J. Phys. Chem. A **2004,** *108,* 6151−6155

Stability, Structure, and Vibrations of Metal-Doped Selenium Clusters

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Received: February 21, 2004; In Final Form: May 11, 2004

Calcium or sodium atoms are added to selenium clusters in the reaction channel of a dual laser vaporization source to study the dependence of the product structures on the number and the valence of the metal atoms. Stabilities of product clusters are investigated by photofragmentation experiments. Several Ca_MSe_N clusters show special stabilities for compositions that can be related to bulklike cuboid structures, while no pattern of geometrical stabilities is found for Na_MSe_N clusters. Keeping a low sodium concentration in the reaction channel generates predominantly Na_2Se_N clusters. They are deposited in a nitrogen matrix and investigated by Raman spectroscopy. A low-frequency Raman band is found which is consistent with calculated frequencies of selenium chains terminated at each end by one sodium atom and bent into horseshoe shapes by an attractive interaction between the two sodium atoms. Structural models for the metal/selenium clusters are discussed which are based on the idea of an electron transfer from the metal atoms to the selenium clusters according to the metal valences.

1. Introduction

Doping of nanostructured semiconductors is a prominent field of current research that is related to the development of smallest semiconductor devices. In contrast to macroscopic semiconductors, where doping with suitable metal atoms provides donor electronic states without substantial changes of the geometric bulk structure,[1] the bonding of metal atoms into nanostructured semiconductor systems is a much more complex problem. Considering the border case of a nanometer sized semiconductor cluster consisting of only a few atoms, the addition of just a single metal atom to this cluster corresponds already to an extremely high dopant concentration in the system. Moreover, the chemical bonding in the pure semiconductor cluster will deviate significantly from its periodic bulk structure and hence electronic band structure approximations will become useless and a molecular orbital approach is necessary.

Metal addition to a small cluster is therefore best described as a molecular reaction which is accompanied by a charge transfer from the metal to the usually more electronegative semiconductor, leading to significant perturbations not only of the electronic but most likely also of the whole geometrical structure of the semiconductor particle. The investigation of such structural effects might become important for the assembly of smallest semiconductor devices[2] and is an interesting research field of physical chemistry.

For a basic understanding of the changes in chemical bonding in a semiconductor cluster because of metal addition, one would choose a system where a simple structural model for the semiconductor particles exists. Clusters of, for example, silicon are not appropriate since they tend to occur in several isomeric structures with complex bonding situations far from the bulk structure.[3,4] Selenium as an element forming bonds with a low coordination number is much more suitable. The Se coordination number of two causes simple ring structures for pure gas-phase Se_N clusters ($N = 5-8$), as shown by several experiments (electron diffraction,[5] photoelectron spectroscopy,[6] Stern-Gerlach experiments[7]) and quantum chemical calculations.[8−10] Similarly, several Se modifications are known for the bulk which consists of such selenium rings or of selenium chains.[11]

From a chemical point of view, it is interesting to compare the effects of the addition of metal atoms with different valences, since the amount of the charge transfer from the dopant metal to the selenium cluster should depend significantly on the number of available valence electrons. We have chosen calcium and sodium, since they have similar electronegativities and their ions Ca^{2+} and Na^{+} have almost the same radii in solid-state compounds[12]. Up to now, for small isolated metal/selenium clusters only mass spectrometric studies on the Cu_MSe_N and Ag_MSe_N systems are reported in the literature[13,14].

In our present work, we focus on the question how the simple structures of Se_N clusters change when a few Ca or Na atoms are added. Products of the metal addition are first isolated in a molecular beam and analyzed by mass spectrometry. To obtain information about the stability of the clusters, photofragmentation experiments are carried out. In addition, Na_MSe_N clusters are deposited in an inert gas matrix and investigated by Raman spectroscopy. With this method, vibrations of the metal/selenium bonds in the clusters can be observed. The formation of a metal/selenium bond is accompanied by a transfer of a weakly bound valence electron from the metal to the selenium resulting in a strong decrease in the overall polarizability.[15] Since the charge transfer between the metal and the selenium should depend sensitively on the distance between these atoms, one can expect a strong dependence of the clusters polarizability on changes of the Na−Se bond lengths that should reflect itself in intense Raman bands for vibrations where these bonds are involved. The equilibrium geometries of some experimentally found clusters are calculated by density functional theory. The vibrational spectra are calculated as well and correlated with those obtained by Raman spectroscopy.

2. Experiments

An overview of the molecular beam apparatus is shown in Figure 1. Metal/selenium clusters are generated in a dual laser

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10.1021/jp049203q CCC: $27.50 © 2004 American Chemical Society
Published on Web 06/29/2004

vaporization source[15] by separate vaporization from a selenium and a metal rod into pulsed helium gas flows. The vapors are mixed in a reaction channel, where metal/selenium clusters are formed and expanded through a nozzle into a second vacuum chamber forming a cluster beam. The beam passes through a differential pressure stage in a third chamber. The clusters are photoionized using an arc xenon flash lamp or an excimer laser. After passing an electrostatically shielded distance of 8 cm, they are accelerated into a home-built Wiley/McLaren time-of-flight mass spectrometer (TOF-MS)[16] with a MicroSphere Plate as detector and the cluster distribution is analyzed. In a fourth vacuum chamber, the cluster deposition rate is determined with a quartz microbalance (Intellemetrics) which can be moved in to and out of the cluster beam. The deposition rate is 5−200 pm/s on a substrate area of 30 mm^2. Lastly, the clusters enter a UHV chamber where they are deposited into a growing argon or nitrogen matrix on a gold-plated sapphire substrate, cooled by a continuous flow liquid He cryostat to a temperature of 15 ± 1 K. The deposition rate of the matrix is measured by means of optical interferometry; the typical matrix thickness is 1−2 mm. High dilution of the clusters (1:1000) prevents them from interacting. Because of the low kinetic energy of the clusters which is determined by means of a retarding electric potential at the TOF-MS to be less than 10 eV, there should be no cluster fragmentation during deposition.[17] The support can be turned toward the optics of a Fourier transform Raman spectrometer (Bruker RFS100/S with modified optics and liquid N_2 cooled Ge detector). The clusters frozen in the matrix are irradiated by Nd:YAG laser light (1064 nm, 10−110 mW) and a Raman spectrum is recorded.

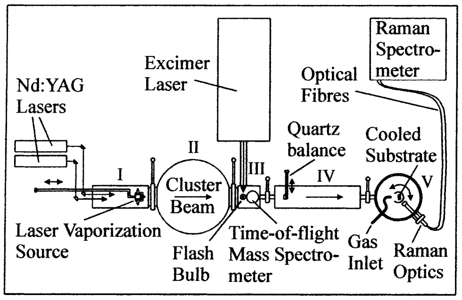

Figure 1. Molecular beam apparatus consisting of five vacuum chambers (I−V) separated by gate valves.

3. Computational Methods

The calculation of the equilibrium geometries and the harmonic vibrational frequencies of Na_MSe_N clusters is carried out by means of density functional theory (B3LYP functional) as implemented in the Gaussian98 program package.[18] Well-known selenium ring and chain structures[10,11] with sodium atoms added at different positions are used as starting geometries. As a first step, the optimization is performed with a 6-31G* basis set, followed by reoptimization with a 6-311G* basis set. Additionally, Mulliken population analysis is used to gain some information about the partial charge distribution.

4. Results and Discussion

In a first experiment, pure selenium clusters are generated by vaporization of selenium only. The conditions in the source can be tuned easily to a state where small selenium clusters with five to eight atoms strongly dominate the cluster beam as observed by the TOF-MS (Figure 2). To avoid multiphoton absorption and cluster fragmentation, ionization is accomplished by an arc xenon flash lamp with a broad spectral range (λ = 120−1100 nm) and a relatively low-light intensity. The obtained cluster distribution is similar to mass spectroscopic investigations of Se_N clusters from other cluster sources[19,20].

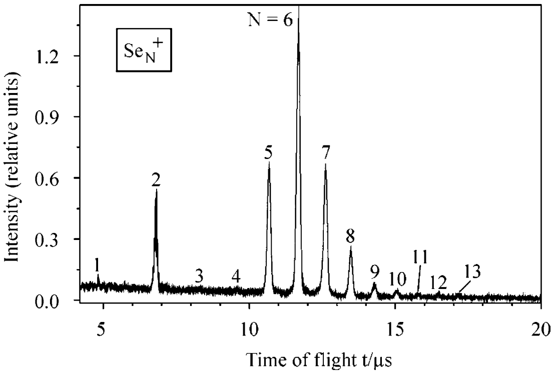

Figure 2. Mass spectrum of Se_N clusters after ionization by a flash lamp.

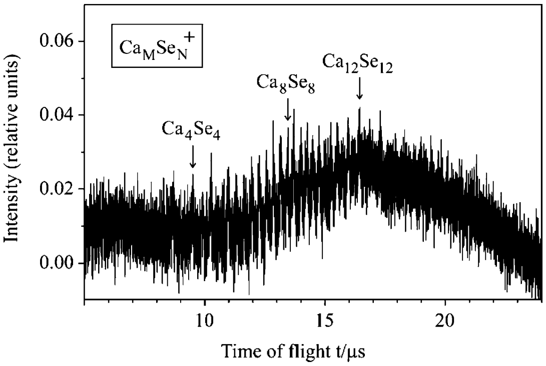

Figure 3. Mass spectrum of Ca_MSe_N clusters after ionization by a flash lamp. Adjacent mass signals are separated by about 40 amu and can be assigned to the series Ca_NSe_N, $Ca_{N+1}Se_N$, and Ca_NSe_{N+1} (cf. text). Some signals are labeled to illustrate the mass range.

Adding calcium by turning on the vaporization of the respective rod leads to a completely different mass spectrum (Figure 3). We observe a distribution with mass steps of about 40 atomic mass units each. The assignment is complicated by the fact that the atomic mass of selenium (79 amu) is almost exactly twice the mass of calcium (40 amu). However, with low-light intensities ensuring the absence of fragmentation, a better mass resolution cannot be obtained. It is most feasible to assign the mass signals to the three cluster series Ca_NSe_N, $Ca_{N+1}Se_N$, and Ca_NSe_{N+1} analogous to the stoichiometry of the only known Ca/Se solid-state compound CaSe. This assignment is supported by the absence of distinct maxima in the spectrum. Under these conditions, no Se_N clusters with only one or two Ca atoms added were observed, even if the calcium concentration in the cluster source was reduced by the use of a lower laser intensity.

Fragmentation becomes important if intense laser light (λ = 193 nm, 100 mJ/cm^2) is used for ionization. The occurrence of multiphoton absorption under such conditions was already shown in other work[21] and can be easily confirmed by comparison of the laser photon density and the typical photon absorption cross sections of semiconductor clusters.[22−24] It is experimentally observed by a nonlinear dependence of the mass signal intensity on the laser intensity.[22] The resulting mass spectrum of Ca_MSe_N clusters contains remarkable maxima at small masses and steps at higher masses (Figure 4). Using the same mass assignment as in Figure 3, the maxima and steps belong to cluster sizes, where the total number of atoms is the product of three integers (Table 1). If one thinks about corresponding geometries, it is self-evident that the maxima and steps reflect the gradual buildup of compact cuboids. Compari-

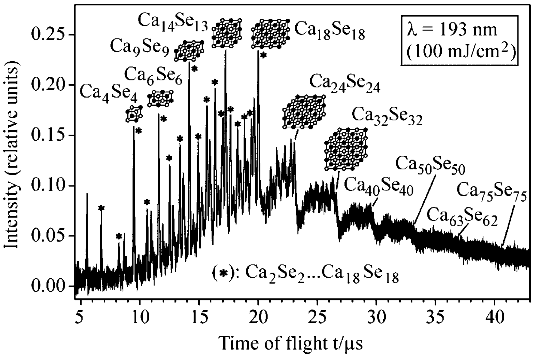

Figure 4. Mass spectrum of Ca_MSe_N clusters after ionization by laser light ($\lambda = 193$ nm, 100 mJ/cm^2) and fragmentation. Stoichiometric clusters (i.e., $M = N = 2, 3, ...18$) are marked with a star.

TABLE 1: Ca_MSe_N Clusters with High Stability

cluster	number of atoms	cuboid a × b × c
Ca_4Se_4	8	2 × 2 × 2
Ca_6Se_6	12	2 × 2 × 3
Ca_9Se_9	18	2 × 3 × 3
$Ca_{14}Se_{13}$	27	3 × 3 × 3
$Ca_{18}Se_{18}$	36	3 × 3 × 4
$Ca_{24}Se_{24}$	48	3 × 4 × 4
$Ca_{32}Se_{32}$	64	4 × 4 × 4
$Ca_{40}Se_{40}$	80	4 × 4 × 5
$Ca_{50}Se_{50}$	100	4 × 5 × 5
$Ca_{63}Se_{62}$	125	5 × 5 × 5
$Ca_{75}Se_{75}$	150	5 × 5 × 6

son with the thermodynamic stable solid-state compound CaSe reveals a striking structural similarity. Bulk CaSe has a NaCl lattice, that is, a packing of alternating cations and anions in a cubic lattice, whose smallest cutouts are just cuboids. The favored formation of complete cuboids after multiphoton absorption can be explained by a simple model. After absorption of several photons, a cluster can reduce its internal energy by fragmentation, that is, by evaporation of atoms or small molecules.[25−27,21] The typical duration of this process is in the range of 1−100 μs,[25,27] well matching our experimental conditions, where clusters fly about 80 μs between irradiation and acceleration into the TOF-MS. The preferred products of such a fragmentation are clusters, where the removal of further atoms needs especially high energies. For systems with a NaCl structure, these are just the complete cuboids. Enhanced stabilities of cuboids or similar structures are also known for other binary clusters, particularly for halides of alkali metals[21,26−31] as well as carbides[32−34] and oxides[35−37] of bivalent metals.

Apart from the especially stable cuboids, we observe in the mass spectrum increased intensities for stoichiometric clusters Ca_NSe_N compared to the respective adjacent signals of nonstoichiometric $Ca_{N+1}Se_N$ and Ca_NSe_{N+1} clusters (Figure 4).

In summary, the Ca_MSe_N stability is determined by the same stoichiometry and the same structure as the solid-state compound CaSe thus strongly suggesting a NaCl-like structure even for the smallest Ca_MSe_N clusters. This is in accordance with the calcium acting as a bivalent metal, that is, a formal transfer of the two valence electrons of the Ca to an adjacent Se atom leading to the formation of Ca^{2+} and Se^{2-} ions. Within this model, both types of ions have (formally) completely filled electron shells and can therefore form no bonds to other atoms apart from ionic interactions. Although in reality covalent bonding contributions might be present as well, the stability of the product clusters can be understood as packings of ions that minimize the lattice energy.

Replacing the calcium by a sodium rod in the cluster source allows the production of Na_MSe_N clusters. Figure 5 shows the cluster distribution after fragmentation. Basically, we observe a periodic mass distribution corresponding to three cluster series $(Na_2Se)_N(Na_2Se_X)Na^+$ with $X = 1-3$ with different intensities and $N = 0, 1, ..., 17$. Interestingly, we obtain essentially the same mass spectrum, regardless of the photon energy ($\lambda = 193$ or 248 nm) we use which is further evidence for the occurrence of multiphoton absorption followed by decay processes. As in Ca_MSe_N, there is a strong relation to the stoichiometry of the known Na/Se solid-state compounds Na_2Se_N with $N = 1, 2, 3, 4, 6$.[38,39] The first Na_MSe_N cluster series ($X = 1$) which can be rewritten in the form $(Na_2Se)_{N+1}Na^+$ and has the highest abundance exactly reflects the composition of the thermodynamically most stable compound Na_2Se consisting of Na^+ and Se^{2-} ions with an additional Na^+ allowing for the positive charge of the cluster ions. The other two series ($X = 2, 3$) also have compositions close to the stoichiometry Na_2Se. However, for a reasonable description of the bonding situation in these clusters, we have to assume the existence of selenium polyanions $Se_2{}^{2-}$ and $Se_3{}^{2-}$ as known from the less stable bulk compounds Na_2Se_2 and Na_2Se_3.

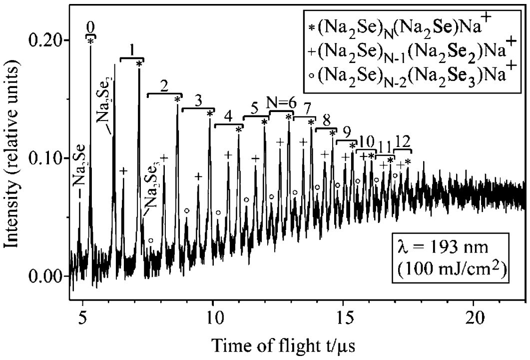

Figure 5. Mass spectrum of Na_MSe_N clusters after ionization by laser light ($\lambda = 193$ nm, 100 mJ/cm^2) and fragmentation.

The enhanced stability of the observed cluster series $(Na_2Se)_N(Na_2Se_X)Na^+$ in the fragmentation process can be explained by the fact that all atoms in those clusters have completely filled electron shells. The latter is obvious for the Na^+ and Se^{2-} ions; however, in the polyanions $Se_X{}^{2-}$ the octet configuration for all atoms is achieved by covalent bonds between adjacent Se atoms leading to a short selenium chain with a singly negative charge at each end. These reflections on the electronic configuration and the stoichiometry already explain the observed fragmentation products. Geometrical influences that mean particular stabilities which can be ascribed to preferred geometries as for the Ca_MSe_N clusters are not observed. This can be understood by the fact that we now have a combination of singly positive and doubly negative charged ions, which require much more complex structures for the minimization of the coulomb energy. The bulk Na_2Se has an antifluorite structure,[40] for which no small cutouts containing only a few atoms are possible that have simultaneously an approximately stoichiometric composition and an especially compact geometry.

The occurrence of small polyanions $Se_2{}^{2-}$ and $Se_3{}^{2-}$ raises the question whether larger aggregates $Se_N{}^{2-}$ with $N > 3$ are possible as well, analogous to the bulk modifications Na_2Se_N. One could even think about generation of clusters with exactly the bulk stoichiometry corresponding to the addition of two Na atoms to a Se_N ring.

By the use of low sodium concentrations in the cluster source, it is indeed possible to carry out this reaction as shown in the mass spectrum in Figure 6. For a direct observation of the product distribution leaving the cluster source, we have used

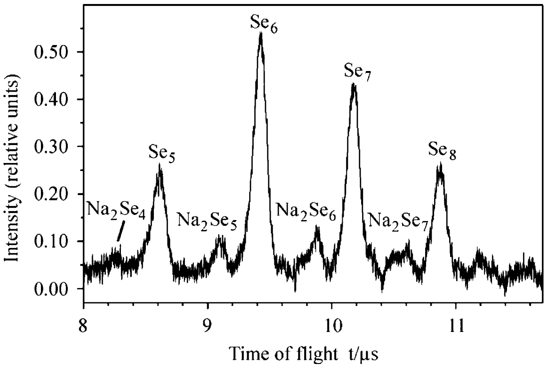

Figure 6. Mass spectrum of Se_N and Na_MSe_N clusters after ionization by a flash lamp.

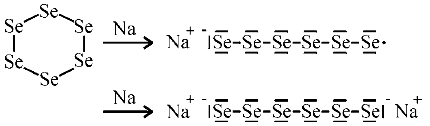

Figure 7. Proposed reaction mechanism for the addition of Na atoms to Se_N rings.

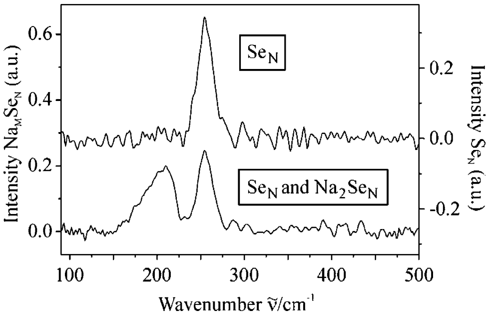

Figure 8. Raman spectra of selenium clusters (top) and sodium/selenium clusters (bottom) in a nitrogen matrix ($T = 15$ K, laser power 110 mW).

the flash lamp again to avoid multiphoton absorption and cluster fragmentation. Besides pure Se_N, one finds predominantly product clusters with two Na atoms, Na_2Se_N ($N = 3-8$). An explanation for the preferred formation of clusters with exactly two Na atoms can be easily found considering the possible reaction mechanism. On addition of the first Na atom to a Se_N ring, the formation of a Na−Se bond, that is, the formal transfer of the valence electron of the Na atom to a Se atom, must be accompanied by the simultaneous breaking of a Se−Se bond. Otherwise, one would get a Se atom with three bonds to adjacent atoms corresponding to more than eight valence electrons at this atom which is rather improbable. This reaction is synonymous with a ring opening leading to a selenium chain with a Na at one end (Figure 7). Since the Se atom at the other end of such a chain would have an unpaired electron, a quick saturation by picking up a second Na in the cluster source is extremely probable. In this way, Na_2Se_N clusters, that is, selenium clusters "doped" with a low amount of sodium, can be formed. The Na/Se ratio is varied by the change of the Se_N cluster size, that is, the length of the formed selenium polyanion.

In Na_MSe_N clusters with both high sodium content and low sodium content the Na seems to act as a monovalent metal. For the fragmentation experiments, we conclude this from the compositions of stable Na_MSe_N clusters. For the Na_2Se_N clusters, the transfer of the only valence electron of the Na to the Se_N clusters is plausible as well, since it can explain the preferred formation of clusters with just two Na atoms accompanied by a structural change from selenium rings to chains. However, especially in the latter case, more arguments are desirable.

We have therefore deposited Na_2Se_N and Se_N clusters in a nitrogen matrix and investigated by Raman spectroscopy. The typical Raman signal of a mixture of pure Se_N clusters ($N = 5-8$, cf. Figure 2) in comparison to that of a mixture of Se_N and Na_2Se_N ($N = 4-8$, cf. Figure 6) is shown in Figure 8. For the pure Se_N, one observes a Raman band in the range of 235−280 cm^{-1} which can be explained by a superposition of Raman signals of Se_N rings with 5−8 atoms according to ab initio calculations.[10] For the mixture of Se_N and Na_2Se_N, we obtain a further Raman band between 165 cm^{-1} and 225 cm^{-1} with a maximum at 210 cm^{-1}. This signal is compared to vibrational wavenumbers calculated by means of density functional theory (Gaussian98,[18] B3LYP/6-311G*) for the equilibrium geometries of Na_2Se_N clusters ($N = 4-6$). We find that vibrations of the Na−Se bonds in the clusters have especially high intensities just in the experimentally observed range of wavenumbers. The high Raman intensities of Na−Se oscillations compared to the other cluster vibrations can be explained by the large polarizability changes during the oscillation of these bonds as explained in the Introduction. The Se−Se vibrations in the Na_2Se_N clusters should contribute much less to the spectrum. Even if these Se−Se vibrations would give an observable signal, it would probably vanish under the signal of the pure Se_N clusters which are much more abundant in the molecular beam than the Na_2Se_N (cf. Figure 6). A more detailed discussion of these Raman spectra and their correlation with calculated wavenumbers was published previously.[15]

The calculated equilibrium geometries of Na_2Se_N clusters ($N = 4-6$) are shown in Figure 9.[15] They can be interpreted in terms of two single Na atoms located at the ends of a selenium chain. This is similar to the known bulk compounds Na_2Se_N which are understood as polyanionic structures $(Na^+)_2(Se_N)^{2-}$ with ionic Na−Se and covalent Se−Se bonds.[41,42] However, the selenium chains in the bulk are stretched, whereas in the clusters they remain strongly bent to a horseshoe shape. This can be explained by an attractive interaction between the two Na atoms. The Na−Na distances in Na_2Se_4 (3.57 Å) and Na_2Se_6 (3.40 Å) are similar to that of a free Na_2^+ ion (3.54 Å[43]). A Mulliken population analysis gives a positive charge of 0.4−0.5 e for each sodium atom in Na_2Se_4 and Na_2Se_6. The corresponding negative charge is located at the two end atoms of the selenium chain.[15] This supports the model of a Na_2^+ ion which is inserted into the selenium ring. In the Na_2Se_5 with an

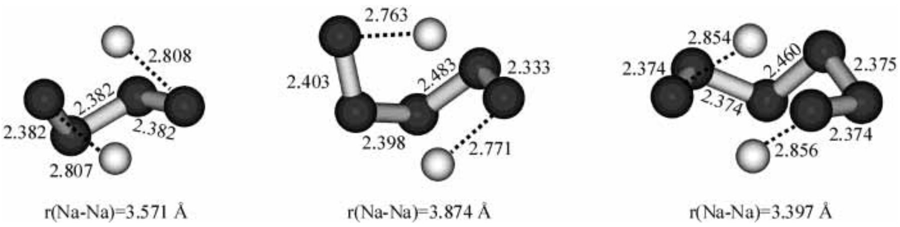

Figure 9. Calculated equilibrium geometries of Na_2Se_4, Na_2Se_5, und Na_2Se_6 (all bond lengths in Å). The two Na atoms are located in the front, above and below the selenium plane.

odd number of Se atoms in the chain, one Na is much closer to a chain end as shown in Figure 9. This leads to a stronger charge transfer to the semiconductor; one obtains a charge of 0.4 e for one Na and 1.0 e for the other. As a consequence, the Na−Na bond is weakened leading to a longer Na−Na distance (3.87 Å).

All these findings support the idea of the isolated Na_2Se_N clusters as being polyanionic selenium chains with positive sodium ions at the ends just as in the bulk compound. However, the amount of charge transfer in the Na−Se bonds varies between the border cases $(Na_2)^+(Se_N)^-$ and $(Na^+)_2(Se_N)^{2-}$.

5. Conclusions

The addition of metal atoms to small selenium clusters leads to structural changes that can be related to the electron transfer from the metal to the semiconductor. In a first approximation, the amount of this charge transfer can be predicted by the metal valence, that is, by the same principles of bonding formation which are applied for bulk compounds. The structural models for the metal/selenium clusters derived from experiments are strongly related to small cutouts of corresponding bulk structures. Addition of bivalent calcium leads to products that show special stabilities for Ca_MSe_N clusters corresponding to cuboids with CaSe bulk structure and can be formally understood as packings of Ca^{2+} and Se^{2-} ions. Addition of monovalent sodium leads to products with highest stabilities for Na_MSe_N clusters corresponding to formally purely ionic compounds consisting of Na^+ and Se^{2-} ions similar to bulk Na_2Se. However, especially for low sodium concentrations, there are further products containing Na^+ ions and polyanionic chains Se_N^{2-} of different lengths. The latter can be regarded as intermediate steps between the purely covalent bonds in Se_N clusters and the purely ionic bonds in $[(Na^+)_2Se^{2-}]_{N+1}Na^+$ clusters.

Although the concept of electron transfer according to the metal valences provides structural models in agreement with mass spectra and fragmentation experiments, quantum chemical calculations show that the electron transfer is rather incomplete. This results in structural features as the bending of the polyanionic selenium chains in Na_2Se_N clusters to a horseshoe shape because of a covalent bonding interaction between the sodium atoms.

The calculated vibrational wavenumbers of the Na_2Se_N clusters are in agreement with the observation of an intense low-frequency Raman band of these clusters deposited in a nitrogen matrix. Moreover, one can understand the high Raman activity through the charge transfer during vibrational Na/Se bond elongation leading to a strong dynamical change of the clusters polarizability.

Acknowledgment. We acknowledge support from the Deutsche Forschungsgemeinschaft for the project “Elektronische und magnetische Struktur von metallhaltigen Halbleiterclustern” (Be-1350/5-1). J. A. Becker is grateful for support from the Fonds der Chemischen Industrie. C. Herwig and M. Schnell thank the Stiftung Stipendien-Fonds des Verbandes der Chemischen Industrie for a PhD grant. Computer time of the Regionales Rechenzentrum Niedersachsen has been essential for this work.

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