Electronic structure of Ga$_{84}$ cluster compounds

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Density functional calculations were carried out to study large bare and ligated gallium clusters and their packing in a three-dimensional crystal structure. In the single clusters, the electronic states are delocalized over the whole cluster and the gallium atoms exhibit no noticeable charge. Band-structure calculations of the crystal do not yield any significant dispersion of the electronic bands. Thus it is concluded that the observed macroscopic electric conductivity is mediated by a hopping mechanism between the clusters rather than by the presence of states, which are delocalized over the whole crystal.

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I. INTRODUCTION

Semiconducting and metallic clusters as building blocks for organized structures are potential candidates for devices in nanoelectronics. In the past years several ligand stabilized aluminium and gallium cluster compounds were synthesized in different sizes.1 Ligated Al$_{77}$ (Ref. 2) and Ga$_{84}$ (Ref. 3) are the largest main group metal clusters characterized so far. Both clusters are surrounded by a ligand shell of 20 N(SiMe$_3$)$_2$ groups. Altogether the number of direct metal-metal contacts exceeds the number of metal-ligand bonds, they can be denoted as “metalloid” clusters.3 Both comprise structural elements that are similar to their bulk modifications. The Al$_{77}$ cluster is built up very similar to the fcc (face-centered-cubic) packing with a coordination number of 12 for the central aluminum atom. In the outer shells the coordination numbers decrease from 10 for the atoms next to the center to 4 for the outer aluminum atoms, as one would expect in a transition from a metallic center to the cluster surface. In contrast, the Ga$_{84}$ cluster is following the typical structural motifs of the low pressure gallium modifications,5 with low coordination numbers of 4 in the cluster center and for the outer gallium atoms and of 8 for the atoms in-between.

In detail, a single cluster [Ga$_{84}$(N(SiMe$_3$)$_2$)$_{20}$]$_{4-}$ is built up from four atomic shells as shown in Fig. 1 of Ref. 3. Figure 1 gives the radial distribution of the atoms. In the center of the cluster one can find a Ga$_2$ dumbbell quite similar to the Ga dimers in $\alpha$-gallium. As Fig. 1 indicates the dumbbell is surrounded by a Ga$_{20}$ shell with a radius of roughly 3.5 Å, and a Ga$_{40}$ shell with a radius of about 5.6 Å. 20 further gallium atoms form the outer shell with a radius of approximately 6.8 Å. These Ga atoms are each bonded to a N(SiMe$_3$)$_2$ group, thus they will be referred to as Ga@N in the following. The two remaining gallium apex atoms are located next to the Ga@N shell on opposite sides of the cluster, but they are ligand free.

In the crystal structure, two adjacent clusters are separated by two toluene molecules, such that chains are formed as shown in Fig. 2. The apex atoms align in the chain direction and exactly point towards the toluene molecules. The distance between an apex atom and the apex atom of the next cluster amounts to 12.9 Å. Finally, the [Ga$_{84}$(N(SiMe$_3$)$_2$)$_{20}$]$_{4-}$ anions follow a slightly disorted cubic close packing (ccp). The tetrahedral holes of this structure are filled with Li(THF)$_2$$^+$ cations and the octahedral holes with dimers of the Li$_2$Br(THF)$_6$$^-$ cation.

In the macroscopic dimension this Ga$_{84}$-cluster-compound gives black, metallic shiny crystals that show semiconducting properties, however, with a very small band gap, which was estimated to 30 meV from a four point measurement of the electrical conductivity.4 Furthermore, Ga$_{84}$-NMR experiments indicate similarities of the gallium atoms in the Ga$_{84}$ cluster and $\alpha$-gallium.5

Often the electronic structure of clusters with delocalized s and sp states can be described by the jellium model. In the case of the similar [Al$_{77}$(N(SiMe$_3$)$_2$)$_{20}$]$^{2-}$-cluster Gong et al.5 studied its electronic shell structure. They could successfully apply the jellium model for the ligand-free and noncharged Al$_{77}$ cluster up to the 1t electronic shell. In the case of the analogous Ga$_{84}$ cluster the jellium shell concept can only be applied for the low lying electronic shells 1s, 1p, 1d2s, 1f, 2p, and 1g. Besides this, Lerme et al. obtained the electronically stable shells from a self-consistent spherical jellium model of gallium clusters according to the following electron

![FIG. 1. The onionlike composition of the Ga$_{84}$ cluster: central Ga$_2$ dumbbell, surrounded by two spheres Ga$_{20}$ and Ga$_{40}$, 20 ligated Ga–N atoms and finally two apex gallium atoms.](image)
numbers \(N_{\text{jellium}} = 39, 93, 138, 198, 267, 339, \ldots\) (see Ref. 7), additional beating structures were found for larger clusters.\(^8,9\) In comparison to these results the noncharged Ga\(_{64}\) cluster kernel constituted by the three inner Ga shell and the two apex atoms exhibits \(N_f = 192\) electrons and the Ga\(_{84}\)-cluster kernel \(N_f = 252\) electrons. In both cases the electronic configurations do not match with the values given in the literature, but come close to it. In conclusion, a simple jellium model does not describe the ligand-free and noncharged Ga\(_{64}\) and Ga\(_{84}\) clusters. Therefore, more sophisticated density-functional based methods will be employed, which have shown to yield structural data on small bare clusters (up to Ga\(_{10}\))\(^10\) and adsorbed Ga\(_{\ast}\) species on the silicon (111) surface\(^11\) in good agreement with experimental data. In the present study, the density functional based tight binding method and a fully self-consistent plane-wave density-functional method were applied for approximants to the large Ga\(_{84}\)-cluster and for the crys-
tal structure built from the Ga\(_{64}\)\(_{20}\)\(^4\)− cluster in Sec. III A, for the free Ga\(_{84}\)(N(SiMe\(_3\))\(_2\))\(_{20}\)\(^4\)− cluster in Sec. III B, and for the crystal structure built from the Ga\(_{84}\)(N(SiMe\(_3\))\(_2\))\(_{20}\)\(^4\)− cluster and counter ions in Sec. III C.

### II. COMPUTATIONAL DETAILS

The two computational methods we used are based on the density functional theory (DFT). The first is the density functional based tight binding method (DFTB)\(^\text{12,13}\) within its self-consistent charge implementation.\(^\text{14}\) In DFTB a linear combination of atomic orbitals (LCAO) ansatz is used to describe the Kohn-Sham (KS) molecular orbitals (MO), and the atomic orbitals are expressed with Slater-type orbital (STO) basis functions. The total energy \(E\) is expressed as the sum of the occupied KS states and a short-range repulsive potential \(U\),

\[
E = \sum_i \varepsilon_i + \frac{1}{2} \sum_{\alpha \neq \beta} U_{\alpha \beta}(\mathbf{R}_{\alpha \beta}).
\]

Only two-center contributions are taken into account. With the SCC extension the total energy is corrected with respect to charge density fluctuations as described in more detail in Ref. 14. The repulsive potential is obtained by the difference of the DFTB energy and the DFT energy of a reference system.

Second, the program ABINIT\(^\text{15}\) was employed mainly to study periodic crystal structures. In ABINIT the electronic density is represented in KS orbitals which are expanded in plane waves. The interaction with the ionic core states is described by pseudopotentials.\(^\text{16}\) The local density approximation (LDA) is used for the exchange-correlation potential. Convergence studies for the \(\alpha\)-Ga structure indicate, that a plane wave cutoff energy of 333 eV is sufficient for reproducing the extended Ga valence states.

To validate the numerical accuracy of the DFTB and DFT calculations we performed further test calculations on the crystalline structures of \(\alpha\)-Ga, \(\beta\)-Ga, \(\gamma\)-Ga, and Ga(III) with DFTB and on \(\alpha\)-Ga with DFT. All calculations were carried out employing experimental lattice constants.\(^\text{17-20}\) The \(k\) points used in all band structure calculations are generated following the special \(k\)-point sampling as introduced by Pack and Monkhorst.\(^\text{21}\) The calculated density of electronic states (DOS) are shown in Fig. 3. The broadening employed in both cases amounts to 0.1 eV (DFTB and DFT). The results obtained with the DFT band structure method are in agreement with data in the literature.\(^\text{22,23}\) The DFTB results show a qualitative reproduction of the electronic states, especially of the characteristic states near the Fermi level, which are responsible for the electronic conductivity.

In the following, the term Fermi level is also employed to describe the electronic structure of finite systems; in this case, it is calculated as one-half the difference of the energies of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO).

### III. RESULTS

#### A. Model clusters

In order to better understand the subtle interactions within the crystals composed of [Ga\(_{64}\)(N(SiMe\(_3\))\(_2\))\(_{20}\)\(^4\)− clusters, toluene molecules, solvent, and counterions, we investigate a number of smaller approximants of the [Ga\(_{84}\)(N(SiMe\(_3\))\(_2\))\(_{20}\)\(^4\)− cluster, mainly with the DFTB method,

\[
\text{[Ga}_{64}\text{L}_{20}]^{4−} = \text{[Ga}_{64}]^{4−} + 20\text{L},
\]

\[
\text{[Ga}_{64}\text{(GaL)}_{20}]^{4−} = \text{[Ga}_{64}]^{4−} + 20\text{GaL},
\]

\[
\text{[Ga}_{64}\text{N}_{20}]^{4−}, \text{[Ga}_{64}\text{(NH}_{2})_{20}]^{4−}\text{ and [Ga}_{64}\text{H}_{20}]^{4−}.
\]

The results of electronic DOS calculations of these Ga\(_{64}\)-cluster models are depicted in Fig. 4 and a compilation of the atomic charges is given in Fig. 5. The electronic DOS of the full free [Ga\(_{64}\)(N(SiMe\(_3\))\(_2\))\(_{20}\)\(^4\)− cluster is qualitatively reproduced by all models. For the [Ga\(_{84}\)(N(SiMe\(_3\))\(_2\))\(_{20}\)\(^4\)− structure a relatively high density of states is obtained at the

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**FIG. 2.** The Ga\(_{84}\) clusters are separated by toluene molecules building tubes/chains through the crystal structure. Thereby the two apex gallium atoms point towards the toluene molecules. In this drawing only the N atoms from the ligand shell are depicted for clarity.
Fermi level. The atom-resolved projection of the DOS shows that one-half of the states is attributed to Ga levels, and the other half is ligand based. Qualitatively, a similar result is obtained for the model $\text{Ga}_{84}\text{N}_{20}^{4-}$. Also $\text{Ga}_{84}^{4-}$, and $\text{Ga}_{64}^{4-}$ display a high density of Ga-derived states at the Fermi level, major peaks at $-1.0$ eV and $-1.5$ eV and pseudogaps at roughly $-0.25$ eV and $0.75$ eV. The other two model clusters, $\text{Ga}_{84}\text{H}_{20}^{4-}$ and $\text{Ga}_{84}\text{NH}_{2}^{20}^{4-}$, also exhibit the pseudogaps at $-0.25$ eV and $0.75$ eV, but a significantly lower DOS at the Fermi level. Additionally, the Ga DOS fingerprint in the valence region between $-2$ eV to $0$ eV is composed of only two sharp features in the bare clusters $\text{Ga}_{64}^{4-}$ and $\text{Ga}_{84}^{4-}$, but exhibits three major peaks in $\text{Ga}_{84}\text{H}_{20}^{4-}$ and $\text{Ga}_{84}\text{NH}_{2}^{20}^{4-}$, and one broad, structured peak in $\text{Ga}_{84}\text{N}_{20}^{4-}$ and $\text{Ga}_{84}\text{(SiMe}_{3})^{20}^{4-}$. The different behavior of the ligated clusters indicates that the interaction with the ligand shell has significant impact on the electronic properties of the gallium cluster core. In order to discuss the influence of the ligand shell in more detail, also the total electronic DOS of the four ligated clusters is given by the grey lines in Fig. 4. For the ligands H and NH$_2$, additional states occur around $-2$ eV, which can hybridize with the Ga valence states and cause the three peak pattern. For N and N(SiMe$_3$)$_2$, however, the N-derived levels occur at lower binding energies with a maximum at roughly $-1$ eV, indicative of an electron transfer to the N atom.

For an analysis of the charge redistribution between the gallium shells and between the gallium core and the ligand shell a Mulliken population analysis was performed (see Fig. 5). The division of the cluster core in the four subshells $\text{Ga}_{3}$ (I), $\text{Ga}_{20}$ (II), $\text{Ga}_{10}$ (III), and $\text{Ga}_{22}$ (IV), is indicated by the vertical lines in Fig. 5. The central two gallium atoms and the outermost shell are always slightly positive, with the exception that the negative charge of the bare clusters accumulates in the outer shell. Overall, the distribution of the atomic charges in the outer shell is reproduced best with the model clusters $\text{Ga}_{84}\text{N}_{20}^{4-}$ and $\text{Ga}_{84}\text{(NH}_{2})^{20}^{4-}$, whereas the inner core is better described by $\text{Ga}_{84}\text{H}_{20}^{3+}$ and $\text{Ga}_{84}\text{(NH}_{2})^{20}^{3+}$.

A closer look at the charge distributions suggests that the four radial shells of the gallium core exhibit the following...

Figure 6 gives a schematic view of the charge distribution in a cut plane through the cluster, where the apex atoms are located at the top and the bottom of the circles, the central Ga2 unit is mapped to the circle in the middle, and the remaining shells with their subshell structures are represented by the other concentric circles and their segments. Dark color denotes positive partial charges, white color negative partial charges. It is obvious, that the additional negative charge accumulates in the outermost shell of the naked clusters. For the ligated clusters, the excess charge is transferred even further to the ligand shell, such that an overall positive charge is obtained for the [Ga84] cluster core. Therefore, the model [Ga84N20]2+ was also investigated in correspondence to the calculated 1.6 electron deficit of the gallium kernel in [Ga84(N(SiMe3)2)20]2+. Its charge distribution exhibits a similar shell structure as the one of the [Ga84(N(SiMe3)2)20]3+ cluster, but the negative partial charges at the apex atoms are not reproduced. In conclusion, only the models [Ga84N20]3+ and [Ga84(NH2)20]3+ correctly reproduce the charge distribution along the cluster axis, which is the relevant direction for intercluster electronic interaction.

These results demonstrate that the specific chemical surrounding, particularly the electronegativity of the ligands, influences the electronic structure of the Ga84 cluster. In the case of the [Ga84(N(SiMe3)2)20]3+ cluster the Ga@N atoms are less strongly positive due to the vicinity of the −N(SiMe3)2 groups because the nitrogen atoms gain additional negative charge from the two electron donating silicon atoms. A similar situation is realized in [Ga84(NH2)20]3+, where the additional electronic charge of the NH2 ligands is transferred from the two [Ga10] rings above and below the equatorial one. This analysis of the charge distributions corroborates the conclusions drawn on the basis of the DOS data that the [Ga84] cluster core is partially positivated and that the correct reproduction of the negative charge at the N centers is crucial for a reasonable modeling of the full [Ga84(N(SiMe3)2)20]4− cluster.

B. Properties of the free [Ga84(N(SiMe3)2)20]4− cluster

As the ligand shell is thus important for the cluster properties we investigate the electronic structure of the single cluster [Ga84(N(SiMe3)2)20]4− in more detail. For this purpose we performed calculations with the DFTB method for...
calculated electronic DOS of the complete cluster structure of projected DOS on the central gallium dumbbell follows that corresponding curves of the bulk gallium modifications. While the inner shells exhibit roughly similarities to the corr-

panels in Fig. 7 show that curves of the electronic DOS of gallium shells we obtain a more detailed picture. The lower electron gas.

maxima follow roughly the square root function of the free from −9 eV to 0 eV, and the positions and heights of the in the top part of Fig. 7. The gallium states occur in the range position of the last maximum in the occupied DOS emerges. 1−
f interchangeable.

The partial charges of the gallium cluster core have been discussed in detail above. The total sum of the atomic charges shows a deficit of 1.6 electrons for all gallium atoms, i.e., an effective overall charge of 1.6 for the [Ga84]-cluster kernel. In the ligand shell the atomic charges of the nitrogen and carbon atoms exhibit negative values while those of silicon and hydrogen are positive.

To study the influence of the formal charge q of the cluster we calculated the electronic structure of the single clusters [Ga84(N(SiMe3)2)20]q− varying q as q=0,−1,−2,−3,−4,−5,−6. Our results are displayed in Table I. Taking into account that the cluster contains 624 atoms, the binding energy differences between the differently charged clusters are rather low. Nevertheless, the two clusters with q=−3,−4 own the highest binding energies of −7.5 eV and −6.9 eV, respectively. Thus, without the counterions those two clusters are electronically more stable than the other ones as shown in Table I. This result is in agreement with the experiment, because a cluster nearly isostructural with the [Ga84(N@N)]4− cluster was synthesized very recently,24 which bears a threefold negative formal charge.

Taking the differences of the atomic charges of the [Ga84(N(SiMe3)2)20]q− cluster and the noncharged [Ga84(N(SiMe3)2)20] one the additional q electrons are distributed for all clusters [Ga84(N(SiMe3)2)20]q− as follows: 50% at outer hydrogen atoms, 20% at carbon atoms, 15% at nitrogen atoms, 10% at gallium atoms, and 5% at silicon atoms.

In order to find a more quantitative expression for the character of the electron distribution in the single cluster structure we define the degree of delocalization \( \Lambda_i \) for the state \( i \) as follows:

\[
\Lambda_i = \sum_{j=1}^{N} N_{ij}.
\]  

\( N_{ij} \) is the Mulliken gross population for the jth atom in state i. Therein one can distinguish two limiting cases: \( \Lambda_i=1 \) for

\[
\begin{array}{c|c}
\text{Charge } q & E_{\text{bind}}^q (\text{eV}) \\
\hline
0 & 0 \\
1− & −4.74 \\
2− & −6.24 \\
3− & −7.49 \\
4− & −6.86 \\
5− & −5.99 \\
6− & −1.25 \\
\end{array}
\]

For the positivated Ga2 dumbbell and the positively charged Ga@N atoms of the outer shell the last maximum occurs at −1.3 eV, the two intermediate, nearly neutral shells exhibit maxima at −1.0 eV, whereas the pronounced maximum of the two negatively charged apex atoms is upward shifted to −0.8 eV. In the DOS projected on Ga@N atoms, one can realize an additional influence of the electron withdrawing nitrogen atoms.

With the projection of the electronic DOS on the different shells of gallium atoms (see Fig. 1). The comparison of the DOS of \( \alpha \)-gallium (dashed) and that of the central gallium dumbbell for the following Ga20 and Ga40 shells the DOS of \( \gamma \)-gallium, respectively (dashed) shows similarities.

the atomic structure as obtained from the x-ray data.

The calculated electronic DOS of the complete cluster structure [Ga84(N(SiMe3)2)20]4− is shown as a grey line in the top part of Fig. 7. As discussed above the [Ga84(N(SiMe3)2)20]4− cluster exhibits a relatively high electronic DOS at the Fermi level and no significant energy gap. The projection of the DOS on the complete [Ga84] core is given by the black line in the top part of Fig. 7. The gallium states occur in the range from −9 eV to 0 eV, and the positions and heights of the maxima follow roughly the square root function of the free electron gas.

With the projection of the electronic DOS on the different gallium shells we obtain a more detailed picture. The lower panels in Fig. 7 show that curves of the electronic DOS of the inner shells exhibit roughly similarities to the corresponding curves of the bulk gallium modifications: While the projected DOS on the central gallium dumbbell follows that of \( \alpha \)-gallium, the two following gallium shells exhibit similarities of the \( \gamma \)-gallium modification. Overall, a correlation between the partial charge on the gallium atoms and the peak position of the last maximum in the occupied DOS emerges.
full localization at one atom and \( \Lambda_e = 1/N \) for complete delocalization over the whole cluster.

For the \([\text{Ga}_{64}(\text{SiMe}_3)_2]^{3-}\) cluster the electrons are completely delocalized if the value of \( \Lambda_e \) amounts to \(1.6 \times 10^{-3}\). The states near the Fermi energy give degrees of delocalization in the range of \( \Lambda_i = 1.3, \ldots, 2.6 \times 10^{-2}\). This means the electronic states are not fully delocalized over the whole cluster structure, but the Mulliken gross population directly shows that they are only delocalized over the gallium, nitrogen, and silicon atoms.

C. Crystal structure

For the packing of the individual clusters into a slightly simplified hexagonal model of the crystal structure we employ again the cluster geometry obtained from the experimental x-ray data, omitting the counterions, \(\text{Li} \text{(THF)}_2^+\) and \(\text{Li}_2\text{Br(THF)}_n^+\). The lattice constants were adjusted accordingly as follows: We assign the axis from the apex atoms of one cluster over the toluene molecules to the apex atoms of the neighboring cluster as \(z\) direction and continue the other directions within an idealized hexagonal packing of the cluster chains. Within this supercell the two toluene molecules were placed at the positions obtained from the x-ray data. Thus, the supercell parameters amount to \(a=b=20.8\) Å and \(c=26.2\) Å. For this periodic model we carried out band structure calculations with a set of 25 \(k\) points, applying the TFB method. The results for the electronic structure are identical to the ones obtained for the single, free cluster. Even for the periodic cluster structure no dispersion of the electronic bands in reciprocal space is obtained. This indicates that the localization of the electronic states discussed above for the free cluster is not lifted due to the packing in the crystal. For a more detailed analysis of the localization, additional calculations were carried out for the same supercell size, but containing either only the toluene molecules or the cluster. A comparison of the atom-resolved Mulliken charges gives no indication for a transfer of electronic charge over the toluene molecules.
Additionally, we tested whether a different orientation of the toluene dimer affects these results, because large temperature factors had been obtained for those atoms in the experiment. The toluene molecules are rotated by 90 degrees in such a way, that the \( \pi \)-systems point to the apex atoms of the \( \text{Ga}_{84} \) clusters. The results for the electronic structure are identical to the ones calculated for the other orientation.

As the DFTB method uses several approximations, in particular a minimal basis set composed of atomic orbitals, we investigated some model clusters with a fully self-consistent plane-wave band-structure DF-formalism (ABINIT). The plane-wave basis set can represent also extended states that may affect the electronic conductivity and are not well represented within the minimum basis used in the DFTB calculations.

First we calculated the electronic DOS (\( \Gamma \)-point approximation) of the clusters \([\text{Ga}_{84}]\), \([\text{Ga}_{84}]\), \([\text{Ga}_{84}N_{20}]\), and \([\text{Ga}_{84}(\text{NH}_2)_{20}]\), without additional toluene molecules in the hexagonal packing described above. The results are shown in Fig. 8 together with the results of the DFTB calculations for these clusters. Overall, the onset of the valence levels is shifted from \(-9.5\) eV in the DFTB calculations to \(-10\) eV in the DFT investigation, but the two curves differ mainly by a homogeneous scaling of the DOS with respect to the energy axis. This difference has already been observed for the DOS of the crystalline \( \alpha \)-gallium modification in Fig. 3. Thus, for all studied clusters, nearly identical DOS curves are obtained by both methods, especially in the region of the occupied states. Some minor differences can be observed for the unoccupied states, which are generally more delocalized and hence better represented by the plane-wave basis set.

Finally, the smaller periodic cluster model \([\text{Ga}_{84}(\text{NH}_2)_{20}]^{2-} \cdot 2\text{toluene}\) was chosen as a computationally feasible alternative to the very large \([\text{Ga}_{84}(\text{SiMe}_3)_{20}]^{2-}\) cluster. In order to ensure the correct charge state, the counter ions, Li\((\text{THF})_2^+\) and Li\(_2\text{Br}(\text{THF})_2^+\), were either replaced by an equivalent homogenous background charge, or modeled by bare Li\(^+\) ions. The even smaller cluster \([\text{Ga}_{84}N_{20}]\), whose DOS had most features in common with the \([\text{Ga}_{84}(\text{SiMe}_3)_{20}]^{2-}\) cluster was not selected for the study, because its smaller size would require an adjustment of the lattice constant of the model cell, which would lead to significantly shorter distances between the counter ions.

Nevertheless, from the band structure calculation on five points along the \( z \) direction no dispersion of the electronic bands is obtained, regardless whether we neglect the counter ions or whether we include them explicitly as four noncoordinated lithium atoms at their relative positions taken from the x-ray data. An analysis of the site- and band-resolved electron density shows, that the states at the Fermi level are mainly cluster based, whereas states with contributions from the toluene molecules occur only at \( 0.8 \) eV above the Fermi level. Hence, in the regular model system there is no indication for electronic conductivity due to easily available extended states close to the Fermi level. Based on the present results one would rather suggest a hopping-type electronic conductivity between the metallic cluster cores.

IV. SUMMARY AND CONCLUSIONS

Density-functional-based tight-binding (DF-TB) and density-functional bands-structure calculations (DFT) were carried out for bare and ligated Ga clusters as models of the compound \([\text{Ga}_{84}(\text{SiMe}_3)_{20}]^{2-}\) and the packing of the ligated clusters in a close-packed three-dimensional crystal structure. In the single clusters, the electronic states are delocalized over the whole metalloid cluster core, and the gallium atoms exhibit no significant charge. Without the ligand shell, the charge distribution of the \( \text{Ga}_{84} \) is quite different, thus the ligands play a crucial role for the stabilization of the structure. This fact coincides with the observation that \( \text{Ga}_{84} \) neither exhibits the atomistic structure of a magic cluster, nor contains a number of valence electrons, which leads to electronic shell closing in a simple spherical jellium model.

Among the simplified models for the complete \([\text{Ga}_{84}(\text{SiMe}_3)_{20}]^{2-}\) cluster \([\text{Ga}_{84}N_{20}]\) describes the electronic DOS best, whereas the correlation between the cluster shells and the charge distribution is reproduced better with the \([\text{Ga}_{84}(\text{NH}_2)_{20}]\) cluster. Band-structure calculations of the crystal composed of the \([\text{Ga}_{84}(\text{SiMe}_3)_{20}]^{2-}\) cluster with or without the counterions present in the experiment do not yield any significant dispersion of the electronic bands. Thus it is concluded that the observed macroscopic electric conductivity is mediated by a hopping mechanism between the clusters rather than by the presence of states, which are delocalized over the whole crystal.

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