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Laser ablation of Co/Ge mixtures: a new type of endohedral structure, a semiconductor cage trapping a metal atom

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In experiments on Co/Ge binary clusters by laser vaporization, a remarkably strong signal in the mass spectrum was presented, which was assigned to the cluster anion consisting of ten germanium atoms and one cobalt atom, $[CoGe_{10}]^-$. For this cluster anion we suggest an endohedral structure – a Ge_{10} cage trapping a Co atom in its interior. Reactions between cobalt clusters and germanium clusters using a laser double ablation reactor also confirmed the endohedral structure. According to the electronic and geometrical shell closures, a bicapped tetragonal antiprism structure was predicted for this endohedral $[CoGe_{10}]^-$ cluster anion. Copyright © 2001 John Wiley & Sons, Ltd.

The fact that an atom or a group of atoms can be trapped in a fullerene cage[1,2] has been generally recognized since 1991 when techniques to produce metallofullerene were developed[3,4] and the samples were produced in bulk. This provided the conditions to directly study the characteristics of a metallofullerene,[4] and consequently numerous experimental explorations of endohedral fullerenes were conducted. Theoretical studies on the structures and the formation mechanism[5,6] of the new complexes were also developed. But for almost a decade, most of the species with endohedral structures produced and studied mainly had carbon fullerene cages.[7–13] Recently, a W-encapsulating Si_{12} cage cluster was reported.[14] Here we give a new experimental result, which might indicate that a transition metal atom (Co) was trapped in a semiconductor cage (Ge_{10}). This recognition comes from the analysis of mass spectra of Co/Ge binary cluster anions produced by laser ablation and also from the reactions between cobalt clusters and germanium clusters in a laser double ablation reactor (LDAR).

EXPERIMENTAL

The binary cluster anions of germanium and cobalt were generated and analyzed under the following conditions. The samples were prepared with germanium (purity 99.99%) and cobalt (purity 99.9%) powders, mixed well in different atomic ratios and pressed to form tablets. The experiments to produce and detect Co/Ge binary cluster anions were performed by a vaporization laser and the first stage of a home-made tandem time-of-flight mass spectrometer (T-TOFMS). A detailed description of the T-TOFMS is given elsewhere.[15] In our experiments the first stage of the T-TOFMS is only used to produce the clusters. Briefly, the second harmonic of a Q-switched Nd: YAG laser (532 nm, 10 mJ/pulse, 10 pulse/s) was focused on the surface of a tablet sample held in the vacuum chamber (at 10^{-6} Torr) of the spectrometer to produce the cluster anions. The produced cluster anions were extracted and accelerated with a pulse voltage of −1.2 kV, and then drifted in a field-free region 3.5 m long. The anions were detected by a dual micro-channel plate detector held in the end of the field-free region, and recorded to give the mass spectrum. Typically, 1000–2000 laser shots were accumulated and stored in an IBM-PC computer.

RESULTS AND DISCUSSION

Figure 1 shows a series of cluster anion distributions resulting from variations in the sample compositions and the vaporization conditions. Figure 1(a) resulted from the sample with atomic ratio Ge/Co = 1:1 and laser power 9.77×10^7 W/cm^2. For Figs 1(b) and 1(c), the atomic ratios of Ge and Co in the samples are 4:1 and 1:4, and the laser powers are 8.76×10^7 and 1.01×10^8 W/cm^2, respectively. It is clear that the resulting cluster distribution is mainly dominated by $[CoGe_{10}]^-$ though the relative intensity of the $[CoGe_{10}]^-$ signal changes somewhat with different laser powers and the compositions of samples, as shown in Fig. 1, which indicates that the stability of $[CoGe_{10}]^-$ is intrinsic. Figure 1 displays the evolvement of $[CoGe_n]^-$ clusters with n (n = 6–11). Aside from the largest peak $[CoGe_{10}]^-$, the other $[CoGe_n]^-$ ($6 \leqslant n < 10$) peaks also increase with n, but are still much less than that of $[CoGe_{10}]^-$. The sudden change

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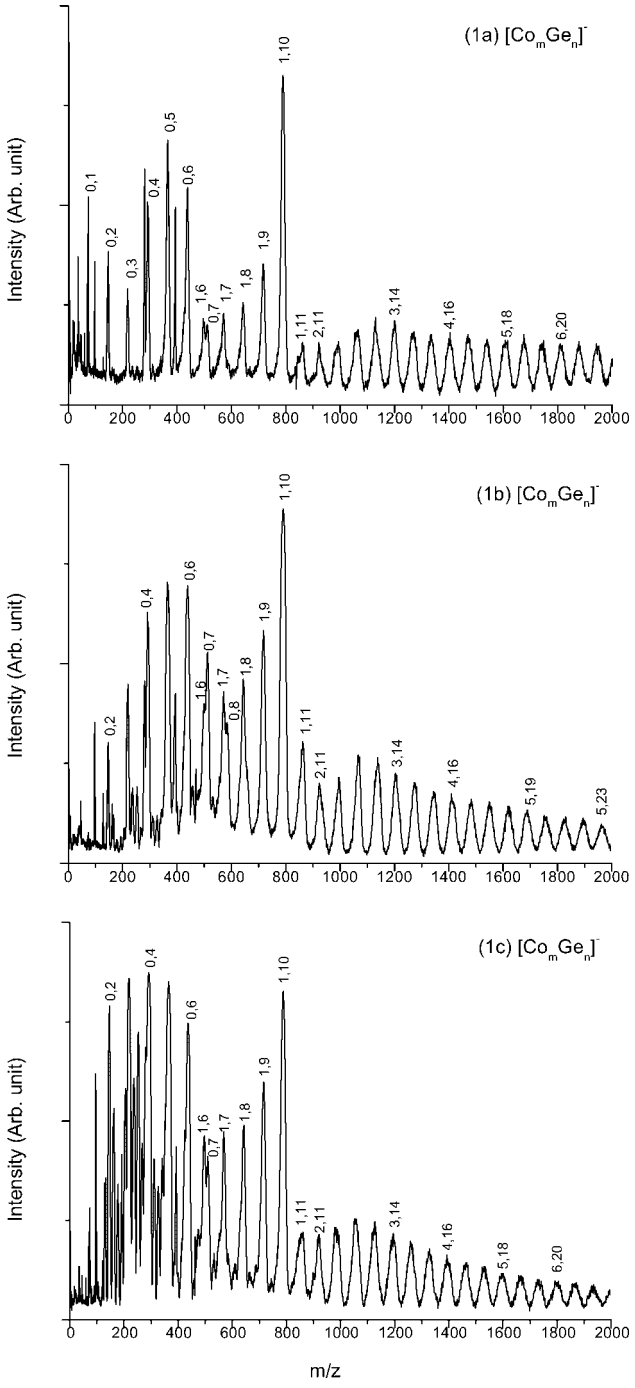

Figure 1. TOF mass spectra of Co/Ge cluster anions $[Co_nGe_m]^-$ produced by laser ablation on mixed samples of Co and Ge with different atomic ratios and laser powers. (a) Ge/Co = 1:1, laser power 9.77×10^7 W/cm^2; (b) Ge/Co = 4:1, laser power 8.76×10^7 W/cm^2; and (c) Ge/Co = 1:4, laser power 1.01×10^8 W/cm^2.

happens at n = 11. The $[CoGe_{11}]^-$ peak is less than all of the other $[CoGe_n]^-$ peaks, especially much less than that of $[CoGe_{10}]^-$. When the time delay between the YAG pulse used to generate the clusters and the high voltage used to extract the clusters ranges from 350 to 490 μs, the relative intensity of the $[CoGe_{10}]^-$ peak changes slightly, but it is always strong. Obviously, the $[CoGe_{11}]^-$ cluster is not sensitive to the time delay like C_{60}^-. These observations

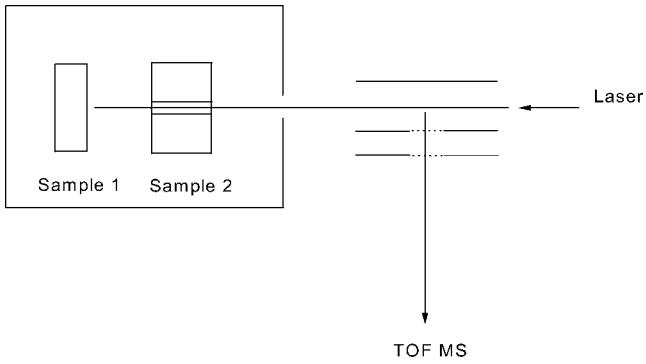

Figure 2. Laser double ablation reactor.

imply that the cobalt atom should be viewed as a reaction site until it is completely covered with germanium atoms. This distribution feature is an evidence[16] that the $[CoGe_{10}]^-$ cluster has a cage structure. It has been reported that Ge_{10} or $[Ge_{10}]^-$ does have a cage structure.[17,18] We should consider, based on the facts from the experiments, whether the cobalt atom is inside the Ge_{10} cage or outside? If the cobalt atom is outside the Ge_{10} cage, the cluster $[CoGe_{10}]^-$ should be the product from the reaction of $[Ge_{10}]^-$ and Co (or Ge_{10} and $[Co]^-$). In order to understand whether this reaction product is a real one, we performed the following experiments using the LDAR.[19]

The LDAR, mounted in the source chamber of the T-TOFMS, contains two solid samples, germanium (purity 99.99%) and cobalt (purity 99.9%), shown in Fig. 2. These two samples were all shaped into disks (thickness ~5 mm, radius ~5 mm) and were separated by 6 mm from each other. A hole (radius ~1 mm) was drilled in the sample Co, and the laser beam (532 nm) was directed through the hole of sample Co, so as to be normal to the surfaces of samples Ge and Co. This arrangement can make the laser ablate the two samples and also satisfy the experimental condition of clustering first and reaction second (CFRS),[19] which can check whether the reaction product $[CoGe_{10}]^-$ is generated. If the Co atom is outside the Ge_{10} cage, by laser double ablation reaction the

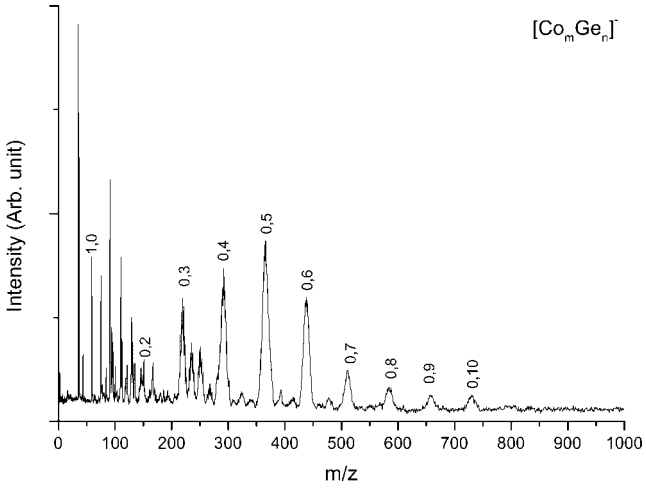

Figure 3. TOF mass spectrum produced by laser double ablation on samples Co and Ge.

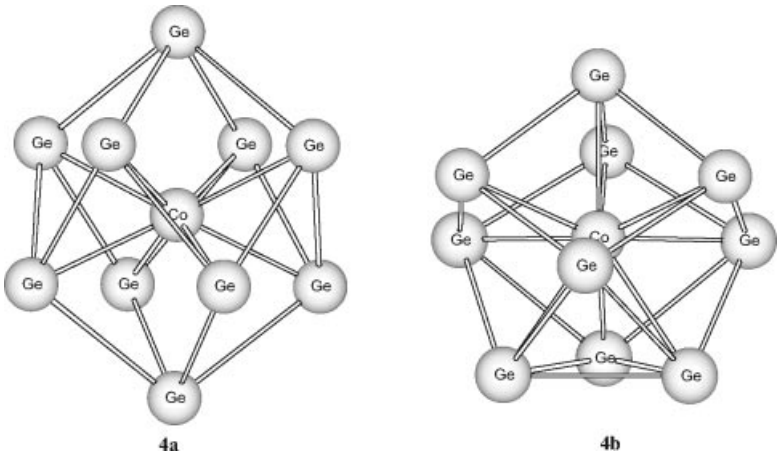

Figure 4. Possible structures of the $[CoGe_{10}]^-$ cluster anion: (a) bicapped tetragonal antiprism structure; and (b) tetracapped trigonal prism structure.

cobalt atom should react with the Ge_{10} cage cluster and the reaction product $[CoGe_{10}]^-$ should be observed in the mass spectrum. Figure 3 gives the mass spectrum obtained from these experiments, and clearly the reaction product $[CoGe_{10}]^-$ did not appear. This result excludes the possibility that the cobalt atom is outside the Ge_{10} cage, and the proposal that the cobalt atom in the cluster $[CoGe_{10}]^-$ is inside the Ge_{10} cage is confirmed.

It has been reported[17,18] that the $[Ge_{10}]^-$ cage has a bicapped tetragonal antiprism ground state structure, with a tetracapped trigonal prism structure being slightly higher in energy, while the Ge_{10} cage has a tetracapped trigonal prism ground state structure with the bicapped tetragonal antiprism structure being 0.7 eV higher. Putting the Co atom into the $[Ge_{10}]^-$ cage gives two possible endohedral structures of the $[CoGe_{10}]^-$ cluster anion, as shown in Fig. 4. Compared with the tetracapped trigonal prism structure (Fig. 4(b)) the bicapped tetragonal antiprism structure **4a** should be more reasonable. There are four valence electrons in one Ge atom and nine in one Co atom. For structure **4a**, assuming that each Ge atom on the vertex of the tetragonal antiprism donates an electron to the central metal Co atom, the Co atom possesses 18 electrons in total (8 electrons from the Ge_{10} cage, 9 valence electrons from itself and one negative charge), resulting in a closed electronic shell, as for Kr. According to the so-called octet[20] (18 electrons[20] or effective atomic number[21]) rule, the $[CoGe_{10}]^-$ cluster anion is therefore expected to be stable. At the same time, three valence electrons are left for each Ge atom on the vertices of the tetragonal antiprism, making it possible to form a Ge polyhedron. Each cap Ge atom bonds with four Ge atoms on the vertices of the tetragonal antiprism, also with closed electronic shells. On the other hand, the Co atom and part Ge atoms in structure **4b** do not have closed electronic shell configurations. Thus, structure **4a** should be a better candidate for the ground state structure of the $[CoGe_{10}]^-$ cluster anion.

CONCLUSIONS

A remarkably stable cluster anion $[CoGe_{10}]^-$ was found by the laser ablation of a cobalt and germanium mixture. For this $[CoGe_{10}]^-$ cluster anion, an endohedral structure – a bicapped tetragonal antiprism Ge_{10} cage trapping a metal Co atom in its interior – was suggested. This endohedral structure is confirmed by the reactions between cobalt clusters and germanium clusters, and is very stable owing to both the electronic and the geometrical shell closures.

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