Atomic scale dynamics of ultrasmall germanium clusters

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Starting from the gas phase, small clusters can be produced and deposited with huge flexibility with regard to composition, materials choice and cluster size. Despite many advances in experimental characterization, a detailed morphology of such clusters is still lacking. Here we present an atomic scale observation as well as the dynamical behaviour of ultrasmall germanium clusters. Using quantitative scanning transmission electron microscopy in combination with ab initio calculations, we are able to characterize the transition between different equilibrium geometries of a germanium cluster consisting of less than 25 atoms. Seven-membered rings, trigonal prisms and some smaller subunits are identified as possible building blocks that stabilize the structure.
Ultrasmall clusters have attracted increasing interest, because they can be thought of as fundamental building blocks leading to metamaterials with physical and chemical properties that are not available in nature\textsuperscript{1,2}. Consequently, the structure of clusters of Ge and other group IV elements has been the subject of many studies. Whereas bulk Ge has the diamond cubic structure, the hitherto-identified structural growth mechanisms for small clusters are much more exotic. Early mass spectrometry observations of species with enhanced stability and fragmentation mass spectrometry have confirmed the existence of small-sized building blocks, in particular Ge\textsubscript{6,11}, with the most stable sizes being Ge\textsubscript{6}, Ge\textsubscript{7}, and Ge\textsubscript{10} (refs 3,4). First structural assignments were based on ion-mobility experiments in combination with density functional theory computations\textsuperscript{5}. Meanwhile, more extensive theoretical studies have revealed structural patterns consistent with stable deltahedral subunits where larger species consist of several of these subunits joined together forming, for example, prolate\textsuperscript{6} (sizes N~30) and platelet\textsuperscript{7} (sizes N~45) -shaped nanoparticles.

Recent advances in the field of transmission electron microscopy (TEM) enable one to obtain two-dimensional (2D) images with a spatial resolution of up to 50 pm. However, it is still not straightforward to determine the three-dimensional (3D) geometry of ultrasmall clusters. One of the problems is that during electron irradiation, clusters may rotate or show structural changes\textsuperscript{8,9}. Even though TEM observations can now be made at lower acceleration voltages or while cooling the sample, still, an intrinsic energy transfer from the impinging electron beam to the sample cannot be fully avoided. This results in the unique possibility to visualize the transformation between energetically excited configurations. Furthermore, the support on which the clusters are deposited may have a strong influence on their structure and dynamics.

Here we determine different equilibrium configurations of ultrasmall Ge clusters deposited on a carbon support using state-of-the-art aberration-corrected TEM. Using statistical parameter estimation theory and \textit{ab initio} calculations, we are able to analyse several metastable configurations that are reproduced as local energy minima. The direct observation of the atomic scale dynamics allows several metastable configurations that are reproduced as local energy minima. The direct observation of the atomic scale dynamics allows a 2D-to-3D transition, as well as a transition from a compact towards an elongated structure of the cluster, which finally breaks up into smaller fragments.

**Results**

**Quantitative 2D electron microscopy.** As explained in the Methods, ultrasmall Ge clusters preformed in the gas phase were deposited on TEM grids coated by a thin layer of amorphous carbon. The clusters are imaged using high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) at 120 kV. Under the electron beam, structural changes of the clusters are observed and the movement of single Ge atoms on the carbon support can be followed.

The cluster shown in Fig. 1 was imaged by acquiring 100 frames with an individual frame time of 0.1 s. A subseries of eight consecutive frames (Fig. 1a–h) is studied here in more detail. Another example of a series of images is presented as Supplementary Fig. S1. The configuration of the cluster in Fig. 1a appears predominantly 2D, whereas the configurations in Fig. 1g,h are observed with enhanced contrast at certain atom positions, suggesting a 3D geometry. To study this transformation, Fig. 1a, Fig. 1h and an intermediate frame (Fig. 1d) have been quantified by statistical parameter estimation theory\textsuperscript{10–12}. Using this approach, a parametric model in which the projection of an atom corresponds to a Gaussian peaked at the atom position has been assumed. The parameters of this model, including the atom positions, the height and width of the intensity peaks, have been determined using the least squares estimator. The refined models, evaluated at these estimated parameters, are shown in Fig. 2a–c. From the estimated parameters, also totally scattered atom intensities, corresponding to volumes under the estimated Gaussian peaks, are determined.

HAADF-STEM intensities scale with the atomic number Z of the atoms present in a sample as well as with the number of atoms. Here all atoms are of the same type and, consequently, the intensity will increase when several atoms are positioned on top of each other. On the basis of such quantitative analysis, we conclude that the estimated peaks correspond to 1, 2 or 3 atoms projected on top of each other. These results are indicated in Fig. 2d–f and confirm that 2D, 3D and intermediate configurations are present.

**3D structure characterization.** To evaluate the stability of these configurations, \textit{ab initio} calculations have been carried out. The x and y coordinates in the starting configuration are directly based on our experimental results (Fig. 2d–f). Along the z direction, we assumed three equally spaced planes that may contain atoms as a starting point. We built up the 3D structure from the 2D projections based on a planar base structure on top of which additional atoms are added (in case of the presence of 2 or 3 atoms at the same 2D-projected position). After full relaxation, the Ge cluster geometries...
Remarkably, the intermediate configuration corresponds to a less stable structure with a binding energy of \(-4.49\) eV per atom. To study the transformation from the 2D configuration to the 3D configuration, we followed the path of each individual atom. Many possibilities exist, but it is a reasonable assumption that the most likely pathway is close to the shortest travelled distance of all atoms. Therefore, the total travelled distance has been minimized over all possible combinations of atoms in two successive frames. The results are presented in Supplementary Fig. S2.

In addition to the analysed configurations shown in Fig. 2, several other configurations of the same cluster have been investigated using the same quantitative approach. One of these configurations, which appears after longer observation, is presented in Fig. 4. The refined model evaluated at the estimated parameters is shown in Fig. 4a, whereas the result of the \textit{ab initio} calculations is presented in Fig. 4b. This shows that the cluster has evolved from compact geometries to an almost planar strongly elongated shape. Also this structure was reproduced by the \textit{ab initio} calculations with an average binding energy per atom of \(-4.24\) eV. In this configuration, it is clear that the cluster is built up from smaller subunits very similar to the predicted configurations for clusters consisting of 3 and 4 atoms. Later observed frames show that the cluster breaks up into smaller fragments of 3–7 atoms.

**Discussion**

In this study, we observe the transition between a 2D and a 3D configuration of a Ge cluster consisting of about 25 atoms. Structural re-arrangements such as the ones observed here were still present when cooling the sample to liquid nitrogen temperatures. In addition, according to Hobbs\(^{14}\), specimen heating is negligible for our specific sample and the beam current that was used. It is therefore likely that the main driving mechanism for the re-arrangements is knock-on momentum transfer\(^{15}\). The transferred kinetic energy is maximal for head-on collisions and depends on the ratio of the electron mass and the mass of the nuclei, as well as the acceleration voltage of the TEM. For Ge clusters imaged using an acceleration voltage of \(\pm 300\) kV, Hobbs\(^{14}\) observed re-arrangements with time constants of \(\approx 10^2\) ms.
Ge trimers and tetramers in their ground state are smaller building blocks that correspond well to the configurations of base structure. The configuration in building blocks in larger 2D and 3D configurations with a planar base structure was also observed to be stable in free space. It is noted that, during the relaxation of the configurations, one will have a large influence on the formation of planar rings, it must be noted, however, that larger clusters also may be present in the cluster beam but will not be registered because of a decreasing detector efficiency with cluster mass.

Methods

Cluster production and deposition. Gas phase clusters were produced using a cluster source based on laser vaporization of a Ge target and condensation and aggregation in pulses of He carrier gas. The cluster source is integrated in an ultrahigh vacuum cluster deposition chamber that is described in detail by Vandamme et al. The size distribution of the clusters in the beam is monitored by time-of-flight mass spectrometry, showing clusters from the monomer to about 130 atom clusters. A mass spectrum of the cationic Ge clusters is shown in Fig. 5a. The cluster size distribution was optimized for small sizes by reduction of the cluster source volume and by operating the source at room temperature, resulting in abundant production of species from Ge$_2$ up to about Ge$_{45}$. Depending on the cluster shape, this corresponds to a diameter up to 7 Å for a planar disk or 13 Å for a sphere. Assuming a circular disk shape for the most abundant cluster, Ge$_{19}$, a diameter of 9 Å is found. It should be noted, however, that larger clusters also may be present in the cluster beam but will not be registered because of a decreasing detector efficiency with cluster mass.

Figure 3 | Two examples of slightly varying starting configurations resulting in significantly altered relaxed structures. (a,b) The left panels represent the top view of a model that corresponds to the experimental picture. The panels in the middle give two different configurations that are indistinguishable if viewed from the top. After relaxation with density functional theory (panels on the right), only one of the two possibilities is still compatible with the experimental image, as can be seen in Figure 2.

Figure 4 | Quantitative analysis of a more elongated prolate configuration. (a) Refined parametric model, peaked at the estimated atomic positions. Green and red dots correspond to 1 atom and 2 atoms, respectively. (b) Outcome of the ab initio calculation. It can be seen that a seven-membered ring is present. In addition, smaller fragments, consisting of 3-4 atoms are found to correspond well to the predicted ground states of trimers and tetramers.

Figure 5 | Aggregation in pulses of He carrier gas.
Statistical parameter estimation. The totally scattered atom intensities estimated by fitting a parametric model to the experimental images are influenced by several factors, including experimental detection noise and the dynamical character of the frames. As a consequence, quantifying the observed intensities, in terms of number of atoms, should be done in a statistical manner\(^\text{10}\). Figure 6, therefore, presents the histogram of all intensities corresponding to the estimated Gaussian peaks shown in Fig. 2. Next, these intensities are regarded as independent statistical draws from a so-called Gaussian mixture model. This model, defined as a superposition of Gaussians, describes the probability that a specific intensity value will be observed. To determine the number of significant peaks of this model, the integrated classification likelihood criterion\(^\text{24}\) was used, indicating the presence of three peaks. Their positions, amplitudes and widths have been estimated using the so-called expectation maximization algorithm. Its aim is to optimize the likelihood that the given intensities are generated by a mixture of Gaussians. The solid curve in Fig. 6 shows the estimated mixture model; the individual Gaussian components are shown by means of dashed curves. Because of the inherent statistical measurement errors as described above, overlap of the Gaussian components is observed in Fig. 6 causing uncertainties for the number of atoms in specific Gaussian peaks. However, by exploiting the boundary conditions determined by the conservation of the total number of atoms in the area of interest, a unique solution for the number of atoms at each estimated position has been found.

Ab initio calculations. All calculations are based on density functional theory and performed using the OpenMX code\(^\text{25,26}\) with periodic boundary conditions. We use the local density approximation functional developed by Ceperly and Alder\(^\text{27}\) to evaluate the exchange-correlation energy of interacting electrons. Double-valence plus single-polarization orbitals are used as the basis set. A large enough vacuum space is used to treat the Ge clusters as isolated from each other. The relaxed structures have been optimized carefully without any constraint (that is, without forcing the clusters to form planar structures). The optimization, implemented in the OpenMX code, was based on the method described by Baker\(^\text{28}\). Starting configurations were based on the experimental measurements as shown in the first and second column of Fig. 2. For the optimized structure calculations, all atoms in the system are relaxed until the forces are less than 0.005 eV/Å.

The resulting beam of Ge clusters is subsequently deposited without size selection at room temperature on TEM grids, which consist of an ultrathin amorphous carbon layer supported by a Cu grid. The clusters were deposited with their inherent low kinetic energy (~0.15 eV per atom). This corresponds to a soft-landing regime, where the kinetic energy is small compared with the atomic binding energy within the cluster, and, consequently, negligible cluster fragmentation is expected owing to the impact\(^\text{21}\). Deposition times were chosen to achieve a low cluster density, well below complete coverage of the substrate.

A histogram of the size distribution of all clusters as imaged by TEM is presented in Fig. 5b. As the clusters change their geometry during the TEM investigation, it is not straightforward to define the diameter. The diameter was measured for each cluster being in its most spherical, compact geometry. It must be noted that, although this histogram contains only clusters with a diameter < 2 nm, larger clusters (with sizes up to 10 nm) also have been observed.

**Figure 5 | Size distribution of the clusters.** (a) Time-of-flight mass abundance spectrum of Ge cluster cations. Of interest are the strong size-dependent features reflecting enhanced stability for a number of sizes in the 6 to 20 atoms range. (b) Histogram illustrating the size distribution of the investigated clusters as deduced from the TEM images. It must be noted that, although this histogram contains only clusters with a diameter < 2 nm, larger clusters (with sizes up to 10 nm) also have been observed.

**Figure 6 | Histogram of the totally scattered intensities.** These intensities are determined from the estimated Gaussian peaks in Fig. 2a–c. The solid curve shows the estimated mixture model; the individual components are shown as dashed curves.

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**Author contributions**

S.B. and E.Y. carried out the TEM experiments. S.V.A. performed the statistical data analysis and interpreted the images together with S.B. and P.L. C.R. and K.L. produced and deposited the clusters. *Ab initio* calculations were carried out by B.S. and B.P.M.V.B., P.L. and G.V.T. designed the study and advised on methodology, experiments and interpretations.

**Additional information**

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