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Gas-Phase Copper/Selenium and Silver/Selenium Clusters

Y. Yamada,† H. T. Deng, and A. W. Castleman, Jr.*

Department of Chemistry, The Pennsylvania State University,
University Park, Pennsylvania 16802

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Binary clusters $Cu_nSe_m^+$ and $Ag_nSe_m^+$ are produced by a gas aggregation source and investigated by time-of-flight mass spectrometry following ionization with a KrF excimer laser. Dominant species in the mass spectra are assigned as $(M_2Se)_n^+$ and $M(M_2Se)_n^+$ (M = Cu or Ag), which reflect stable compositions of neutral precursors and charged clusters. In these series, magic numbers appear at $n = 6$. Additionally, especially prominent peaks are observed for $M_nSe_m^+$; $(n,m) = (7,4)$, (9,5), and (11,6). From an investigation of the magic numbers and prominent abundances of various species, it is suggested that these binary clusters have structures related to an antifluorite structure.

Introduction

A study of metal alloy or binary clusters is very interesting and informative since the importance of the electronic and geometric contributions to stability can be investigated by examining the influences of substituting various atom in a cluster. Cu and Ag atoms have sufficient free-electron behavior that the pure clusters of these metals obey jellium shell model, as reflected in their observed abundances. When these metals, Cu and Ag, are aggregated together or mixed with certain other metals such as Al, In, Pb,[1] Sb, and Bi,[2] distributions of the alloy clusters are influenced by the electronic stability and they are observed to still obey the jellium shell model, especially in the Cu-rich or Ag-rich cluster composition range. One of the objectives of the present study is to investigate whether the electronic stability (jellium shell model) is a useful model in the case of mixtures of coinage metals and Se, where the Se atom is expected to display a certain limited degree of metallic nature.

In the case of pure Se clusters, they have been observed to form stable small molecules such as Se_5, Se_6, Se_7, and Se_8 in the gas phase, and their photoelectron spectra have been reported.[3,4] In the series of larger Se clusters, a periodicity of 6–8 has been observed in the mass spectral distributions of the clusters,[5] and their nucleation processes have been studied. The magic cluster sequence was explained in terms of the packing structure of Se_8 molecules.

In bulk systems, Cu/Se and Ag/Se have the compositions Cu_2Se and Ag_2Se, but the structures of the high-temperature form are not simple. In the high-temperature form of $Cu_{2-x}Se$ (berzelianite), the Se atoms form a fcc lattice and the Cu atoms are randomly distributed over the tetrahedral and trigonal sites.[7] The low-temperature form has a cubic antifluorite type base structure, but still their detailed structure is not clear even though they have been studied extensively.[8,9] The abundance of the clusters in a mass spectrum often reflects their particular geometrical structures. Studies of gas-phase MgO[10–12] and CaO[13] clusters show that these systems form compact cubic structures similar to pieces of their crystal lattice. We have reported that the distributions in a mass spectrum of copper carbide clusters reflect their stable geometric structure, which is an antifluorite structure.[14] Investigations of the mass spectral distributions of the Cu/Se and Ag/Se clusters provide information on factors governing the stabilities of the clusters, i.e., electronic stability or stable geometrical form.

Using a laser vaporization technique, negative cluster ions, $Cu_nSe_m^-$, $Cu_nTe_m^-$, $Ag_nSe_m^-$, and $Ag_nTe_m^-$ have been studied.[15,16] In the $Cu_nSe_m^-$ system, it has been reported that they a magic number at $(n,m) = (29,15)$, which has been related to the known cluster compound[17]in condensed-phase chemistry. Additionally, there has been a study of the $Cu_nSe_m^+$ system, in which Se-rich clusters were observed,[18] but no particular magic numbers were found.

Experimental Section

Details of the apparatus are described elsewhere.[19] Briefly, a gas aggregation source is used in the present work to form species of selected composition. The pure powder sample or mixture

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† Permanent address: Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken, Japan.

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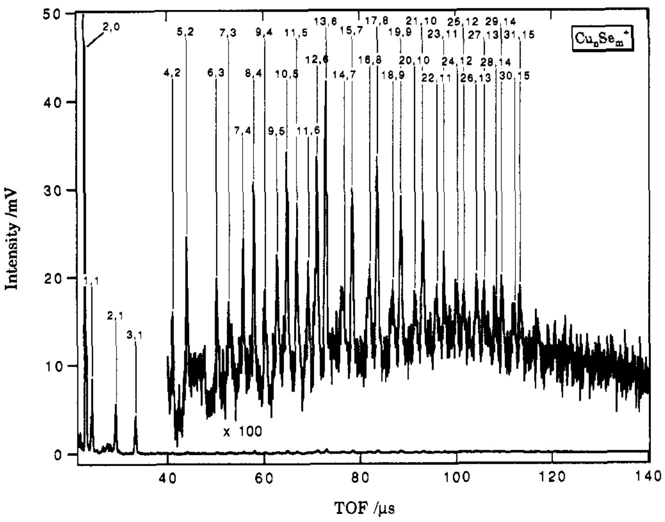

Figure 1. Time-of-flight mass spectrum of $Cu_nSe_m^+$ binary clusters. Indicated numbers in this figure correspond to $Cu_nSe_m^+$; *n*,*m*.

powder is resistively heated in a boron nitride crucible and evaporated into a flow of He gas (3.5 sscm). The carrier gas is cooled to liquid nitrogen temperature after it is mixed with metal vapor. A 0.062-in. hole in the apex of a cone serves to sample a small fraction of the flow and most of the gas is pumped out in front of the cone. The clusters are introduced into a low pressure ionization region between the electrostatic grids of a time-of-flight (TOF) spectrometer.

The neutral clusters are photoionized by slightly focused light from a KrF excimer laser (4.98 eV). The laser beam (pulse width 20 ns) is focused with a convex lens to obtain 170–330 mJ/cm^2/pulse in the ionization region, enabling detection of the desired cluster ions. The ionized clusters are accelerated with double stage acceleration grids, and detected by a microchannel plate particle multiplier (MCP) after traversing a 186-cm differentially pumped field-free region. The ion signals from the MCP are accumulated using a 100-MHz transient digitizer and the TOF spectra are transferred to a microcomputer for analysis.

Results and Discussion

Before studying the binary system, pure Cu, Ag, and Se clusters were examined to observe their distributions and any magic numbers reflecting their stabilities. The usual magic numbers at the Cu_n^+ (Ag_n^+) $n = 9$ and 21 which are 8- and 20-electron species corresponding to 1p and 2s jellium shell closings, and observation of the well-known even–odd alternations as described in the literature were verified in the pure Cu_n^+ (Ag_n^+) cluster systems.[1] On the other hand, pure Se_n^+ clusters show magic numbers at $n = 5$, 6, 7, and 8 under our experimental conditions, reflecting the fact that these are stable molecules in the gas phase.

To measure the mass spectra of Cu/Se clusters, we vaporized the component samples in a single crucible and observed the spectra with various mixing ratios employed in different experiments. A typical mass spectrum of $Cu_nSe_m^+$ is displayed in Figure 1. Generally, in the study of metal alloy clusters,[1,2] binary clusters with various mixing ratios can be obtained by changing the initial sample compositions in the crucible. However, in the Cu/Se system, binary clusters with large size are obtained only under conditions (typical initial sample composition is 20% atomic percent of Se) in which the distributions displayed in the figure were taken. When we change the mixture ratio of the sample powders introduced into the crucible and increase, beyond the composition, the amount of Cu or Se powder (<5% or >65% of Se), the only clusters we could obtain were pure Cu_n^+ or pure Se_n^+ clusters, rather than Cu-rich or Se-rich binary clusters. Therefore, it appears that these elements do not form binary clusters at most composition ratios.

Two series of intense peaks are observed in the spectrum (Figure 1), which are assigned to $(Cu_{2n+1}Se_n)^+$ and $(Cu_{2n}Se_n)^+$ clusters ($n = 1$–15). There are only four exceptional peaks in this system, which correspond to other compositions, namely, $(Cu_nSe_m)^+$; where $(n,m) = (1,1)$, (7,4), (9,5), and (11,6). The species (1,1) may appear because of a large probability of formation, leaving the last three to be explained (see below). Smaller clusters such as (2,1), (3,1), and (5,2) are relatively strong because of the general effect that small size clusters have high intensities. There are clear magic numbers at (13,6) and (12,6) in the series of $(Cu_{2n+1}Se_n)^+$ and $(Cu_{2n}Se_n)^+$, respectively. The numbers of excess electrons in the cluster ions $(Cu_{2n+1}Se_n)^+$ are zero, assuming that the Cu atoms donate one electron (Cu^+) and Se atoms accept two electrons (Se^{2-}), which thereby satisfy the total charge of the observed clusters (+1). Similarly, the clusters $Cu_{2n}Se_n$ have no excess electrons, and may be stable as neutral precursors. It seems that the abundance of the clusters in this system is explainable in terms of the compound Cu_2Se, which is a stable compound assuming Cu^+ and Se^{2-} ions.

The electronic configuration of a Se atom is [Ar]3d^{10}4s^{2}p^4, and it may donate four or six valence electrons to the cluster if it has free electron behavior. Evidently a Cu ([Ar]3d^{10}4s^1) atom donates one electron to the cluster. If consideration is given to finding clusters which fit with the jellium shell model, $Cu_{11}Se_6^+$ and $Cu_{11}Se_5^+$ may have 34 and 40 valence electrons (corresponding to 1f and 2p shell closings) assuming the contribution of four and six valence electrons from each Se atom, respectively. However, $Cu_{11}Se_5^+$ is not a magic number in the spectrum (Figure 1), which would be expected on the basis of the foregoing considerations. While $Cu_{11}Se_6^+$ is the one of the peaks which do not belong to either of the two series, there are no other clusters observed than these two that could possibly correspond to other jellium shell closings. If the species $Cu_{11}Se_5^+$ reflects the stability of a jellium shell closing at 40 electrons, we should obtain other species that correspond to other jellium shell closings. Therefore, we conclude that the jellium shell model cannot be applied to this system and the free electron nature of a Se atom is insufficient to yield a donation of valence electrons to the cluster. In this system, the components evidently form compoundlike clusters having the stoichiometry Cu_2Se, rather than clusters with free valence electrons. This is consistent with the fact that Cu/Se do not mix well in other compositions at the temperature we employed to vaporize the sample mixtures (>1000 K). Cu_2Se is stable at higher temperature up to 1403 K, while other stable crystals such as Cu_3Se_2, CuSe, and $CuSe_2$ are found at lower temperature (<385, 650, and <605 K, respectively) in the Cu/Se system.[20]

To further understand the structure of Cu/Se clusters, the bulk structure and the abundances in the mass spectra may be important clues. We can use similar arguments as used in the study of gas-phase copper carbide clusters

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[20] *Binary Alloy Phse Diagrams*, 2nd ed.; Massalski, T. B., et al., Eds.; ASM International (USA); 1990; Vol. 1, p 88; Vol. 2, p 1475.

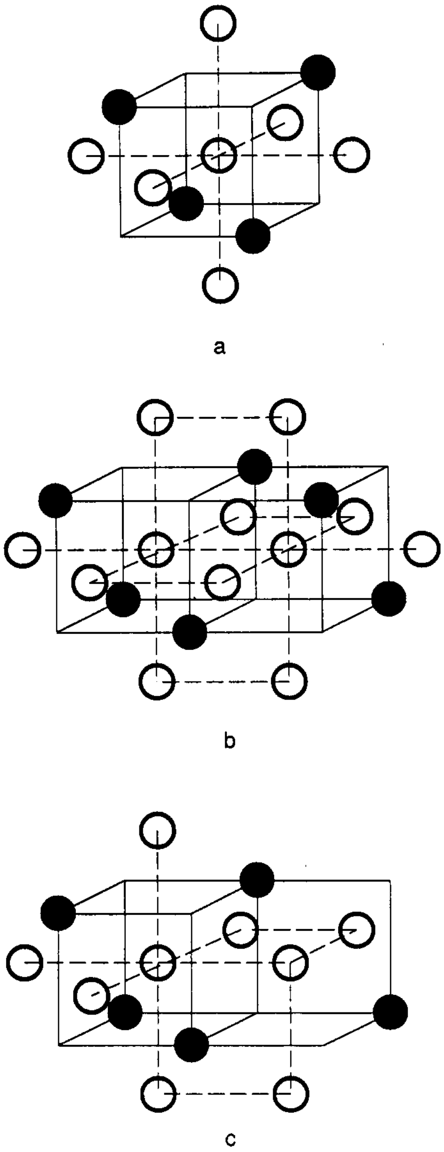

Figure 2. Stable structure of Cu/Se (Ag/Se) binary clusters. Black and white circles represent Se and Cu (Ag) atoms. (a) Cu_7Se_4 (Ag_7Se_4), (b) $Cu_{12}Se_6$ ($Ag_{12}Se_6$), and (c) Cu_9Se_5 (Ag_9Se_5).

whose geometries are related to antifluorite structures.[14] When we cut some parts of the bulk structure of Cu_2Se, assuming it has an antifluorite structure, we obtain small entities as displayed in Figure 2a,b, which are 2 × 2 × 2 and 2 × 2 × 3, respectively. Cu atoms sit on the middle and outer positions of the cage made of Se^{2-} anions. The compositions are (a) Cu_7Se_4 and (b) $Cu_{12}Se_6$. These structures may be the stable structures of the neutral clusters. Counting the number of electron in the neutral clusters, Cu_7Se_4 and $Cu_{12}Se_6$ have −1 and 0, respectively, assuming a Cu atom gives one electron and a Se atom attracts two electrons. Therefore $Cu_{12}Se_6$ is more stable than Cu_7Se_4 because it has no excess charge. The magic number at $Cu_{13}Se_6^+$ in the series of $Cu_{2n+1}Se_n^+$ can be explained by the attachment of one additional Cu cation having charge (+1) to $Cu_{12}Se_6$, which is the stable neutral species. Similarly, the magic number at $Cu_{12}Se_6^+$ in the series of $Cu_{2n}Se_n^+$ is also explainable in terms of the stable structure of neutral cluster, which are precursors of the observed species. They are stable as neutrals, though they do not satisfy the total charge of the expected stable cluster ions. The peak at $Cu_7Se_4^+$ that does not belong to either of the two series corresponds to a 2 × 2 × 2 structures (Figure 2a). The next large stable structure predicted from the antifluorite structure is a 2 × 3 × 3 ($Cu_{20}Se_9$), but it is not observed in the spectrum. This is possibly due to the fact that it is not electronically stable and thus its abundance may be very small.

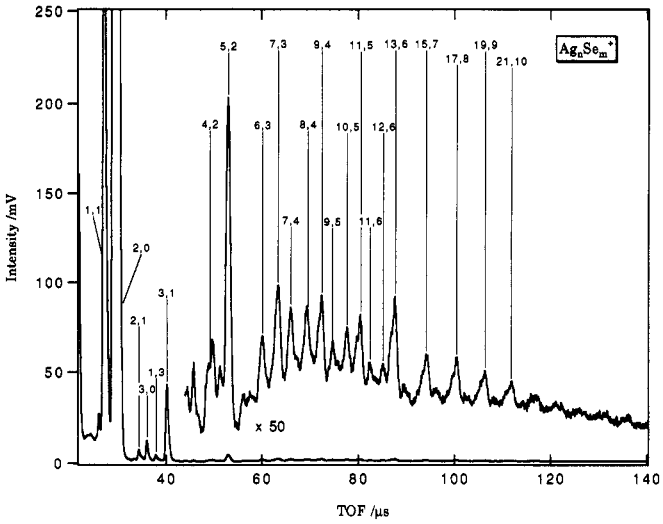

Figure 3. Time-of-flight mass spectrum of $Ag_nSe_m^+$ binary clusters. Indicated numbers in this figure correspond to $Ag_nSe_m^+$; n,m.

While the complete structures 2 × 2 × 2 and 2 × 2 × 3 are very stable, the structures having small defects may be also more stable than other proximate species having different composition ratios. Upon the removal of one Se^{2-} from the corner of $Cu_{12}Se_6$ (2 × 2 × 2, Figure 2b), a structure of Cu_9Se_5 (Figure 2c) is obtained. There are two ways to remove Se^{2-} from a 2 × 2 × 2 cage; the removal of Se^{2-} from a corner loses three Cu atoms to form Cu_9Se_5, and removal of the center Se^{2-} on the edge leads to the loss of four Cu atoms to form Cu_8Se_5. But, Cu_8Se_5 is not observed in the spectrum (Figure 1). The appearance of $Cu_{11}Se_6^+$ may due to the fragmentation of the stable structure $Cu_{12}Se_6$.

Similar distributions to those discussed above are also observed in the $Ag_nSe_m^+$ system (Figure 3). The series of $Ag_{2n}Se_n^+$ and $Ag_{2n+1}Se_n^+$ are observed with the magic numbers at $n = 6$, as well as $Ag_nSe_m^+$ (n,m) = (7,4), (9,5), and (11,6). In this case, the series of $Ag_{2n}Se_n^+$ do not have strong intensities, and thus the magic number at $Ag_{12}Se_6$ is not evident as it is in the $Cu_nSe_m^+$ system. The magic number at $Ag_{13}Se_6^+$ in the series $Ag_{2n+1}Se_n^+$ and the peaks at $Ag_7Se_4^+$, $Ag_9Se_5^+$, and $Ag_{11}Se_6^+$ support the conclusion that these binary clusters have similar structures to those of the $Cu_nSe_m^+$ system (and hence also related to the antifluorite structure). The intensity of $Ag_5Se_2^+$ is high, because of the general distributions, i.e., clusters with small masses have higher intensities.

It is reported that the low-temperature crystal structure of Ag_2Se in the condensed phase is orthorhombic and that the high-temperature structure is bcc.[20] Although Ag_2Se in the condensed phase does not form an antifluorite structure, this result suggests that it forms fragments of antifluorite structures in small clusters in the gas phase.

Te([Kr]$4d^{10}5s^2p^4$) atoms are expected to have the same nature as Se atom. We also produced binary clusters of Ag/Te, which show almost the same distributions as in Cu/Se and Ag/Se system. However, in the Ag/Te system, the elements mix more easily to form a wider variety of combinations, and we obtained some additional binary species other than those observed in the Cu/Se and Ag/Se systems. The series of $Ag_{2n}Te_n^+$ also have relatively high intensities, as do $Ag_7Te_4^+$, $Ag_9Te_5^+$, and $Ag_{11}Te_6^+$, which supports the suggestion that most of the binary clusters are related to the structure of the Cu/Se or Ag/Se systems. Additionally, there are some species which have never been seen in Cu/Se or Ag/Se systems such as $Ag_6Te_2^+$, $Ag_{11}Te_2^+$, $Ag_nTe_3^+$ (n = 11–14), and $Ag_{15}Te_4^+$.

In a similar manner, Cu/Te binary clusters were also investigated. Unfortunately the difference between the masses of two Cu atoms and that of one Te atom is only 0.51 amu; therefore mass overlaps of different species make it difficult to separate and estimate intensities of each peak in the Cu/Te system. Though we can assign the peak from their isotope patterns in the small mass range, it is impossible to make assignments at large sizes which is more important for the objectives of the present study. However, the patterns of each peak are consistent with the patterns observed in the Cu/Se, Ag/Se, and Ag/Te systems.

Conclusion

Binary clusters $Cu_nSe_m^+$ and $Ag_nSe_m^+$ produced by a gas aggregation source reveal dominant peaks corresponding to $(M_2Se)_n^+$ and $M(M_2Se)_n^+$ (M = Cu, Ag), with those for n = 6 being magic numbers in these series. Additionally, $M_7Se_4^+$, $M_9Se_5^+$, and $M_{11}Se_6^+$ have high intensities. The jellium shell model cannot account for the magic numbers observed in this system because the Se atoms do not display sufficiently free electronic behavior. Rather, compound-like clusters are observed in this system and the distribution of clusters reflect the stability of neutral clusters with particularly stable geometrical arrangements.

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