I. INTRODUCTION

A general goal of cluster physics is to study the emergence of bulk behavior right from the molecular limit, by building clusters of increasing size and following the size evolution of selected properties. From the theoretical point of view, this ambitious plan has been largely impeded because of the slow and nonmonotonic size evolution observed in many properties. The predicted cluster structures are not simply related to the corresponding bulk structures in many cases, which precludes the possibility of a meaningful extrapolation to the bulk limit. Moreover, cluster structure is difficult to determine theoretically due to the huge increase in the number of isomers with size, and experimentally due to the small number of scatterers compared with the bulk case. Nevertheless, recent advances involving ion mobility measurements, electron diffraction from trapped cluster ions, or the use of photoelectron spectra as a fingerprint of structures, have been successful in elucidating the structures of several ionic and covalent clusters.

Abundance patterns obtained from the mass spectra of binary ionic clusters like the alkali halides and alkaline-earth oxides point toward a prompt establishment of bulk rock-salt symmetry. Theoretical calculations have shown, however, that small sodium iodide and lithium halide clusters adopt ground state structures based on the stacking of hexagonal rings. In the case of alkaline-earth oxide clusters, the large and coordination-dependent values of the oxide polarizabilities favor the formation of structures with a large proportion of ions in surface sites, inducing a delay in the emergence of bulk structural properties. Turning to the alkali halides, bulk CsCl, CsBr, and CsI crystallize in the CsCl-type structure, while both experimental mass spectra and theoretical calculations indicate that small clusters of those materials adopt ground state structures which are fragments of a rock-salt lattice. This implies that there has to be a structural phase transition as the cluster size is increased. Ion mobility measurements performed by Löffler suggest that (CsCl)$_n$Cs$^+$ cluster ions with $n=32$ are specially compact, which might be explained by the presence of isomers with the shape of a perfect three-shell rhombic dodecahedron (that is with bulk CsCl symmetry) in the cluster beam. The electron diffraction experiments performed recently in the group of Park show that there is a substantial proportion of isomers with bulk CsCl symmetry for the same size.

In this theoretical work we analyze the above mentioned size-induced phase transition in (CsCl)$_n$Cs$^+$ cluster ions. We consider only those sizes that correspond to geometrical shell closings for the CsCl-type (perfect rhombic dodecahedra with $n=32, 87, 184, 335, 552$) and rock-salt (perfect cubes with $n=13, 62, 171, 364, 665$) structural series. In doing so, we try to avoid any nonmonotonic size evolution in the calculated properties. In the upper part of Fig. 1 we display the relative number of atoms with a given coordination as a function of $N^{-1/3}$, where $N=2n+1$ is the total number of atoms in the cluster. In the lower part we show the number of atoms with nonbulk coordination relative to the total number of surface atoms. For the largest sizes considered the proportion of bulklike atoms is dominant, and within the surface the proportion of face-like atoms is already much larger than those of edge and vertex-like atoms. From those sizes to the bulk, the only meaningful size evolution of these proportions will be a slow approach to zero of the face-like atoms. We thus expect to capture all the physical information relevant to the phase transition by studying this set of clusters and the corresponding bulk phases, which have been studied both with the same theoretical model. In this way inaccuracies related to the use of different methodologies are avoided and a meaningful extrapolation to the bulk limit can be done.

In a second part of the work, we explicitly analyze the structures adopted by (CsCl)$_n$Cs$^+$ cluster ions in the size range $n=31–33$, in order to explain the experimental findings of Refs. 1 and 4.

The rest of the paper is organized as follows: Section II includes just a brief description of the theoretical model employed in the calculations, as a full account of it has been given in previous publications. In Section III we present and discuss the results of the calculations, and Section IV summarizes the main conclusions.
II. THEORETICAL MODEL

Cluster energies have been obtained by performing Perturbed Ion (PI) plus polarization calculations. This is a well tested method that describes accurately both bulk and cluster limits. Its theoretical foundation lies in the theory of electronic separability. Very briefly, the cluster wave function is broken into local group functions (ionic in nature in our case) that are optimised in a stepwise procedure. In each iteration, the total energy is minimized with respect to variations of the electron density localized in a given ion, with the electron densities of the other ions kept frozen. In the subsequent iterations each frozen ion assumes the role of nonfrozen ion. When the self-consistent process finishes the outputs are the total cluster energy and a set of localized wave functions, one for each geometrically nonequivalent ion of the cluster. This procedure leads to a linear scaling of the computational effort with cluster size, which allows the investigation of large clusters with an explicit inclusion of the electronic structure. The cluster binding energy can be decomposed into ionic additive contributions

$$E_{\text{clus}}^{\text{bind}} = \sum_{R \in \text{clus}} (E_{\text{add}}^R - E_{0}^R),$$

being $E_{\text{add}}^R$ the contribution of the ion R to the total cluster energy and $E_0^R$ the energy of the ion R in vacuo. In this way the contribution of ions with different coordinations to the binding energy can be separately analyzed, which is particularly convenient for our study. Each additive energy can be decomposed in turn as a sum of deformation and interaction terms

$$E_{\text{clus}}^{\text{bind}} = \sum_{R \in \text{clus}} (E_{\text{def}}^R + 1/2 E_{\text{int}}^R),$$

where $E_{\text{def}}^R$ is the self-energy of the ion R, measured relative to the vacuum state, and $E_{\text{int}}^R$ contains electrostatic, exchange and repulsive overlap energy terms. The polarization contribution to the cluster binding energy is not computed in the actual version of the PI code, as it assumes (for computational simplicity) that the electronic charge distribution of each ion in the cluster is spherically symmetric. Thus, a polarization correction to the PI energy is computed semiempirically as described in Refs. 2-3. Bulk polarizabilities are used for both Cs$^+$ and Cl$^-$ ions. This is a good approximation for the Cs$^+$ cations. The main effect on the anion polarizabilities when passing from the bulk to a cluster environment is an increase of the polarizabilities of those ions located on the cluster surface, due to the lower average coordination compared to the bulk. However, we have checked that our main conclusions are not affected by an increase in the surface chloride polarizabilities as large as 10–20%, which are typical values for halides. The short-range induction damping parameters have been obtained through the scaling procedure validated in Ref. 24. The reliability for cluster calculations of the mixed quantum-mechanical/semiempirical energy model thus obtained has been checked and shown to be high in previous publications. 22-24

III. RESULTS

A. The rock-salt to CsCl-type structural transition

Fig. 2 shows the size evolution of the binding energy per ion. First of all, we note that the PI model properly reproduces the stability trend in the bulk, predicting the CsCl structure as the most stable one. This is a tough problem for semiempirical methods, as Pyper has shown that a full account of the coordination number dependence of the self-energy and overlap contributions is necessary to obtain the correct ground state structure. The values of the binding energy, plotted as a function of $N^{-1/3}$, lie neatly on a straight line. The regression coefficients obtained from a fit are 0.9998 in all cases if we exclude from the fitting the NaCl-type cluster with $n=13$, which is the smallest one. We have calculated after the fitting procedure the energy of the $5 \times 5 \times 7$ cuboid (also included in Fig. 2), and checked that it lies on the fitted NaCl-type energy curve. This shows that a consideration of perfect cubes (or cuboids) on one hand, and rhombic dodecahedra on the other hand removes the non-monotonic behavior from the size evolution of the binding energies. Our results predict that the rhombic dodecahedra become definitely more stable after the completion of the fifth shell of atoms, that is for $n=184$. The four-shell rhombic dodecahedron and the $5 \times 5 \times 7$ cuboid are essentially degenerate, so both of them will contribute to the enhanced abundance observed experimentally for $n=87$. 25 We have not found any experimental mass spectrum for values of $n$ as high as 184, but we predict that a new set of magic numbers, corresponding to the closing of rhombic dodecahedral atomic shells, should emerge from this size on. The magic numbers corresponding to the closing of perfect cubic shells will probably not disappear still at that specific size from the mass spectra, because they do not coincide with the CsCl shell closings, and complete cubes can remain more stable than incomplete rhombic dodecahedra until larger values of $n$ are reached. Polarization has little influence on these general results, and only affects the energetic ordering of the two essentially degenerate isomers mentioned above.

Now we turn to an analysis of the physical factors responsible for this transition. In Fig. 3 we show the binding energy per ion, averaged over subsets of ions with a fixed coordination. The contribution of bulklike ions to the binding energy favors always the formation of CsCl-type structures. However, the contribution of face-like ions favors the formation of rock-salt fragments. As soon as the proportion of bulk ions is larger than that of surface atoms, which occurs after the completion of the fifth rhombic dodecahedral atomic shell, fragments of the CsCl-type lattice become more stable. The energy contribution of those ions in edge positions is approximately the same for both structural families except for the smallest clusters; finally, corner atoms favor the CsCl-type structures, but their small relative number results in a very small contribution to the total energy for those sizes where the transition occurs.

Fig. 3 has reduced the structural phase transition in (CsCl)$_n$Cs$^+$ cluster ions to an essentially bulk effect. By
this we mean that CsCl-type structures become more stable as soon as the proportion of bulklike atoms is dominant. To complete our discussion we have then to address the stability question in the bulk. This is more easily understood by analyzing the reasons why other alkali halides like NaCl or CsF do not crystallize in the CsCl-type lattice. The largest contribution to the binding energy of an ionic crystal is the Madelung energy term $E_M = \frac{1}{2} \frac{e^2}{R}$, with $M$ the Madelung constant and $R$ the equilibrium interionic distance. The Madelung constant of the CsCl-type lattice (1.762675) is larger than that of the rock-salt lattice (1.747565), so were the value of $R$ the same for both structures, the CsCl-type would always be more stable. We have solved for the electronic structure of NaCl and CsF crystals in the CsCl-type structure at a nonequilibrium value of the interionic distance, chosen in such a way that the Madelung energy term is exactly the same as in the corresponding rock-salt lattice at equilibrium. In the case of NaCl, $E_{add}(Na^+)$ favors the CsCl-type structure, but $E_{add}(Cl^-)$ largely favors the rock-salt phase. The main reason is the large anion-anion overlap at that artificial distance, that is the $Na^+$ cation is so small compared to the $Cl^-$ anion that eight anions can not be packed efficiently around a cation. In CsF the situation is reversed, and it is the cationcation overlap that is too large. This demonstrates that the stability situation in the bulk is a purely packing effect: in CsCl, CsBr and CsI, the large value of the cation-anion size ratio allows for an equilibrium interionic approach in the CsCl-type structure close enough as to obtain a Madelung energy term more negative than in the rock-salt phase, without a large overlap interaction between like ions. The same is true for the bulklike ions in the clusters studied, and so when those ions begin to dominate the energetics, the bulklike fragments become more stable.

We have made a prediction above that can be tested experimentally, namely the emergence of a new set of magic numbers from $n=184$ on. Here we propose another, perhaps more indirect, experimental test. In Fig. 4, the eigenvalues of the 3p orbitals of $Cl^-$ (with opposite sign) are plotted as a function of $N^{-1/3}$. We have a band of eigenvalues for each size because the anions occupy nonequivalent positions in the clusters. As the clusters under study are formed by closed shell ions whose wave functions are strongly localized, it can be assumed that an electron is extracted from a specific localized orbital when the cluster is ionized. This is the lowest bound 3p orbital, which corresponds always to a chloride anion with a low coordination. Thus the dashed lines represent the size evolution of the vertical ionization potential IP (in the Koopmans’ approximation) for both structural families. For the rock-salt series, that size evolution is approximately linear in $N^{-1/3}$, but for the CsCl-type series it shows a more or less oscillating behavior, which should be detected in experimental measurements of the vertical IP if rhombic dodecahedra actually are the ground state structures from a given size on. We can explain these different electronic behaviors in a very simple way: in the rock-salt clusters the eight corner sites are always occupied by Cs$^+$ cations. The weakest bound electron corresponds always to a Cl$^-$ anion with fourfold coordination, namely anyone of those closer to the corner cation sites. On the other hand, rhombic dodecahedra have fourteen corner sites. When the number of atomic shells is even, all these sites are occupied by Cs$^+$ cations, but when that number is odd, eight of them are cationic sites and the other six anionic sites. Thus the nonmonotonic behavior of the vertical IP is due to the different local coordination of the Cl$^-$ anion to which the weakest bound electron is attached as the number of atomic shells increases.

### B. Structures of $(CsCl)_{n}Cs^+$ (n=31–33) and comparison to experiment

We finish our study with an explicit consideration of $(CsCl)_{n}Cs^+$ clusters in the size range $n=31–33$, the range covered in the experiments of Löffler and Parks. Specifically, we have considered the most compact $7 \times 3 \times 3$, $4 \times 4 \times 4$ and $5 \times 4 \times 3$ rock-salt structures, and the three-shell rhombic dodecahedron, with some atoms added or removed from different positions. The binding energies are shown in Table I. The ground state (GS) structure of $(CsCl)_{31}Cs^+$ is a complete $7 \times 3 \times 3$ cuboid. The $4 \times 4 \times 4$ fragment with an anion removed from a corner position is slightly less stable, and the lowest energy rhombic dodecahedral isomer we have obtained has a still lower stability. For $n=32$, the complete three-shell rhombic dodecahedron becomes the GS isomer. All the different incomplete rock-salt fragments have a smaller binding energy. For $n=33$, the different rock-salt isomers are essentially degenerate, but the CsCl-type structure is found again at a higher energy. This sequence of GS structures for $(CsCl)_{n}Cs^+$ clusters is consistent with the experimental findings. The relative mobility is a local maximum for $n=32$, as the perfect three-shell rhombic dodecahedron is evidently more compact than the complete $7 \times 3 \times 3$ $(CsCl)_{31}Cs^+$ cuboid or any of the incomplete rock-salt structures obtained for $n=33$. Also, the energetical ordering of the isomers is consistent with the large proportion of CsCl-type isomers found for $n=32$ in the electron diffraction experiments.

### IV. SUMMARY

We have reported a computational study of the size-induced rock-salt to CsCl-type structural phase transition in $(CsCl)_{n}Cs^+$ cluster ions. For this purpose, the Perturbed Ion (PI) method, supplemented with a semiempirical account of polarization effects, has been employed. Only cluster ions with an atomic closed-shell configuration have been considered in order to avoid nonmonotonic behavior in the calculated properties. Moreover, we have employed the same theoretical model to study both cluster and bulk limits, which allows for a meaningful extrapolation strategy. The main result is that rhombic dodecahedral isomers become definitely more stable than rock-salt structures after the completion of the fifth rhombic-dodecahedral atomic shell, that is for a size $n=184$. Thus, it is predicted that a new set of
magic numbers, reflecting the establishment of the new structural symmetry, should emerge from that size on. The size evolution of the vertical ionization potential of the cluster ions should also be a good experimental fingerprint of the transition. In order to explain the nature of the transition, an analysis of the binding energy into ionic components has been performed. The result is quite simple: bulklike ions always prefer to have a CsCl-type environment, even for the smallest cluster sizes (this has been shown to be a purely packing effect), while surface-like atoms prefer to adopt rock-salt structures. The transition occurs as soon as the proportion of bulklike atoms is large enough to dominate the energetics of the whole cluster. One of the possibilities advanced by Parks consistent with his experimental results is the existence of isomers with mixed symmetry. Our results indicate that the formation of isomers with a CsCl-type core and a rock-salt-type surface could be energetically favored, if the strain accumulated in the bonds at the interface region separating both phases can be conveniently relaxed. This point deserves further investigation.

The structures adopted by \((\text{CsCl})_n\text{Cs}^+\) cluster ions have been more carefully studied in the size range \(n=31–33\), which has been covered in the experimental investigations. Our results are consistent with the experimental findings, and show that the three-shell rhombic dodecahedron is the lowest energy isomer for \(n=32\).

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**Captions of Tables.**

**Table I** Binding energy, in eV/ion, of the different rock-salt and CsCl-type structures for the size range \(n=31–33\).

**Captions of Figures.**

**Figure 1** Size evolution of the number of atoms with a given coordination, relative to the total number of atoms (upper half) or to the total number of surface atoms (lower half). The left half refers to CsCl-type symmetry and the right half to rock-salt symmetry.

**Figure 2** Size evolution of the binding energy per ion for both CsCl-type and rock-salt structural families, with (lower half) and without (upper half) the inclusion of polarization corrections. The value of \(N^{-1/3}\) at the transition point has been indicated with an arrow.

**Figure 3** Size evolution of the binding energy contributions from ions with different coordinations. Full circles represent ions in the CsCl-type structures and squares represent ions in the rock-salt structures.

**Figure 4** Size evolution of the 3p orbital eigenvalues of chloride anions. The dashed line represents the variation of the vertical ionization potential in the Koopmans’ approximation with size.

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| n=31 | Structure | Energy (eV/ion) | n=32 | Structure | Energy (eV/ion) | n=33 | Structure | Energy (eV/ion) |
|------|-----------|----------------|------|-----------|----------------|------|-----------|----------------|
|      | 7×3×3     | 3.032          |      | 7×3×3+2   | 3.021          |      | 7×3×3+4   | 3.025          |
|      | 4×4×4-1   | 3.026          |      | 4×4×4+1   | 3.032          |      | 4×4×4+3   | 3.027          |
|      | 5×4×3+3   | 3.019          |      | 5×4×3+5   | 2.998          |      | 5×4×3+7   | 3.028          |
|      | CsCl-type | 2.983          |      | CsCl-type | 3.048          |      | CsCl-type+2| 2.980          |
