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# Close-packing structure of small barium clusters

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Barium clusters are produced by the inert-gas condensation technique. The observed size distribution shows large peaks at $n=13$, 19, 23, 26, 29, 32, as well for singly charged clusters as for doubly and triply charged clusters. These results can be interpreted by icosahedral close-packing structures, similar to those observed in noble-gas clusters.

One of the main challenges of cluster science is to understand how the atomic structure leads to the physical and chemical bulk properties. From this point of view, the divalent metals are particularly interesting. The atom has a $s^2$ closed-shell structure and these materials should be, in principle, insulator in the bulk, the metallic character resulting only from the overlap betwen the $s$ and $p$ bands.[1] Recently this problem has been extensively studied in the mercury clusters[2-4] and a transition from a van der Waals structure to a metallic one has been observed beyond $n=12$ atoms in the cluster. However, up to now, despite theoretical calculations on berryllium[5-7] and magnesium[8] clusters, no experimental results have been carried out in column II*A* elements such as Be, Mg, Ca, Sr, and Ba for which the atomic $s$-$p$ band gap is much lower.

In the present paper we report the first observation of barium clusters generated by the inert-gas condensation technique. The observed mass spectra exhibit very clear magic numbers which may be easily explained by icosahedral packing geometry.

The barium clusters are generated by the gas aggregation technique. The clusters source is very similar to that developed by Sattler *et al.*[9] and has been described in previous papers.[10] Briefly, the barium metal heated at about 730 °C is vaporized in a helium atmosphere at a pressure which varies typically from 1 to 4 Torr. The helium gas, as well as the copper walls of the condensation chamber, are cooled at liquid-nitrogen temperature. The helium cluster's gas is then expanded through a 2-mm nozzle into an intermediate chamber maintained at $10^{-4}$ Torr by a 1800-liter/s pump. Finally the beam goes into a high-vacuum chamber where the clusters are ionized by electron impact at energies varying from 5 to 100 eV. The ionized clusters are then analyzed by a time-of-flight mass spectrometer.

Figure 1 shows typical mass spectra of barium clusters recorded at rather low electron energy (12 eV). Intense peaks may be easily remarked on the spectrum corresponding to the following magic sequence 13, 19, 23, 26, 29, 32. These results are confirmed by the study of the mass spectrum as a function of the generation conditions. As recently demonstrated,[11] the cluster's mass distribution produced by the inert-gas condensation technique may be easily shifted, when the helium pressure varies. The results obtained for barium clusters are shown in Fig. 2. The same magic sequence 13, 19, 23, 26, 29, 32 emerges very clearly whatever the averaged mass of the clusters distribution. Sometimes, other peaks (11, 17, 35, and 37) may be almost as intense as those of the "magic sequence," but if we average in the large number of recorded mass spectra, they are definitively less intense. The high intensity observed for a given number of atoms suggests that they correspond to very stable structure. The numbers 13 and 19 are in favor of icosahedral structures observed in the rare-gas cluster's molecular beam in mass spectra studies.[12-14] Icosahedral structures are also observed for larger clusters in electron-diffraction experiments.[15] In fact, Harris, Kiowell, and Northby[16] have already observed exactly the same magic sequence 13, 19, 23, 26, 29, 32 in the mass spectra of singly charged argon clusters directly produced in the free-jet expansion. Their results are interpreted by icosahedral close-packing structure: They consider an icosahedron of 13 atoms which constitutes the core structure of the cluster. Atoms are then added on the faces of the icosahedron (fc sites) or the vertices of an atom of the icosahedral core ($V$ sites). Harris *et al.*[16] have shown that the sequence 13, 19, 23, 26, 29, 32, 34 corresponds to the most stable clusters because the number of bonds is maximum. These structures are obtained by adding atoms at fc sites around our atom of the core and then an atom on the enclosed vertex site, the added atoms forming a cap. Then an adjacent cap is filled. The structures of 19, 23, 26, 29, 32, 34 atoms correspond to the completion of one, two, three, four, five, six

 

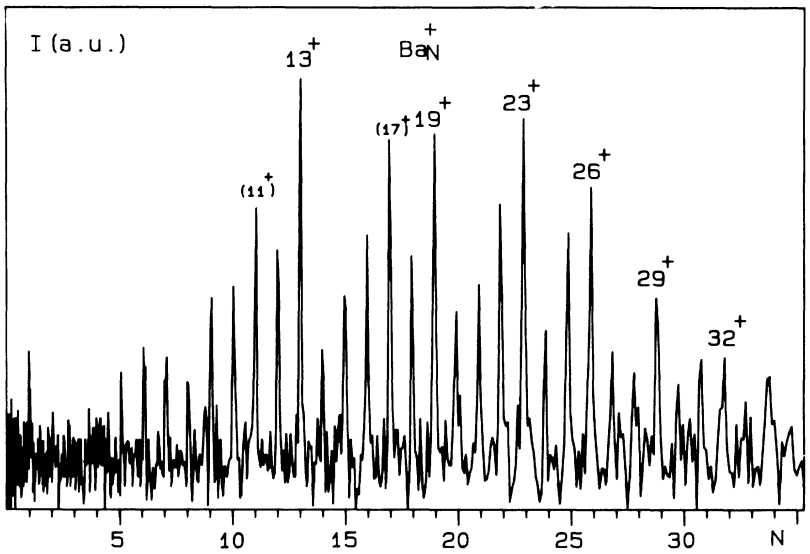


FIG. 1. Mass spectrum of barium clusters obtained at low-ionization electron energy (12 eV). The helium pressure is 3 mbar. The magic sequence (13, 19, 23, 26, 29, 32) clearly emerges from the spectrum.

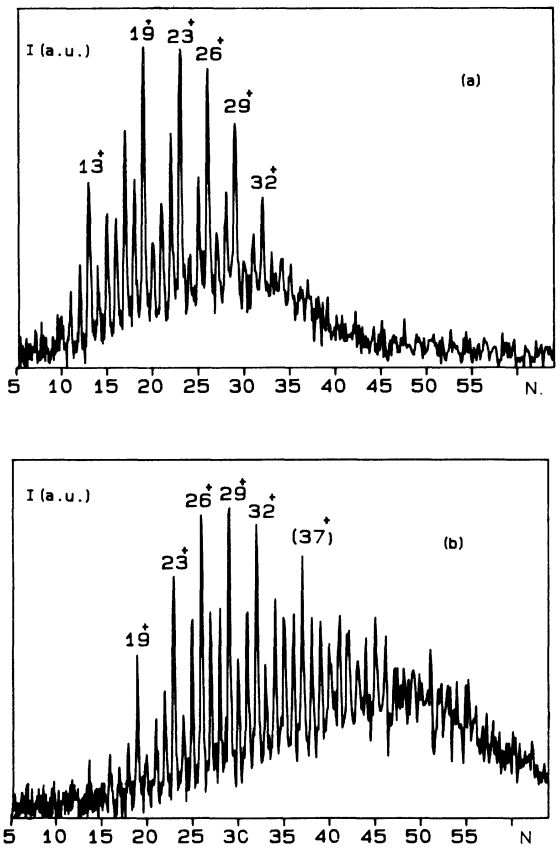


FIG. 2. Influence of the helium pressure: (a) $p_{He}=4.5$ mbar; (b) $p_{He}=2.2$ mbar. When the helium pressure increases, the mass spectrum is shifted to low masses, but the magic sequence emerges in both cases. For both spectra, the ionizing electron energy is 20 eV.

adjacent caps.

As already demonstrated for mercury clusters,[17] intense small doubly charged clusters of divalent metals may be easily obtained by electron-impact ionization. Figure 3 shows the barium cluster's mass spectrum recorded at 30 eV for two different generation conditions. The observed critical size for doubly charged barium clusters is $n_c^2=9$ [Fig. 3(a)]. However, the most interesting feature of Fig. 3 is the observation of the same magic sequence (13, 19, 23, 26, 29, 32) on the doubly charged clusters series. Triply charged clusters may also be observed at higher electron energy and Fig. 4 displays the obtained results at 55 eV in two different generation conditions. The critical size for triply charged clusters is found to be $n_c^3=22$ in Fig. 4(a) for which the size distribution is centered around $n\approx 25$. It is striking to remark that the magic sequence 23, 26, 29, 32 may still be observed in the triply charged clusters. Our results concerning these multiply charged clusters clearly indicate that the observed magic sequence is not dependent on the clusters charge. This is not in contradiction with the present model because the stability of these icosahedral structures is mainly due to the number of bounds which only depend on the geometry. It is also interesting to remark that the observed mass spectra are almost independent on the electron energy. They are not strongly shifted toward small masses when the electron energy increases, as it has been observed for lead[11] or antimony clusters.[18] This probably means that the fragmentation phenomena are not very important in barium clusters or at least that they are almost independent on the ionization energy which in our experiment is always well above the ionization threshold.

Above $n=32$, we no longer observed clear magic numbers. The cluster having 34 atoms corresponds to six adjacent caps in the previously described model. The peaks $Ba_{34}^+$ [Fig. 2(b)] and $Ba_{34}^{3+}$ [Fig. 4(b)] do not clearly

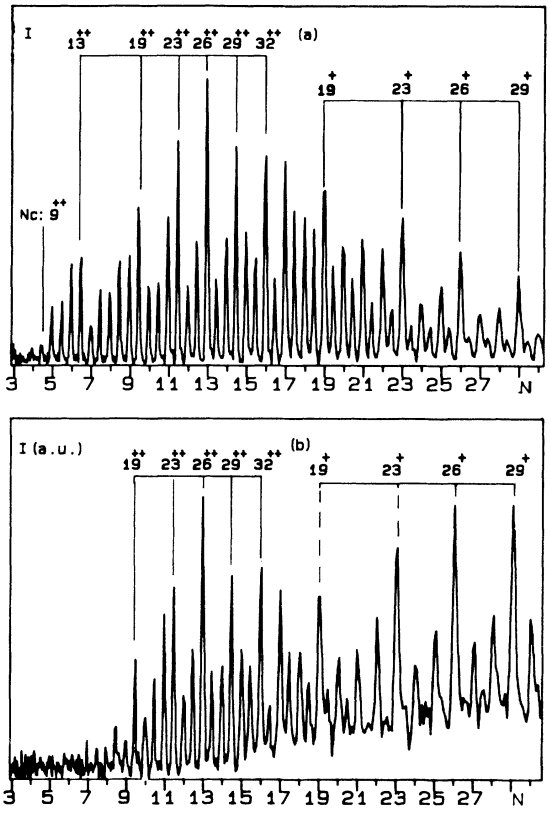


FIG. 3. Doubly charged barium clusters for two different nucleation conditions: (a) $p_{He}=4.5$ mbar; (b) $p_{He}=3$ mbar. In spectrum (a) the critical size $n_c=9$ is observed. In both spectra, the magic sequence (13, 19, 23, 26, 29, 32) is observed in singly charged and doubly charged clusters. The ionization energy is 30 eV.

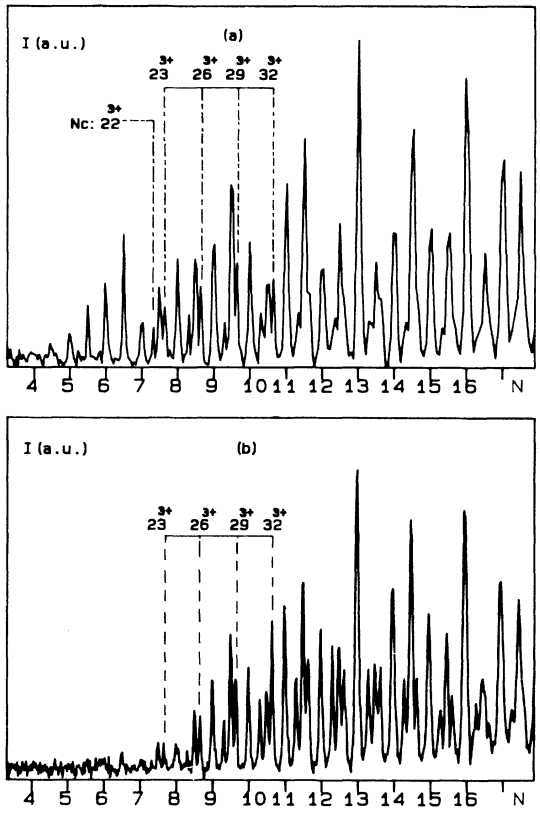


FIG. 4. Triply charged barium clusters for two different nucleation conditions: (a) $p_{He}=4.5$ mbar; (b) $p_{He}=3$ mbar. The observed critical size is $n_c=22$. The ionization energy is 55 eV. The magic sequence (23, 26, 29, 32) is also observed in triply charged clusters.

emerge in the spectra. In the case of $Ar_n^+$ clusters,[16] $Ar_{34}^+$ is very intense but the mass spectrum is blurred after $n=34$ due to the fact that a different arrangement occurs corresponding to a multilayer icosahedral structure and a very high intensity is observed for $n=55$ for which a two-shell icosahedral structure is expected. In our case, neither the intensity of $Ba_{55}^+$ [Fig. 2(b)] and $Ba_{55}^{2+}$ [Fig. 3(a)] exhibits a particular behavior as compared to neighboring peaks.

This lack of clear structure beyond $n=32$ might be due to the fact that larger clusters may have higher temperatures. In the intert-gas condensation source, an important velocity slip[10] is observed between helium atoms and the clusters, which could support this hypothesis. However, we detect ionic clusters which are ionized well above the threshold. As recently demonstrated in sodium clusters,[19] under such conditions the mass spectra reflect the ions intensity just after the extraction region of the time-of-flight mass spectrometer. The temperature of the ionic clusters is then mainly due to the dynamic process following the ionization and to the residence time of the cluster in this extraction region.[19] In any case, our ionic barium clusters cannot be very cold. Their temperature is probably a few hundred K.

As already noted at the beginning of the paper, the small clusters of divalent metals are expected to be van der Waals and a transition toward a metallic structure must occur as a function of the size. This effect has been well-characterized experimentally[2,3] in mercury clusters $Hg_n$ and a progressive delocalization of the electrons has been observed from $n>12$. Zinc and cadmium clusters[20] have been studied by the secondary-ion mass spectrometry (SIMS). For $n\geq 10$, the observed mass spectrum is tentatively interpretated by the shell model[21] which has been introduced to interpret the electronic structure of alkaline clusters and assumes the delocalization of the electrons. The experimental results are not very clear because several observed intense peaks are not interpreted in the shell-model frame. However the whole set of "magic numbers" is rather in favor of the shell model than in favor of icosahedral structures. This would mean that in zinc and cadmium clusters, the electron delocalization occurs from $n\geq 10$.

In the case of column II*A* elements, theoretical calculations have been performed mainly in berryllium clusters.[5,6] In magnesium and calcium clusters,[7] results have been obtained up to 4 atoms. The general tendency is clear, the *s-p* hybridization[7] is weaker in magnesium and calcium than in berryllium. This leads to a rather small

binding energy per atom in $Mg_4$ and $Ca_4$. This effect is due to the diffuse character of the $np$ orbital which increases with $n$. It compenses the decrease of the $ns(^1S_0)$-$np(^3P_0)$ gap with $n$. In barium the $6p$ orbital is yet more diffuse but the $6s(^1S_0)$-$6p(^3P_0)$ gap is slightly smaller than in calcium (1.5 eV in barium as correspond to 1.9 eV in calcium). Moreover, the situation is complicated by the $5d$ level which takes place just between the $6s(^1S_0)$ and the $6p(^3P_0)$ level. This makes the theoretical calculations in barium clusters quite difficult. However, the binding energy of small barium clusters is probably weak and the bonding mainly of van der Waals character. Our experimental results, which demonstrate clear icosahedral structures, are in favor of this hypothesis. Indeed, the complete delocalization of the electrons leads to the shell model for which the highest stabilities are obtained for other "magic numbers" (8, 20, 34, 40, ... , electrons). In alkaline clusters, the icosahedron (13 atoms) is not specially stable[22] because the Jahn-Teller effect lowers the symmetry of electronically degenerate states. The icosahedron having a half-filled degenerate $d$-like orbital shell is submitted to Jahn-Teller distortions. In the ellipsoidal shell model, the 13 atoms alkaline cluster has an ellipsoidal shape arising from a deformation of the sphere and this is also due to generated half-filled $1d$ orbitals.[23] This problem of degeneracy does not occur in van der Waals clusters.

In conclusion, we have observed icosahedral structures in singly, doubly, and triply charged barium clusters up to 32 atoms. Our results indicate that the structure of small barium clusters is not dominated by the shell model, which corresponds to the complete delocalization of the electrons, and they are in favor of a van der Waals structure.

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