement. Thus, the calculations show that it is not possible to maintain the $Al_{12}Si$ clusters in a solid but the clusters will coalesce to a bulk Al metal with substitutional Si impurities.

[1] S. N. Khanna and P. Jena, Phys. Rev. Lett. **69**, 1664 (1992).

[2] M. Manninen, J. Mansikka-aho, S. N. Khanna, and P. Jena, Solid State Commun. **85**, 11 (1993).

[3] We use the computer code CASTEP (Cambridge Serial Total Energy Package) developed by M. C. Payne and V. Milman; see also M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

[4] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[5] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[6] G. P. Kerker, J. Phys. C **13**, L189 (1980); L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[7] M. P. Teter, M. C. Payne, and D. C. Allen, Phys. Rev. B **40**, 12255 (1989).

BRIEF REPORTS

[8] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[9] C.-L. Fu and K. M. Ho, Phys. Rev. B **28**, 5480 (1983); R. J. Needs, R. M. Martin, and O. H. Nielsen, *ibid.* **33**, 3778 (1986).

[10] B. Delley, J. Chem. Phys. **92**, 508 (1990).

[11] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature (London) **347**, 354 (1990); A. F. Hebard,

in *Physics and Chemistry of Finite Systems: From Clusters to Crystals*, edited by P. Jena, S. N. Khanna, and B. K. Rao (Kluwer, Dortrecht, 1992).

[12] B. C. Guo, K. P. Kerns, and A. W. Castleman, Jr., Science **255**, 1411 (1992).

[13] S. Saito and A. Oshiyama, Phys. Rev. Lett. **66**, 2637 (1991).