Structure of CA12
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I. INTRODUCTION

Interest in clusters and their assemblies has rapidly increased during the last decade. Not only do clusters provide a good testing ground for theories and computational methods, but they can also be used to explore the manner in which solids and alloys are formed from single atoms or molecules. Furthermore, the finite size and large ratio of atoms at the surface vs in the interior gives a unique frame for studying finite-size and surface effects.

An interesting situation occurs when the clusters are positioned into a regularly arranged lattice. If the composition and properties of the cluster is preserved in the lattice a molecular crystal has been formed. The everyday example is ice, or in the liquid form water. Moreover, the recent discovery of the third solid form of carbon, the fullerenes, has led to an enormous number of studies of their properties.

Recently Khanna and Jena proposed that molecular crystals similar to fullerenes, made of cluster constituents, could be prepared by a suitable choice of the atomic and electronic arrangement of the clusters. There would be two main criteria for the composition of the molecular crystals: (i) the intramolecular interaction should be strong, i.e., the isolated cluster must be very stable and (ii) the intermolecular interaction should be weak, i.e., of van der Waals type. To achieve the first requirement Khanna and Jena proposed to use atomic constituents whose total number of valence electrons corresponds to “magic” numbers, since such clusters have been found to be very stable. In particular, Khanna and Jena suggested a compact, icosahedral assembly unit with 12 atoms on the outer shell and a single atom at the center of this shell.

The requirements lead Khanna and Jena to the choice of XAl$_{12}$, X=C,Si, where twelve atoms surrounding a central (C,Si) atom are arranged in an icosahedral structure, and the clusters into an fcc crystal. These clusters have 40 valence electrons on closed electronic shells, which is a magic number for jellium clusters. Thus, the high icosahedral symmetry is not subject to symmetry-lowering Jahn-Teller distortions. Such clusters were found to have a high dissociation energy. Khanna and Jena also argued that CAl$_{12}$ is resistant to reactions with atomic hydrogen.

Here, we report an extension of a previous study of SiAl$_{12}$ (Ref. 9) to CAl$_{12}$ by using ab initio molecular dynamics within the density functional theory (DFT), as proposed by Car and Parrinello (Ref. 10). We employ a novel pseudopotential scheme of Vanderbilt (Ref. 11) to reduce the computational cost. We make comparisons to a conventional pseudopotential and an all-electron calculational method.

Our major results are that the cluster is indeed very stable even at high temperatures, but there is no (local) minimum in the total energy which would be required for the formation of a molecular crystal composed of the CAl$_{12}$ units. We further discuss the general trends of the icosahedral XAl$_{12}$ clusters and possible crystals formed of them.

This paper is organized as follows. Section II briefly introduces the calculational methods. Section III contains the results for the different studies of the isolated CAl$_{12}$ cluster and Sec. IV illustrates the energetics of the proposed cluster-assembled solid. In Sec. V we discuss the results in light of the previous findings for pure aluminium clusters, and in Sec. VI we summarize the main results of this paper.

II. METHODS

For most calculations we have employed the Car-Parrinello (CP) method based on the density functional theory. In our implementation the Kohn-Sham orbitals are expressed with plane waves and only the valence electrons are treated explicitly. The core electrons are replaced by pseudopotentials. For aluminium we use a Bachelet-Hamann-Schlüter (BHS) type pseudopotential with $sp$ nonlocality in the cluster calculations and $s$ nonlocality in the...
calculations for the solid if not otherwise stated. For carbon we use the ultrasoft pseudopotential (USPP) of Vanderbilt.\textsuperscript{11} The use of the ultrasoft pseudopotential is convenient here because a low cutoff can be used and the additional cost due to the overlap operators\textsuperscript{13} is negligible because only one atom (four in the case of the solid) is treated with this approach. For details of the implementation of the Vanderbilt pseudopotential scheme one should see Refs. 13 and 14. We find that a cutoff of 15 Rydberg is sufficient to describe the C–Al interaction. For the exchange-correlation terms we use the local density approximation parametrization by Perdew and Zunger.\textsuperscript{15}

We also did a few calculations with ordinary norm-conserving pseudopotentials, using the CASTEP code developed by Payne and co-workers.\textsuperscript{16} The code employs the optimized Kerker-type pseudopotentials. When applying the code we were mostly limited by the large memory and CPU time requirements due to the large cutoff energy needed. The binding energy of the cluster decreased by $\sim 0.2$ eV when going from 40 to 51 Rydberg (see the following), and we were not able to go to higher cutoff energies. The unit cell was smaller than when using the Vanderbilt pseudopotential. We stress that the difference is only due to the efficiency of using the ultrasoft pseudopotential for carbon. The energy of an isolated Al atom is converged to better than 0.1 meV at these cutoff’s.

To verify the accuracy of the two pseudopotential methods described, we also calculated the properties of the cluster using an all-electron program DMOL.\textsuperscript{17} This method employs a numerical atomic wave function basis set and the whole calculation is done in real space; thus no artificial periodically repeated box was used. The necessary integrals are performed using the discrete variational method.\textsuperscript{18} We applied both the local density approximation (LDA) and gradient-corrected (GC) functionals\textsuperscript{19} for the description of exchange and correlation.

### III. CAI$_{12}$ CLUSTER

Figure 1 shows the ideal geometry of the icosahedral XAl$_{12}$ cluster. Due to the plane wave expansion, one is forced to use periodically repeated images. To decouple the clusters we used a 30 a.u. fcc cell. This cell is found to be sufficient, because at the nearest cluster neighbor distance (21.2 a.u.) the total energy is converged to below 10 meV of the total energy at a cluster distance of 28 a.u. We first confirmed the icosahedral equilibrium structure with the simulated annealing method.\textsuperscript{20} The initial condition was a distorted icosahedron at a temperature of $\sim 930$ K with the carbon atom at the center of the 12 Al atoms. Two exponential cooling rates were used which brought the temperature to about 1 K in 1.7 and 5.1 ps. The resulting geometry of the both simulations was the icosahedral one with carbon atom at the center.

The effect of the nonlocal Al pseudopotential was investigated by optimizing the structure of the clusters. At the minimum, the C–Al distance was 4.84 a.u. with the s nonlocal pseudopotential for Al and 4.69 a.u. with sp nonlocality, and the icosahedral symmetry was perfectly preserved. The C–Al distance is somewhat smaller than in the previous works\textsuperscript{2,21} and the binding energy is larger. The USPP results are very similar to the values obtained with DMOL and a standard pseudopotential for carbon (see Table I). The short Al–Al distances (compared to bulk Al) are due to the relatively strong and short C–Al bonds that have the tendency to shrink the whole cluster. Overall, our results are in better agreement with the results of Gong and Kumar’s\textsuperscript{21} than with the original results of Khanna and Jena;\textsuperscript{2} the agreement is improved with the corrected results of Khanna and Jena.\textsuperscript{8}

We also calculated the structure and binding energy of the XAl$_{12}$ using DMOL with a gradient-corrected exchange-correlation functional.\textsuperscript{19} The gradient correction decreases significantly the binding energy and increases the distances

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|}
\hline
Method & \multicolumn{1}{|l|}{$d$(C–Al) (a.u.)} & \multicolumn{1}{|l|}{$d$(Al–Al) (a.u.)} & $E_{\text{bind}}$ (eV) \\
\hline
CPV (s) & 4.84 & 5.09 & 41.5 \\
CPV (sp) & 4.69 & 4.93 & 45.3 \\
DMOL & 4.75 & 5.00 & 43.1 \\
DMOL (GC) & 4.83 & 5.08 & 36.6 \\
CASTEP & 4.70 & 4.95 & 44.8 \\
Gong and Kumar\textsuperscript{a} & 5.05 & 5.31 & 40.6 \\
Khanna and Jena\textsuperscript{b} & 5.04 & 5.30 & 41.1 \\
Bulk Al\textsuperscript{c} & 5.41 & 5.41 & 3.39 \\
\hline
\end{tabular}
\caption{Calculated properties of the CAI$_{12}$ cluster. The bond distances and the binding energy of the cluster are shown. The $s$ and $sp$ refer to calculations with Vanderbilt pseudo potentials using $s$ and $sp$ nonlocal components for the aluminum pseudopotential, respectively. GC refers to a calculation using a gradient-corrected exchange-correlation functional.}
\end{table}

\textsuperscript{a}Reference 21.
\textsuperscript{b}Reference 8.
\textsuperscript{c}Experimental values.
between the atoms. Such reduction the overbinding of LDA and increasing the bond lengths are general trends of gradient corrections.

From the point of view of coordination a twelvefold coordinated carbon is very unusual. This unnatural coordination might break the icosahedral symmetry or even result in an unstable cluster. To test the stability of the cluster we performed a molecular dynamics simulation at a relatively high temperature. The same 30 a.u. fcc cell was used, the time step was 5 a.u. and the effective electronic mass was $m = 500$ a.u. We started from the cluster of the radius of 4.5 a.u. and with small random displacements to the atomic positions to excite all the vibrational modes. The length of the MD run was 7.7 ps ($\approx 64 \times 200$ steps). The average temperature of the run was $\approx 930$ K.

The main result of the MD run was that the icosahedral structure is stable up to the melting point of bulk Al $\approx 933$ K and time of several picoseconds. One could expect that the outer shell of the icosahedron would break into two subshells of 4 and 8 atoms and thus result in a "natural" coordination for the carbon. This did not happen and the structure remained closely icosahedral during the whole run. To give some measure of the structure of the cluster we calculated the angular distribution of the nearest-neighbor atoms, the pair correlation functions, and the velocity autocorrelation functions.

The atomic pair correlation function is shown in Fig. 2. The C–Al pair correlation function $g(r)$ is shown with a dashed line and the Al–Al pair correlation function $g(r)$ with a solid line. The Al–Al (C–Al) distances in the ideal, optimized icosahedral structure are shown with solid (open) arrows.

Such low rotation does not effect the results, except for very low frequency vibrations.

The velocity autocorrelation function

$$Z(t) = \frac{\langle \mathbf{v}(t+s) \cdot \mathbf{v}(s) \rangle_s}{\langle \mathbf{v}(s) \cdot \mathbf{v}(s) \rangle_s},$$  

where $s$ denotes the initial states, is shown in Fig. 4. The correlation is not completely vanished during the simulation, which we assign to the small size of the cluster and thus to an incomplete sampling of the whole phase space. The calculated cosine Fourier transform of $Z(t)$,

$$Z(\omega) = \frac{2}{\pi} \int_0^\infty Z(t) \cos(\omega t) dt,$$

is given in Fig. 5. The peak at $\approx 62$ THz is close to the vibrational frequency of an Al dimer, 66 THz. Using the harmonic approximation $E(r) = E_0 + \frac{1}{2} M \omega^2 r^2$ for the radial breathing mode relaxation we obtain a frequency 60 THz. Thus the radial vibration frequency is largely due to the compression of the pairwise Al–Al bonds.
The carbon centered cluster is stable up to \( \sim 1000 \) K. Although the atomic displacements for the Al atoms become large, the C–Al distance is always larger than 3.7 a.u. Thus the Al atoms remain on single shell around the carbon atom and the carbon does not leave the center.

We also tested if an icosahedral cluster where the carbon is on the surface of the cluster would be stable and if it would have an energy lower than the carbon centered cluster. We performed a MD simulation with a time step of 8 a.u. and fictitious electron mass of 500 a.u. The duration of the run amounted to 1.9 ps (=10 000 steps) and the temperature was 940 K. Within the simulation time the cluster was stable, but the average potential energy was 1.4 eV higher than for the carbon centered cluster. We did not minimize this structure because it clearly is higher in energy than the carbon centered structure.

We observed rapid diffusion of the atoms at the surface of the cluster. This is not unexpected since the temperature is above the melting temperature of Al (933 K). The surface atoms were jumping rather frequently, but the carbon did not jump inside the cluster where it would have a lower energy. Thus the “diffusion” on the surface is much faster than the center-to-surface atom exchange. This reflects the very different nature of the center and the surface of the cluster. The overall icosahedral structure was preserved, but was strongly distorted.

### IV. CAI\(_{12}\) Cluster Assembly

Khanna and Jena speculated that one could construct sophisticated molecular solids (MS) from XAl\(_{12}\)-type clusters. Such MS have been produced from fullerenes (C\(_{60},\)C\(_{70}\)). In fact a very large variety of MS are known, starting from materials as simple as ice (water) to as complicated as crystalline proteins. Common to all these MS is the existence of strong intramolecular bonds and relatively weak intermolecular bonds. This is necessary to preserve the molecular character of the solid, i.e., too strong intermolecular interactions would break the molecules. As an example, one could mention ice at high pressure. At modest pressures ice is formed from water molecules, but at very high pressures when the molecules are pushed close to each other the “weak” hydrogen bonds have become as strong as the O–H bonds and a new type of ice is formed where the hydrogen are located between the oxygens. One still has the same chemical composition of ice, but it is no more built of water molecules. Thus it is not sufficient only to have stable clusters to form MS but also the intermolecular interactions have to be small.

A conventional way to view the stability of fullerenes and other clusters forming MS is to consider them as closed shell systems that do not easily change their electronic structure by forming covalent bonds or changing the shape of the molecule. Such systems will still interact via weak bonds. A high one-electron (HOMO-LUMO) gap is characteristic for closed shell systems (\( \sim 10 \) eV for water, 20–30 eV for noble gases and \( \sim 2 \) eV for C\(_{60}\)). Thus the HOMO-LUMO gap of 2 eV for CAI\(_{12}\) obtained with DMOL indicates a fairly strong closed shell character for such a cluster.

The intramolecular interactions are properties of the molecules themselves and thus can be studied with few molecules. In the examples mentioned, the MS are bonded with either hydrogen or van der Waals (vdW) bonds but it is questionable whether aluminium would form such weak, nonmetallic bonds. Very small magnesium and mercury clusters are known to be van der Waals bonded, but in larger clusters the vdW character is replaced with metallic bonding.

The SiAl\(_{12}\) clusters turned out not to form a stable cluster phase. Like similar studies presented earlier for SiAl\(_{12}\), the molecules break and the resulting structure is basically fcc aluminium with interstitial dopants. Both our calculations and those of and Gong and Kumar\(^{21}\) give a significantly higher binding energy to the CAI\(_{12}\) cluster than to SiAl\(_{12}\), making CAI\(_{12}\) a better candidate for a MS than SiAl\(_{12}\).

To study solid CAI\(_{12}\) we chose a cubic unit cell with a varying lattice parameter. The clusters were assumed to form a fcc lattice which is a reasonable assumption for weakly interacting spherical molecules. Thus, we placed four molecules in the simulation cell. Only the \( \Gamma \)-point was used in the simulations. This is equivalent to 4 \( k \) points in the fcc lattice.

First we calculated the total energies with the fcc lattice parameter \( A_{\text{lat}} \) varying between 20 and 30 a.u. The radii of the clusters were always set to 4.84 a.u. and one of the symmetry axes of the clusters were chosen in the \((0,[(5-\sqrt{5})/2]^{-1/2},[(5+\sqrt{5})/2]^{-1/2})\) direction. Only the nonlocality was used for the Al pseudopotential. The total energy vs lattice constant is shown in Table II. The total energy

### TABLE II. Total energy vs lattice parameter for solid CAI\(_{12}\) (\( R_0\sim 4.84 \) a.u.).

<table>
<thead>
<tr>
<th>( A_{\text{lat}} ) (a.u.)</th>
<th>( E_{\text{lat}} ) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>(-121.413)</td>
</tr>
<tr>
<td>21.0</td>
<td>(-121.298)</td>
</tr>
<tr>
<td>21.1</td>
<td>(-121.284)</td>
</tr>
<tr>
<td>21.5</td>
<td>(-121.263)</td>
</tr>
<tr>
<td>22.0</td>
<td>(-121.249)</td>
</tr>
<tr>
<td>23.0</td>
<td>(-121.233)</td>
</tr>
<tr>
<td>24.0</td>
<td>(-121.218)</td>
</tr>
<tr>
<td>30.0</td>
<td>(-121.118)</td>
</tr>
</tbody>
</table>
The C–Al distances are shown with a dashed line and the Al–Al distances with a solid line.

The Al–Al and C–Al pair correlation functions are shown in Fig. 6. Both of them are clearly different from those that would arise from the molecular solid phase. The Al–Al pair correlation function is very similar to that for liquid aluminium (see Ref. 23) and the clear first peak of the C–Al pair correlation function has shifted from the 4.8 a.u. of the cluster to 3.9 a.u., while the peak width has reduced from 2.4 to 1.0 a.u. These are dramatic changes and indicate significant changes in the bonding behavior. Indeed, the carbon is now fourfold coordinated. The coordination number is 4.3±0.1, which has been obtained by integrating the C–Al pair correlation function to its first minimum at 5.3±0.2 a.u. From the point of view of the electronic structure of carbon the fourfold coordination is of course very natural. The icosahedral complexes are also very stable. This is reflected by the close separation of the first C–Al peak from the rest of the pair correlation function and also by simply looking at the atomic configurations. Thus, the final state of this system can be described by carbons (or CAI4 complexes) solvated to liquid aluminium. Clearly, the cluster phase is not stable for the chosen unit cell parameter.

The melting of the cluster phase is not very surprising, because with the 20 a.u. lattice constant the aluminium atoms from the next cluster were only at a distance of 5.3 a.u., compared with the nearest-neighbor distance in the cluster of 5.1 a.u. To test the further the stability of the cluster phase we studied a somewhat larger cell with the lattice parameter of 22 a.u. corresponding to the density of 1.4 g/cm³. In this cell the nearest intramolecular Al–Al distance is 6.4 a.u. Here, the atomic positions were minimized starting from the fcc packing of the ideal clusters. After a short minimization the cluster phase again turned out not to be stable. The structure is qualitatively similar to before; the shortest C–Al distance being 3.8 a.u. The coordination of the carbons is again close to four.

V. DISCUSSION

Calculations24–27 and experiments28–30 have predicted and confirmed the existence of aluminium clusters. The results show that the icosahedral cluster with 13 atoms is very stable. Furthermore, it is known that Al transition metal (TM) alloys form icosahedral units when rapidly quenched.31 In modeling these quasicrystals,32 most units used consist of Mackay icosahedra33 or Al12TM clusters, arranged in a bcc lattice.34,27 Thus, the latter is equivalent to the structure of a cluster-assembled solid proposed by Khanna and Jena2 except that (i) the clusters would be in a bcc arrangement, not fcc, and (ii) the carbon atom at the center of the icosahedron is replaced with a transition metal atom (see the following for a discussion of the relative stability of XAl12 clusters). Transition metal clusters often form icosahedral structures.

Our results show that the total energy curve of the cluster-assembled solid is monotonically decreasing to from \( A_{\text{lat}} = 30 \) to 20 a.u. and that the cluster phase breaks down already at \( A_{\text{lat}} = 22 \) a.u., giving strong evidence that the cluster phase is not stable. We do not find any sign of the a weakly interacting van der Waals region in our calculations (e.g., a shallow local minimum for large lattice parameters). One should keep in mind that our calculations are based on LDA, which has a tendency to exaggerate weak bonds like hydrogen or van der Waals bonds. Because the breaking mechanism of the clusters is the forming of intramolecular Al–Al bonds, we believe that LDA is capable to describe this correctly. Even if there would be computationally a MS phase with \( A_{\text{lat}} > 21 \) a.u. the density of that phase would be unrealistically low and thermal fluctuations would destroy the MS phase. In any case, calculated results should always be checked with respect to the exchange-correlation functional if a weak bonding is to be expected.

Why does the apparently closed-shell CAI12 molecule not form a molecular solid? The electron density is not as well localized as in materials such as carbon (fullerenes) and water, thus requiring a relatively large Al–Al distance to avoid strong intermolecular interactions. Moreover, the cluster has built-in instabilities due to the unnatural bonding environment for the carbon atom. The stability of a single cluster is due to the aluminium atoms. They prefer a high coordination and spherical shape, but this structure is not very stable towards external perturbations. The carbon would like to break the 12 atom outer shell to two shells of 4 and 8 atoms. We see clear evidence for this in the solid phase.

The isolated cluster is very stable, but the observed very large fluctuations on the C–Al distance, 2.4 a.u. or 50% from the average bond length, are not in agreement with the concept of strong covalent or metallic bond. The picture that
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