Mass spectra of metal-doped carbon and fullerene clusters

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We present a systematic study of the abundancies of metal-doped cluster cations $M_x C_n^+$ (M=Ca, Sc, Y, La, Ce, Gd; $x=1,2$) produced in a laser vaporization source. The mass spectra of MC_n^+ and $M_2 C_n^+$ reveal the onset of endohedrally doped fullerenes from which the smallest possible cage sizes can be deduced. $Y_2 C_n$ and $La_2 C_n$ show a distinct transition from alternation odd–even to even–odd at $n=69$ and $n=71$, respectively, which can be explained by a substantial change in the doped fullerene structure, i.e., from networked to bi-endohedral systems. A metal induced cluster formation pathway is briefly discussed. © *2000 American Institute of Physics.* [S0021-9606(00)01428-8]

I. INTRODUCTION

A short time after having suggested the fullerene structure of small carbon clusters,[1] Smalley *et al.* found evidence for the existence of carbon cages with a single lanthanum atom trapped inside.[2] In laser fragmentation experiments LaC_{60}^+ shrank by successive C_2 losses, and it was "difficult to fragment past LaC_{44}^+ and impossible to go past LaC_{36}^+ without bursting the cluster." [3,4] This observation was the dawn of an extensive research activity on endohedrally doped carbon cages, since they were expected to exhibit unique properties controlled by the attributes of the encapsulated atoms.[5] Even now, 15 years after the initial discovery, basic properties are still not understood, e.g., the vanishing density of states at the Fermi level in bulk La@C_{82},[6] which is supposed to be metallic according to a simple charge transfer picture.

So far, only a few metallofullerene compounds (e.g., La@C_{82}) are available in larger quantities amenable to conventional investigation methods in solid state spectroscopy. Among these doped fullerenes are only clusters with 60 or more than 70 carbon atoms. They have been investigated by, e.g., resonant photoelectron spectroscopy,[6] x-ray photoelectron spectroscopy,[7–9] x-ray scattering,[10,11] absorption spectroscopy,[12] electron spin resonance,[13–15] and density-functional theory.[16] Comparatively little is known about metal–carbon compounds containing more than one metal atom, since only several species $M_2 C_n$ have been isolated by, e.g., high-pressure liquid chromatography.[17,18] On the other hand, gas-phase molecular beam studies have proven the existence of a multitude of endohedrally doped fullerenes covering a far wider range of masses. Information on those metal–carbon compounds that are not available in macroscopic quantities is limited to theoretical approaches[19–21] and gas-phase experiments, namely anion laser photoelectron spectroscopy[22] and ion mobility measurements.[23–28] Most of these experiments are on La-doped fullerenes, whereby some recent ion mobility studies have also been extended to Nb and Zr. In order to build a bridge to the studies on chemically extractable fullerenes we here largely want to concentrate on clusters doped with rare earth atoms as well as their counterparts without *f*-electrons. A recent publication dealing with the mass spectroscopy characterization of metallocarbon clusters incorporation Sc, Y, and Ca reveals data similar to the present ones.[29] However, our extended studies lead to somewhat different conclusions, in particular concerning the onset of bi-endohedral fullerenes.

In the present paper we, therefore, present mass spectrum of carbon cluster cations doped with calcium, scandium, yttrium, lanthanum, cerium, and gadolinium. Characteristics intensity patterns in the mass spectra allow drawing conclusions about the geometrical structure of the generated metal-doped fullerene cations. Especially the smallest possible endohedrally doped cage sizes can be deduced from the spectra. Moreover, a clue about the electronic structure of some of the clusters is obtained.

II. EXPERIMENT

The experimental setup used in the present work is devoted to the mass selected deposition of cluster ions onto a substrate under UHV conditions.[30] It consists of a three-stage setup containing a laser evaporation source, a magnetic-field mass selector, and a deposition chamber. Metal-doped carbon clusters have been produced by evaporation of a mixed metal–carbon and prepared as described earlier[31] and subsequent condensation of the plasma in a pulsed helium jet at a pressure between one and two bar. After adiabatic expansion the cluster cations are accelerated electrostatically to a kinetic energy of 4 keV prior to passing the entrance slit of the magnetic mass analyzer. The current results have been obtained using a mass resolution of $m/\Delta m \approx 250$. By scanning the magnetic flux density the cluster cations have been mass selected. They have been detected with a secondary electron multiplier behind the exit slit of the mass analyzer. Due to the high impact energies constant detector sensitivity for all masses is expected.
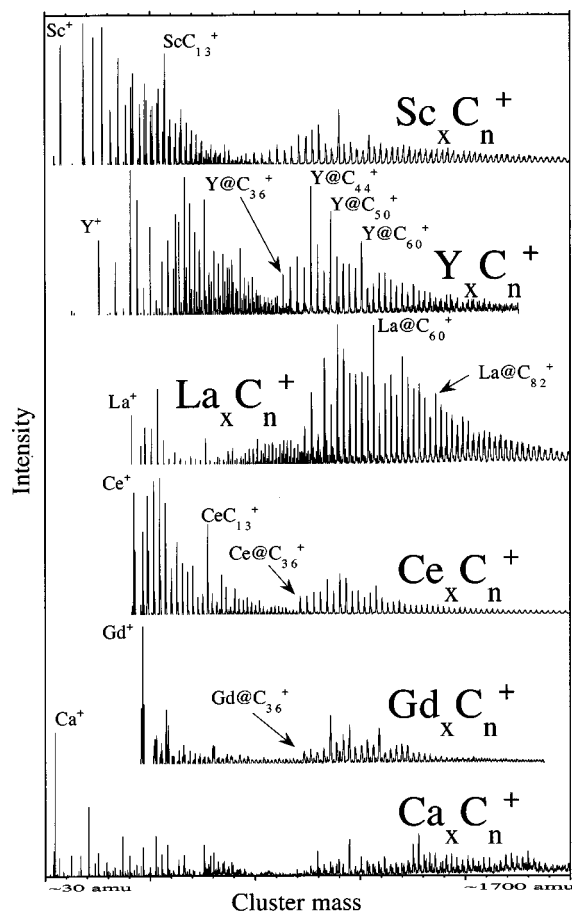

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FIG. 1. Mass spectra of metal-doped carbon cluster cations as produced from metal-doped carbon rods in a laser evaporation source. Metal–carbon compounds cover a wide range of cluster masses.

III. RESULTS AND DISCUSSION

Figure 1 shows the mass spectra of the metal-doped carbon cluster cations $M_xC_n^+$ as produced in the laser evaporation source. Clusters between 30 amu and about 1700 amu are shown in the spectra. The spectra can be divided into two domains. On the left hand side the spectra always start with the metal monomer, followed by mass peaks corresponding to singly metal-doped carbon clusters MC_n^+. Pure carbon clusters with masses smaller than the metal monomer are not observed. The high mass domain on the right-hand-side of each spectrum is dominated by metal-carbon cage structures.

A. Endohedrally doped fullerenes

Figure 2 shows the intensities of singly metal-doped carbon cluster cations MC_n^+ as a function of n, the number of carbon atoms in the cluster. The spectra reveal the onset of distinct even–odd alternations at certain cluster sizes. The distance between two consecutive mass peaks is 24 amu, which corresponds to one C_2 unit, thus labelling the onset of fullerenes. Since the abundance spectra of metal-doped carbon cluster cations differ clearly from the pristine one, exohedral doping can be excluded. We, therefore, consider these intensity patterns to be a strong indicators for endohedrally doped cages $M@C_n^+$. Thus, the present mass spectra represent a systematic and extensive investigation of the smallest possible endohedrally doped cage size for dopants that are
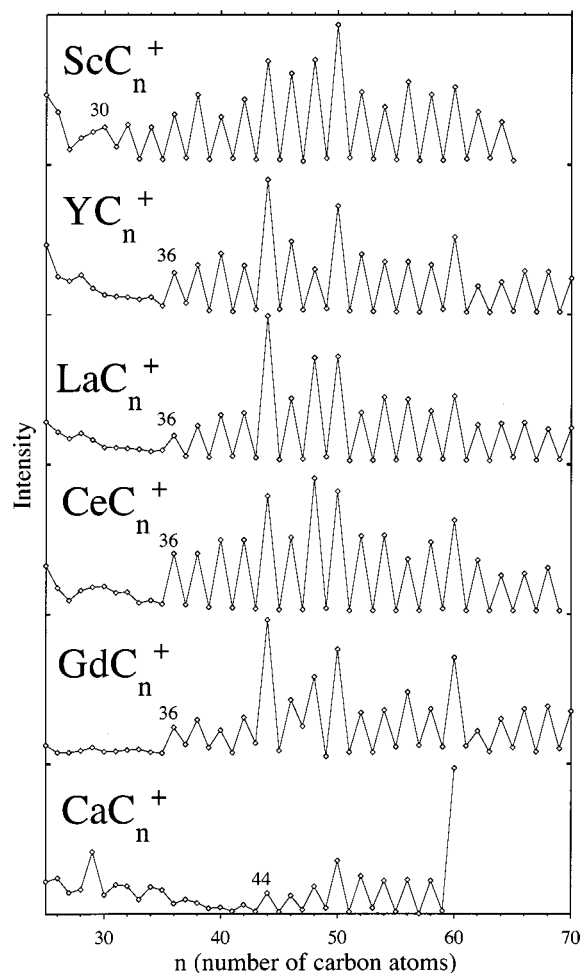

FIG. 2. Intensities of singly doped carbon cluster cations as a function of the number of carbon atoms in the clusters (n). The intensity oscillations are characteristic for cage structures. From the onset of the oscillations the smallest possible endohedrally doped cage sizes $M@C_n^+$ can be deduced.

chemically equivalent to La (and Ca). The smallest observed cage structures are $n = 30$ for Sc, $n = 36$ for Y, La, Ce, Gd, and $n = 44$ for Ca. The intensity patterns are very similar for YC_n^+, LaC_n^+, CeC_n^+, and GdC_n^+, and it appears that the smallest possible cage size is the same for the latter compounds. Prominent species are $M@C_{44}^+$, $M@C_{50}^+$, and $M@C_{60}^+$, in agreement with a recent publication.[32]

The observation of $La@C_{36}^+$ as the smallest possible endohedrally doped fullerene matches the results of the ‘‘shrink-wrapping’’ experiments performed by Smalley et al.[4] As the formation pathway of $La@C_{36}$ is either via shrinkage of bigger compounds or/and via growth of smaller compounds, the existence of endohedral $La@C_{34}$ seems possible. Indeed, when operating the cluster source at a particular low helium background pressure (800 mbar), $La@C_{34}^+$ gains intensity with respect to the neighboring $La@C_{33,35}^+$. This can be taken as indication that LaC_{34}^+ is an endohedrally doped carbon cage too, although it would have to be significantly less stable than $La@C_{n\geq36}^+$. Hence we infer from the data the existence of endohedrally doped metallofullerenes $La@C_n^+$ for $n \geq 34$, and they are the most stabile isomers for $n \geq 36$. This result is in perfect agreement with the results of ion mobility measurements.[25]
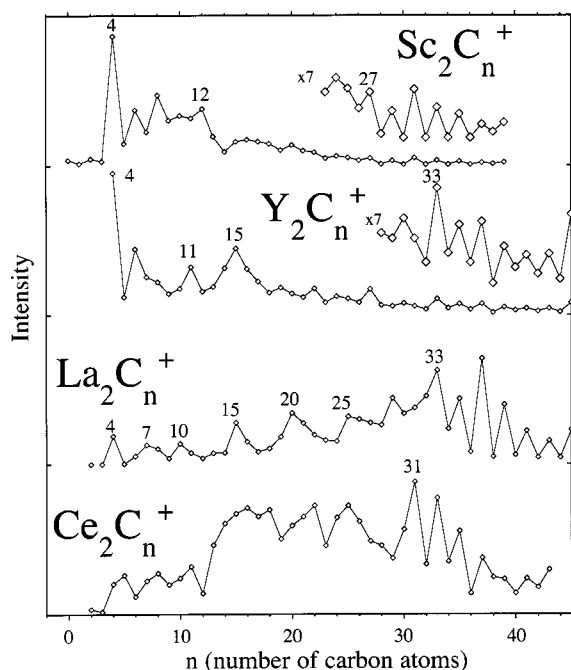
FIG. 3. Intensities of twofold doped carbon cluster cations as a function of the number of carbon atoms in the clusters (n). The intensity oscillations are characteristic for cage structures. From the onset of the oscillations the smallest possible endohedrally doped networked cage sizes $M@(MC_n)^{nw+}$ can be deduced.

FIG. 4. Intensities of $Y_2C_n^+$ and $La_2C_n^+$ as a function of the number of carbon atoms in the clusters (n). The transition from alternation odd–even to even–odd at $n=69$ and $n=71$, respectively, indicates a structural transition from endohedrally doped networked cages $M@(MC_n)^{nw+}$ to bi-endohedrally doped cages $M_2@C_n^+$, as depicted by the two sketches.

A similar statement can be made for YC_n^+ cluster. $Y@C_{36}^+$ labels the onset of a distinct even–odd oscillation. When the source is driven at a certain condition (helium background pressure=400 mbar), the spectra show enhanced intensities for YC_{32}^+ and YC_{34}^+ with respect to their odd-numbered neighbor peaks. This points to the existence of endohedral $Y@C_n^+$ for $n \geqslant 32$ developing into the most stable isomers for $n \geqslant 36$.

Similar deductions can be derived for CaC_n^+ and CeC_n^+. At $n \geqslant 44$ and $n \geqslant 36$, respectively, a strong even–odd alternation is observed, which identifies the endohedral isomers to be the most stable ones. Again, at slightly different conditions, an oscillation with considerably lower amplitude starts at $n=40$ and $n=32$, respectively.

Concerning Sc and Y, the present investigation reveals smaller endohedrally doped cage sizes than a recent publication,[29] in which $M@C_{44}$ are suggested to be the smallest metal encapsulating species. However, concerning La as dopant the present results are in agreement with earlier observations published by Smalley *et al.*[4] and Jarrold *et al.*[25]

B. Twofold doped carbon cages

Figure 3 shows the intensities of twofold metal-doped carbon cluster cations $M_2C_n^+$ (M=Sc, Y, La, Ce) as a function of n. The most interesting feature in these plots in the onset of an odd–even alternation at a certain cluster size, that is $n=27$ for Sc, $n=33$ for Y and La, and $n=31$ for Ce. As already mentioned we consider this kind of oscillation to be a strong indicator for cagelike structures. But why should odd-numbered cages be more stable than their even-numbered neighbors? A likely explanation is that one of the
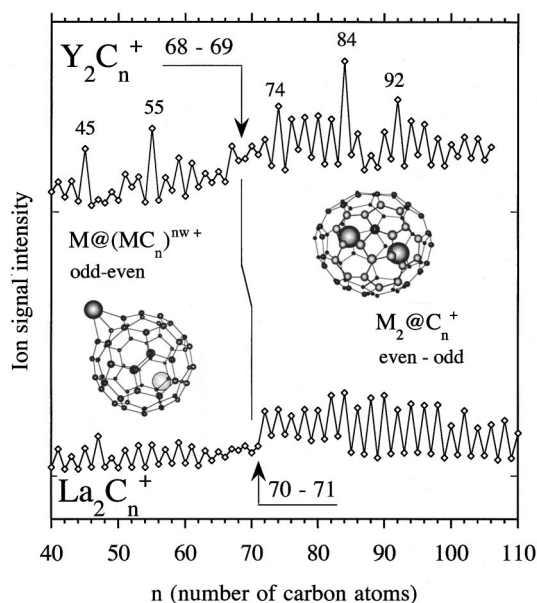
metal atoms is integral into the network of the odd-numbered carbon cage, thus stabilizing a fullerenelike cluster, as proposed by Shelimov *et al.* in the case of LaC_n^+.[25] This kind of cage will be referred to as "networked" in the following, $(MC_n)^{nw}$. Since the onset of this oscillation is in the same size range as the one of the endohedrally doped pure carbon cages, the second metal atom is most likely an endohedral rather than an exohedral one. Thus, just like in the case of singly doped carbon cages, the present mass spectra represent a direct way to reveal the smallest *networked* carbon cage capable of encapsulating a metal atom.

The intensity patterns of twofold doped $Y_2C_n^+$ and $La_2C_n^+$ show another specific feature at higher masses, namely a sharp transition from an alternation odd–even to even–odd at $n=69$ and $n=71$, respectively (Fig. 4). At this point even-numbered cages become more stable than the odd-numbered ones. Thus it is very likely that twofold doped carbon cages exceeding a certain size provide sufficient space to encapsulate both metal atoms inside ($M_2@C_n$), while cages smaller than a certain size n prefer endohedrally doped networked structures with one metal atom as part of the carbon web ($M@(MC_n)^{nw}$). Thus, a structural transition occurs as a function of n, and the present investigation indicates $n=70$ and $n=72$ to be the smallest pure cage size capable of encapsulating two Y and La atoms, respectively. Taking into consideration our results concerning the smallest possible endohedrally doped cage sizes for the other metals investigated, we suspect $Ce_2C_n^+$ and $Gd_2C_n^+$ to have this transition around $n=70$, too, and $Sc_2C_n^+$ at a slightly smaller cage size. Concerning La_2C_n, these results are in agreement with the findings of Shelimov *et al.*, who report the appearance of a fullerene isomer around $n=72$ where both metal atoms are endohedral.[24] Concerning Y_2C_n, a recent publica-

TABLE I. Ionic radii and smallest possible cage sizes of endohedral pure and networked cages. The values in parantheses pertain to the onset of the leading even–odd alternations (see text for details).

Element	Oxidation state	Endohedral pure cage size	Endohedral networked cage size	Bi-endohedral cage size	Ionic radius/Å^a
Sc	+3	30	27		0.89
Y	+3	36(32)	33	70	1.04
La	+3	36(34)	33	72	1.17
Ce	+3	36(32)	31		1.15
	+4	36(32)	31		1.01
Gd	+3	36			1.08
Ca	+2	44(40)			1.14

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tion suggests $Y_2@C_{62}$ to be the onset of di-metallo-fullerenes.[29] The discrepancy might arise from different cluster source conditions, which could lead to the preferential stabilization of different isomers.

Within the mass range of the endohedrally doped networked cages ($35 \leqslant n \leqslant 69$) $Y@(YC_n)^{nw+}$ clusters show $Y@(YC_{45})^{nw+}$ and $Y@(YC_{55})^{nw+}$ as prominent species, which are smaller than their endohedrally doped pure fullerene cage counterparts $Y@C_{50}^+$ and $Y@C_{60}^+$ by five carbon atoms. The reason for the enhanced stability should be found in the specific electronic structure of these clusters rather than in their geometrical structure, since 46 and 56 atoms membered cages (including the networked Y atom) are not supposed to exhibit extraordinary symmetry features similar to a C_{50} or a C_{60} fullerene. In the case of bi-endohedrally doped cages ($n \geqslant 70$) $Y_2@C_{74}^+$, $Y_2@C_{84}^+$, and $Y_2@C_{92}^+$ are prominent species.

C. Smallest cage size of doped fullerenes

Table I summarizes the results on the smallest possible cage sizes of endohedrally doped pure and networked carbon cages. A major spread of the smallest possible $n(n_{min})$ as a function of the metal ionic radius is not found, since the ionic radii of the metals studied in the present work are close to each other. Thus, the present results support the hypothesis that the smallest endohedral fullerene that can be formed for a given element is a function of its ionic radius, as formulated by Guo *et al.*[19] Taking into consideration the reduced n_{min} for Sc and its smaller ionic radius with respect to the other metal ions, the general trend of increasing n_{min} with increasing ionic radius is confirmed. The different behavior of Ca, which exhibits $Ca@C_{44}^+$ as smallest endohedrally doped compound, might be due to its different chemical behavior.

The differences in the smallest possible sizes between pure carbon cages and networked cages are two atoms (three carbon atoms minus the networked metal atom) for the group IIIb transition metals, and four atoms for cerium. The smallest possible endohedrally doped networked cage size is smaller than the smallest possible endohedrally doped pure carbon cage size. Thus, networking seems to stabilize the
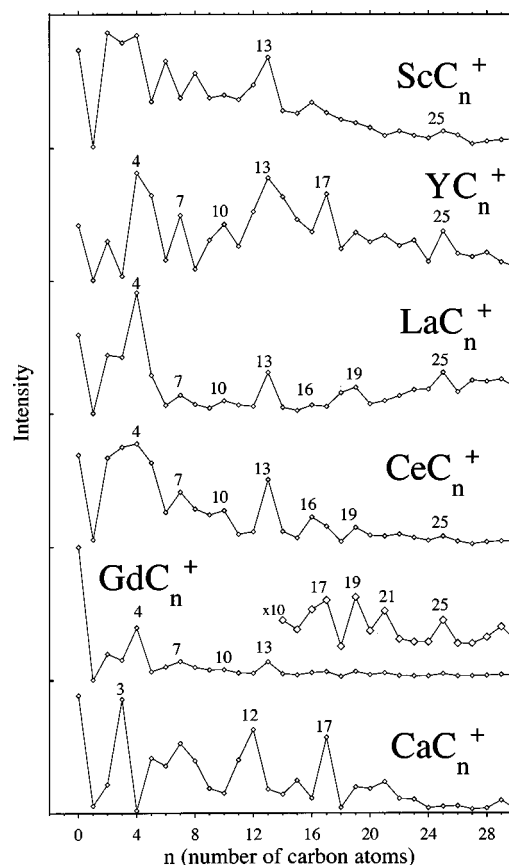

FIG. 5. Intensities of singly doped carbon cluster cations as a function of the number of carbon atoms in the clusters (n) in the low mass domain. Common to all spectra, except for ScC_n^+ and CaC_n^+, is the threefold oscillation starting at $n=4$.

endohedrally doped cluster with respect to disintegration upon shrinkage, and the $4f$ metal cerium is more successful in doing so than the group IIIb transition metals. Consider a pristine carbon cage, take away one of the carbon atoms with its four valence electrons, and replace it by a lanthanum atom, which has got three valence electrons. In order to replace the missing carbon atom, the lanthanum atom needs to form three bonds with the neighboring carbon atoms, and three electrons are required. Thus, the networked cage lacks one π-system electron compared to the pristine cage, and the electron density both outside and inside the carbon shell is reduced. This reduced charge density should be the decisive feature for encapsulating a metal atom at the smaller cage sizes. The question remains why cerium is more effective, although it has got four valence electrons. However, since the cerium valence region contains strongly localized $4f$ character, a reduced ability to contribute to the Ce–C bonds may be expected.

D. Small MC_n^+ and $M_2C_n^+$ clusters

The mass spectra always start with the metal monomer for all metals investigated in this work, and they show similar gross features for all singly metal-doped species except for CaC_n^+. The intensities of MC_n^+ as a function of n reveal a huddle of peculiarities that have to be investigated (Fig. 5).

Common to all spectra, except for CaC_n^+, is the enhanced intensity of MC_4^+ and MC_{13}^+, which are the prominent features in this mass domain. In contrast to this, the Ca-doped carbon cluster cations exhibit CaC_3^+ and CaC_{12}^+ as prominent species, which are smaller than the other prominent MC_n^+ (M=Sc, Y, La, Ce, Gd) by one carbon atom. The intensity of CeC_n^+ as a function of n shows local maxima at CeC_{3k+1}^+. This threefold periodicity covers the mass range from CeC_4^+ up to CeC_{25}^+. Similar threefold intensity patterns are found for ScC_{10}^+ to ScC_{25}^+, for YC_4^+ to YC_{13}^+, for LaC_4^+ to LaC_{25}^+, and for GdC_4^+ to GdC_{13}^+. YC_n^+ and GdC_n^+ show another interesting intensity pattern, an odd–even alternation starting at $n=17$ up to $n=25$ and $n=21$, respectively. Metal monocarbide cations MC^+ are not observed in any of the spectra.

The low mass region of neutral LaC_n has been investigated by anion photoelectron spectroscopy[22] and by density functional theory.[33] Clusters with $n\leqslant4$ adopt a fan shaped ground state geometry, and for $n>4$ a metal terminated chain isomer occurs. In contrast to this, ion mobility measurements[23] and density functional investigations[34] have revealed ring structures as the most stable isomers in this size region. However, none of the methods reveal a threefold periodicity like the one observed in the present spectra. Jarrold *et al.* have reported the loss of LaC_4^+ units to be the main dissociation pathway for most of the LaC_{2n}^+ ring structures ($2n>4$), which is also the case for large odd-numbered LaC_{2n+1}^+ ($2n+1>15$) rings. Small odd-numbered LaC_{2n+1}^+ rings undergo both LaC_4^+ and C_3-loss in comparable extend.[23] Moreover, C_3-loss is a main dissociation pathway for pristine C_{10-30} rings.[35] The enhanced stability of C_3 (which cannot be detected in the cation mass spectra) and LaC_4^+ as well as their particular role during the cluster formation process might be the reason for the observed threefold periodicity. Taking this into account, a $LaC_4^+ + n\text{-}C_3$ cluster condensation pathway is likely.

The enhanced stability of LaC_{13}^+ might be due to its special geometry. Density-functional calculations reveal a cyclic cation with La^+ at the center of the carbon ring, whereas the most stable LaC_{12}^+ isomer prefers a ground-state geometry in which La^+ is inserted into a C_{12} ring.[36] With respect to the close similarities in the intensity patterns of LaC_n^+ and the other metal carbon compounds, we suspect them to show similar ground-state geometries for $n=13$. Concerning CaC_n^+ we suspect CaC_{12}^+ to have a ground-state isomer which incorporates the Ca cation at the center of the ring, and $CaC_{n<12}^+$ to prefer ring insertion.

There are two further hints to the possible cluster formation mechanism: First, the lack of pure carbon clusters at lower masses than the metal monomer. This indicates a metal induced cluster growth mechanism with the metal cation being a nucleus for carbon atom or fragment aggregation. This scenario has been proposed by Maruyama *et al.*[32] Secondly, the poor abundance of pristine fullerenes in the mass spectra. The relative abundance of $M@C_{60}^+$ compared to pristine C_{60}^+ (which depends on the particular source conditions, but seems not to depend proportionally on the metal-to-carbon ratio in the sample rod) decreases from La to Y to Sc, as already shown previously.[22,32] The spectra taken from a mixed Ca–C rod show comparable intensities for doped and

pristine fullerenes, and the 4f metals Ce and Gd show a $M@C_{60}^+$ to C_{60}^+ ratio of about four. However, when using a mixed metal-graphite rod, the relative abundance of C_{50}^+ and C_{60}^+ with respect to the other pristine carbon clusters is much higher than in the spectra taken from pure graphite rods.

The most striking feature concerning small $M_2C_n^+$ clusters is the prominence of $n=4$, which is common to all group IIIb transition metals (see Fig. 3). Moreover, $Sc_2C_n^+$ shows an even–odd alternation for $n=4-12$, and $La_2C_n^+$ shows enhanced intensities at $n=10, 15, 20,$ and 25. The latter feature might be linked with the observation of C_5-loss as a dissociation pathway for clusters in this size regime (where rings are the dominant isomer), which is a major dissociation pathway for pure C_n^+ rings ($n=10-30$).[35]

IV. CONCLUSIONS

We have presented a comparative study of the formation of endohedral and networked endohedral fullerenes with a whole series of mostly isoelectronic dopants. The mass spectra of metal-doped cluster cations $M_xC_n^+$ (M=Ca, Sc, Y, La, Ce, Gd; $x=1,2$) reveal the smallest possible endohedrally doped fullerenes as most stable isomers at $n=44$ (Ca), 30 (Sc), 36 (Y), 36 (La), 36 (Ce), and 36 (Gd). The metal-networked cages are capable to encapsulate a metal atom at a smaller size than the pure carbon cages. $Y_2C_n^+$ and $La_2C_n^+$ show structural transitions from networked endohedrally doped cages to bi-endohedrally doped species at cage sizes $n=69$ and $n=71$, respectively. The smallest pure cage sizes capable to encapsulate a metal atom correlate with the metal ionic radii as suggested earlier.[19]

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