

Emergence of metallic properties in alkali-rich alkali-halide clusters

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We have used photoelectron spectroscopy to study alkali-rich sodium iodide and cesium chloride clusters in order to determine how their composition affects their electronic properties. Spectral features of $(\text{Na } 1)_n\text{Na}_m^-$ ($m \geq 2$) are remarkably similar to those of isolated metal clusters Na_m^- for all sizes of n that we investigated. This result suggests that the clusters are comprised of phase separated metallic and ionic components. In contrast, photoelectron spectra of $(\text{CsCl})_n\text{Cs}_m^-$ clusters are unlike those of pure metal clusters, suggesting that the excess metal atoms are mixed into the ionic portion of the cluster. Such mixing may make it possible for these cesium chloride clusters to exhibit the finite system equivalent of a metal-insulator transition. [S0163-1829(97)05015-7]

I. INTRODUCTION

In the bulk, alkali and alkali halide systems are prototypical metals and insulators, respectively. Even at the cluster level, these materials maintain the bonding characteristics of their bulk counterparts. Metallic bonding and electron delocalization have been demonstrated both experimentally and theoretically for small alkali clusters,¹⁻³ and ionic bonding—including a large band gap—has been observed for finite alkali halide aggregates.³⁻⁵ Mixtures of these two materials therefore present a promising regime in which to observe a metal-nonmetal transition.

In this fashion, Rajagopal, Barnett, and Landman² studied theoretically a “metalization” sequence in which the halogen anions in fully ionic sodium fluoride clusters were successively replaced by electrons, resulting in a metal-rich cluster. In particular, these calculations predicted phase-separated metal and ionic parts in Na_{14}F_9 , in which a $2 \times 3 \times 3$ substrate supported a metallic layer comprised of five sodium atoms (or, equivalently, five sodium ions and five electrons). In a more recent theoretical work, Hakkinen, Barnett, and Landman⁶ observed a similar segregation in $\text{Na}_{14}\text{Cl}_9^+$, in which a layer of five sodium ions and four electrons was supported by an ionic component. Moreover, electron-density calculations revealed a remarkable similarity between the metallic layer and an isolated Na_5^+ cluster, both in terms of the spatial arrangement of ions and in the electron distribution.

Phase separation between metallic and ionic components has also been observed experimentally. Through photoionization and electron-impact ionization, Pollack, Wang, and Kappes⁷ demonstrated a closed electronic shell structure, akin to that of Na_8 and Na_9^+ , in the mixed clusters $(\text{NaCl})\text{Na}_8$, $(\text{NaCl})_2\text{Na}_8$, $(\text{NaCl})\text{Na}_9^+$, and $(\text{NaCl})_2\text{Na}_9^+$. Vezin *et al.*⁸ later linked mixed clusters to the corresponding free-metal clusters with their measurements of the optical absorption and ionization potentials of Li_nH and Li_nH_2 . They found these clusters to be similar to Li_{n-1} and Li_{n-2} , respectively, indicating that each hydrogen atom localizes the electron from one lithium atom. More recently, Xia and Bloomfield⁹ found that the photoelectron spectra of $(\text{NaCl})_3\text{Na}_m^-$ and $(\text{KI})_3\text{K}_m^-$ ($m \geq 2$) resembled the Na_m^-

and K_m^- spectra obtained by McHugh *et al.*¹⁰ suggesting a metal-nonmetal phase separation.

Studies of ionic aggregates have demonstrated the dependence of electron localization and cluster structure on both the number and size of the individual atomic ions comprising the cluster.¹¹⁻¹⁵ In the present work, we extended the study of metal-rich alkali halides $(MX)_nM_m^-$ to systems at two extremes of constituent atomic ion size. Sodium iodide clusters lie at one extreme, with small alkali ions and large halogen ions. Cesium chloride clusters lie at the other extreme, with atomic ions of nearly equal sizes. The ratio of free atomic cation radius to free atomic anion radius in these two materials is approximately 0.45 and 0.92, respectively.

Our photoelectron spectroscopy measurements of $(\text{Na } 1)_n\text{Na}_m^-$ ($m \geq 2$) clusters are indicative of metal-nonmetal phase separations for all sizes of n that we studied. However, photoelectron spectra of $(\text{CsCl})_n\text{Cs}_m^-$ bear little resemblance to those of isolated metal clusters, indicating that cesium-rich cesium halide systems have a higher degree of mixing between the metallic and ionic components.

II. EXPERIMENT

The clusters are produced in a room-temperature laser vaporization cluster source.^{4,16} The pulsed beam from an ArF excimer laser (193 nm) strikes the surface of an alkali halide disk, sending a plume of vapor into a narrow helium-filled channel. The helium, released by a pulsed valve, cools the vapor and sweeps it out of the channel into the surrounding vacuum chamber.

After leaving the channel, the beam of clusters passes through a skimmer to a time-of-flight mass spectrometer.⁴ The pulsed-field plates of the mass spectrometer extract the cluster anions and direct them toward a magnetic bottle photoelectron spectrometer.¹³ When the $(MX)_nM_m^-$ anions reach the magnetic bottle, they are exposed to light from a pulsed Nd:YAG (yttrium aluminum garnet) laser, photodetaching electrons which then travel through the electron spectrometer to a dual microchannel plate detector.

We determine the kinetic energies of photodetached electrons from their travel times through the spectrometer. By subtracting their kinetic energies from the photon energy, we

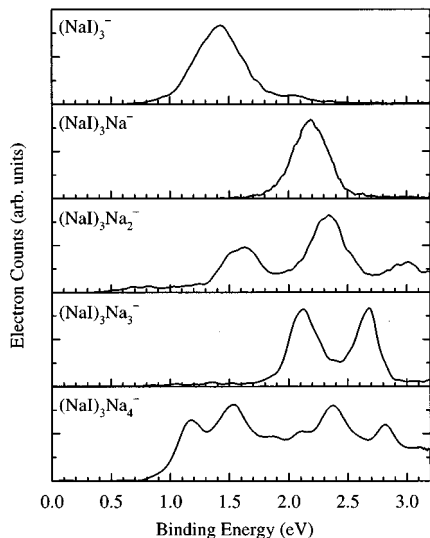


FIG. 1. Photoelectron spectra of $(\text{NaI})_3\text{Na}_m^-$ ($m=0-4$) taken with 3.49-eV photons.

are able to determine how much energy was needed to remove each electron from its cluster anion. We record a large number of photodetachment events to obtain a complete photoelectron spectrum. The resolution of the spectrometer depends on the speed of the outgoing electron, with the ratio of the uncertainty in photoelectron kinetic energy to the total kinetic energy being about 0.1. This resolution is high enough that most of the broadening in each spectral feature arises from the large number of final vibrational states that can result from photodetachment. The location of the first intensity maximum defines the electron vertical binding energy (EVBE)—the energy required to remove the most weakly bound electron from the ground-state cluster anion without permitting the remaining neutral cluster to relax.¹⁷

All of the clusters were studied with 2.33-eV photons from the second-harmonic beam of the Nd:YAG laser. However, since the electrons in sodium iodide clusters are especially tightly bound, these systems were also probed with 3.49-eV photons from the laser's third harmonic. Because the spectra obtained for $(\text{NaI})_n\text{Na}_m^-$ ($m \geq 2$) with the second harmonic contain no information not included in the third-harmonic spectra, only the photoelectron spectra taken with higher-energy photons are shown in the figures.

III. RESULTS AND DISCUSSION

A. $(\text{NaI})_n\text{Na}_m^-$ clusters

Figure 1 presents photoelectron spectra for $(\text{NaI})_3\text{Na}_m^-$ ($m=0-4$). In analogy with the case for $(\text{NaCl})_3\text{Na}_m^-$,⁹ we see that for $m \geq 2$, the spectrum for a cluster of a given m is similar to that obtained by McHugh *et al.*¹⁰ for the corresponding metal cluster Na_m^- . For example, both $(\text{NaI})_3\text{Na}_2^-$ and Na_2^- exhibit three peaks in their photoelectron spectra, with the central one dominant. Figure 1 shows that the first peak, at 1.63 eV, is slightly larger than the third peak, just as was the case for Na_2^- . Similar comparisons can be made for the cases of $m=3$ and 4. We note that while four peaks are seen for $(\text{NaI})_3\text{Na}_4^-$, only three

peaks were observed for Na_4^- , since the fourth peak lies beyond the 2.54-eV photon energy used in that experiment.¹⁰

The similarity shown between the mixed aggregates and the alkali clusters suggests a metal-nonmetal phase separation, in which a Na_m^- cluster is joined to a fully ionic $(\text{NaI})_3$ cluster. Earlier reports predicted a high stability for neutral alkali halide clusters containing six ions.^{18,19} It is thus likely that such an arrangement, predicted to be a hexagonal ring, would resist the reorganization needed to incorporate the Na_m^- particle into its structure. The photoelectron spectra reflect the character of the metallic segment, since the electrons in the ionic component are especially tightly bound and cannot be detached with 3.49-eV photons. The principle characteristic differentiating the mixed clusters from the pure alkali ones, an overall blueshift in the electron binding energies, is probably due to polarization of the ionic lattice induced by the metallic overlayer.

The details of the photoelectron spectra for $(\text{NaI})_3\text{Na}_m^-$ illustrate properties characteristic of metal clusters. While the first peak in each spectrum corresponds to photodetachment events in which the remaining neutral clusters are left in their ground electronic states, the more tightly bound peaks correspond to photodetachment events in which the remaining neutral clusters are left in electronically excited states. The spectra thus provide information about the electronic states of the neutral clusters. Most importantly, we can determine the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the neutral cluster by measuring the energy difference between the maxima of the first two peaks in each spectrum. This HOMO-LUMO gap is the finite system equivalent of the band gap in a bulk solid.

However, because photodetachment occurs on a time scale much shorter than that required for ionic reorganization, the HOMO-LUMO gap that we measure is that of a neutral cluster with its ions arranged as they were in the cluster anion, and the anion and the neutral cluster may have somewhat different ground-state geometries.

Previous experimental and theoretical work has shown that the HOMO-LUMO gap for various metal clusters decreases with increasing particle size and approaches zero in the bulk.^{20,21} We also observe a diminishing HOMO-LUMO gap in the $n=3$ sequence for sodium iodide. The measured gaps are, from Fig. 1, 0.71, 0.56, and 0.35 eV, for $m=2, 3$, and 4, respectively. These gaps are very similar to those observed for the pure sodium clusters. From the spectra reported in Ref. 10, we infer HOMO-LUMO gaps for Na_2 , Na_3 , and Na_4 of approximately 0.7, 0.6, and 0.4 eV, respectively.

Metallic clusters also exhibit oscillations in their electron binding energies according to whether the number of delocalized electrons is even or odd. Clusters with even numbers of delocalized electrons bind those electrons tightly in spin pairs, while clusters with odd numbers of delocalized electrons contain lone, relatively weakly bound electrons. This even-odd alternation has been observed in alkali cluster anions in experiments and calculations.^{10,21} From Fig. 1, we infer EVBE's of 1.63, 2.12, and 1.17 eV for $m=2, 3$, and 4, respectively, consistent with there being $m+1$ delocalized or "excess" electrons in these three clusters, just as there are in the corresponding pure alkali clusters.

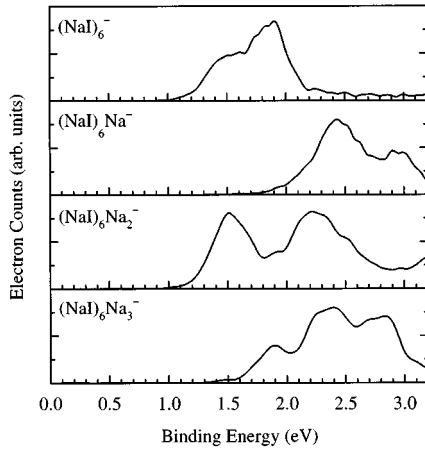


FIG. 2. Photoelectron spectra of $(\text{NaI})_6\text{Na}_m^-$ ($m=0-3$) taken with 3.49-eV photons.

We also studied metal-rich clusters for the $n=6, 7$, and 8 sequences, as shown in Figs. 2, 3, and 4 (the abundances of clusters in other sequences were insufficient for producing photoelectron spectra). Again, metal-nonmetal phase separation is evident for $m \geq 2$. The intensity ratios for the separate peaks in each spectrum in the $n=7$ and 8 sequences are remarkably similar to those observed for the corresponding metal clusters, and all three sequences exhibit diminishing HOMO-LUMO gaps and even-odd alternations in the electron binding energies (see Table I).

Since alkali-halide clusters with hexagonal and cubic geometries exhibit exceptional stability,^{18,19} the ionic substrate in $(\text{NaI})_6\text{Na}_m^-$ is probably either stacked hexagonal rings or a $2 \times 2 \times 3$ cubic structure. Similarly, the ionic substrate in $(\text{NaI})_8\text{Na}_m^-$ is most likely a $2 \times 2 \times 4$ cubic arrangement. However, the phase separation that occurs in the $(\text{NaI})_7\text{Na}_m^-$ clusters is somewhat surprising because the $(\text{NaI})_7$ ionic substrate cannot take a cubic or hexagonal form.

B. $(\text{CsCl})_n\text{Cs}_m^-$ clusters

We also examined cesium-rich cesium halide clusters, as shown in Figs. 5, 6, 7, and 8. None of the sequences for

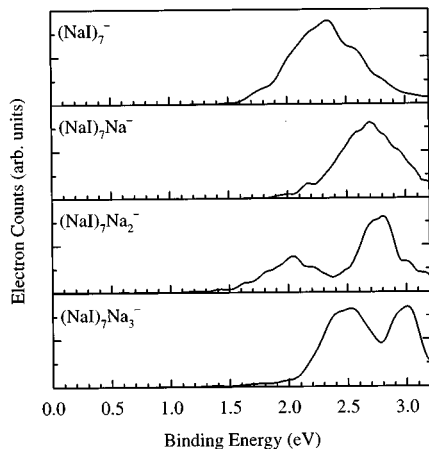


FIG. 3. Photoelectron spectra of $(\text{NaI})_7\text{Na}_m^-$ ($m=0-3$) taken with 3.49-eV photons.

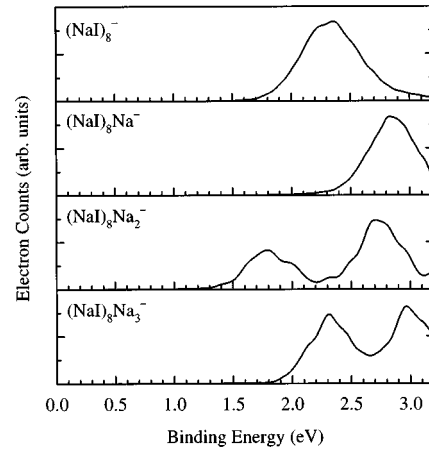


FIG. 4. Photoelectron spectra of $(\text{NaI})_8\text{Na}_m^-$ ($m=0-3$) taken with 3.49-eV photons.

which we obtained photoelectron data ($n=2, 3, 5$, and 7) exhibit close similarities to corresponding alkali-metal clusters that were seen with sodium iodide clusters.

As noted above, we see clear evidence of a metal-nonmetal phase separation in the $(\text{NaI})_3\text{Na}_m^-$ and

TABLE I. Electron vertical binding energies (EVBE) of clusters $(\text{NaI})_n\text{Na}_m^-$ ($n=3, 6, 7$, and 8; $m=2-4$) and $(\text{CsCl})_n\text{Cs}_m^-$ ($n=2, 3, 5$, and 7; $m=2-4$), and the HOMO-LUMO gap in corresponding neutral clusters, obtained from the energy difference between the two lowest binding energy peaks in the photoelectron spectra of the cluster anions.

$(MX)_nM_m^-$	EVBE (eV)	HOMO-LUMO gap (eV)
$(\text{NaI})_3\text{Na}_2^-$	1.63	0.71
$(\text{NaI})_3\text{Na}_3^-$	2.12	0.56
$(\text{NaI})_3\text{Na}_4^-$	1.17	0.35
$(\text{NaI})_6\text{Na}_2^-$	1.51	0.71
$(\text{NaI})_6\text{Na}_3^-$	1.90	0.50
$(\text{NaI})_7\text{Na}_2^-$	2.04	0.77
$(\text{NaI})_7\text{Na}_3^-$	2.53	0.48
$(\text{NaI})_8\text{Na}_2^-$	1.79	0.92
$(\text{NaI})_8\text{Na}_3^-$	2.31	0.66
$(\text{CsCl})_2\text{Cs}_2^-$	0.62	0.25
$(\text{CsCl})_2\text{Cs}_3^-$	0.80	0.35
$(\text{CsCl})_2\text{Cs}_4^-$	0.94	0.31
$(\text{CsCl})_3\text{Cs}_2^-$	0.52	0.35
$(\text{CsCl})_3\text{Cs}_3^-$	0.97	0.18
$(\text{CsCl})_5\text{Cs}_2^-$	0.84	0.25
$(\text{CsCl})_5\text{Cs}_3^-$	1.05	0.24
$(\text{CsCl})_5\text{Cs}_4^-$	0.93	0.22
$(\text{CsCl})_7\text{Cs}_2^-$	0.97	0.20
$(\text{CsCl})_7\text{Cs}_3^-$	1.27	0.11

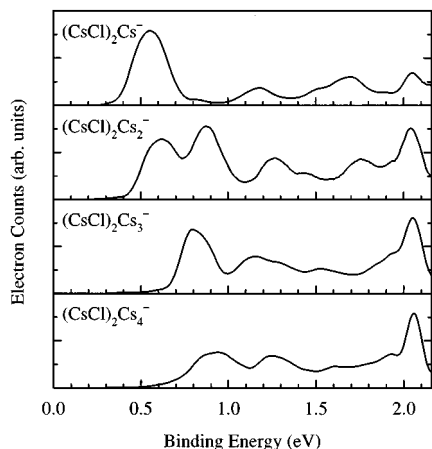


FIG. 5. Photoelectron spectra of $(\text{CsCl})_2\text{Cs}_m^-$ ($m=1-4$) taken with 2.33-eV photons.

$(\text{Na}1)_7\text{Na}_m^-$ cluster sequences. However, we do not see such evidence in the $(\text{CsCl})_3\text{Cs}_m^-$ and $(\text{CsCl})_7\text{Cs}_m^-$ sequences. Both the number and the intensity ratios of peaks in each photoelectron spectrum are completely unlike those seen in pure cesium clusters. Furthermore, while metalization sequences for $n=3$ and 7 both exhibit even-odd alternations in the electron binding energy, the HOMO-LUMO gaps in these cesium halide clusters do not correlate well with those of the pure alkali clusters. We infer HOMO-LUMO gaps of 0.5 and 0.4 eV, respectively, from the spectra of Cs_2^- and Cs_3^- in Ref. 10. The HOMO-LUMO gaps we measured in $(\text{CsCl})_n\text{Cs}_m^-$ clusters ($m=2-3$) are much lower in comparison. For $n=3$, the HOMO-LUMO gap drops with increasing m from 0.35 to 0.18 eV, while for $n=7$, it drops from 0.20 to 0.11 eV.

We can make the same observations for the $n=5$ series. The number and relative heights of peaks in $(\text{CsCl})_5\text{Cs}_m^-$ are markedly different from those of pure cesium clusters. In addition, the spacing between the peaks in each spectrum is too small to resemble a pure metal cluster accurately. We infer HOMO-LUMO gaps of only 0.25 and 0.24 eV for $m=2$ and 3, respectively.

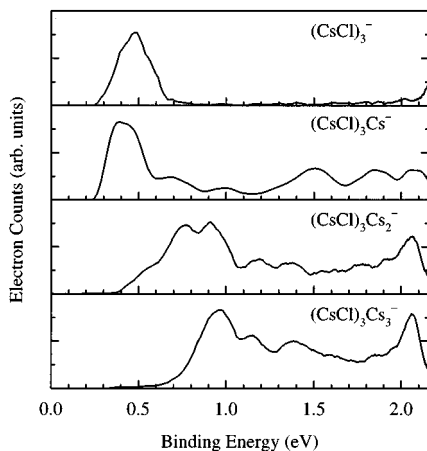


FIG. 6. Photoelectron spectra of $(\text{CsCl})_3\text{Cs}_m^-$ ($m=0-3$) taken with 2.33-eV photons.

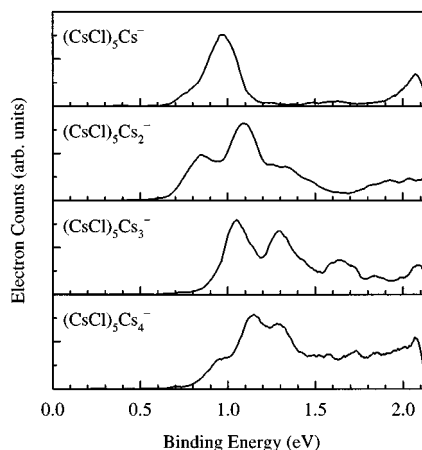


FIG. 7. Photoelectron spectra of $(\text{CsCl})_5\text{Cs}_m^-$ ($m=1-4$) taken with 2.33-eV photons.

Photoelectron spectra of the $n=2$ sequence of cesium chloride clusters depart even more sharply from those of the corresponding pure cesium clusters. Not only is there little correlation between the peak heights observed in the corresponding cesium chloride and pure cesium clusters, the HOMO-LUMO gap in the $(\text{CsCl})_2\text{Cs}_m^-$ clusters is actually smaller for $m=2$ than it is for $m \geq 3$. Moreover, the electron binding energy for $m=4$ is larger than that for $m=3$, even though the $m=3$ cluster ought to contain an even number of excess electrons. Evidently, there is substantial mixing of the alkali and alkali halide portions of these clusters, a result that is probably due in part to the fact that the $(\text{CsCl})_2$ cluster is a rhombus with very little surface area on which to build a separate metal cluster.²²

Overall, we find that the photoelectron spectra of $(\text{CsCl})_n\text{Cs}_m^-$ clusters are substantially different from isolated Cs_m^- clusters. This result suggests that the $(\text{CsCl})_n\text{Cs}_m^-$ clusters may not be divided into separate alkali and alkali halide portions. They have large numbers of low-energy electronic states, a feature which is typical of “metallic” clusters, yet these clusters do not consistently exhibit the spectral features of the alkali-metal clusters them-

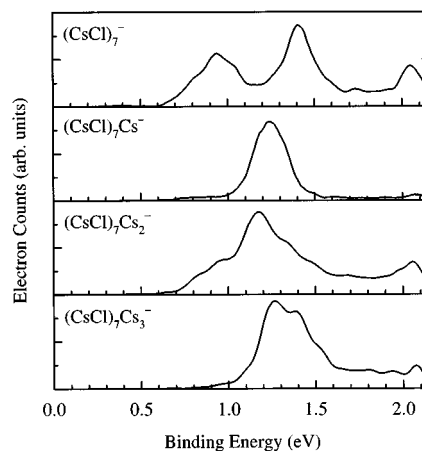


FIG. 8. Photoelectron spectra of $(\text{CsCl})_7\text{Cs}_m^-$ ($m=0-3$) taken with 2.33-eV photons.

selves. Because the $(\text{CsCl})_n\text{Cs}_m^-$ clusters do not exhibit any obvious phase separation, they appear to be true intermediates between cesium metal clusters and cesium halide insulator clusters.

Our observations are similar to those for alkali-alkali halide ($M-MX$) melts consisting of a metal and a salt of that same metal.²³ Studies of these melts have shown that the degree of miscibility of the salt with the metal improves with increasing alkali size. Thus the degree of mixing between metal and metal halide is poor in Na-NaX liquids but very good in Cs-CsX solutions. In addition, experiments on melts have demonstrated that Cs-CsX solutions differ from all other $M-MX$ melts (except for RbBr) in that they lack a miscibility gap. The miscibility gap is a range of metal:salt ratio in which the liquid separates into two distinct phases, one rich in metal and the other rich in salt. The size of this gap increases with decreasing alkali size and is especially large in Na-NaX solutions. For example, separation between metal-rich and salt-rich phases occurs in Na-NaI melts for metal mole fractions ranging from 1.6 to 98.6. In contrast, there is no metal concentration that results in phase separation in any Cs-CsX solution. These solution study results were attributed to the fact that the cohesive forces between metal ions decrease with increasing alkali size. For the same reason, phase segregation between metallic and ionic components within clusters is more likely in $(\text{NaX})_n\text{Na}_m^-$ systems than in $(\text{CsX})_n\text{Cs}_m^-$ systems.

IV. CONCLUSION

In summary, we have studied metal-rich alkali halide clusters, and compared our photoelectron spectra to those of corresponding free-metal clusters. We have shown evidence that the way in which excess metal atoms are incorporated into salt clusters depends on the number of atoms in the aggregate and on the types of the constituent atoms. $(\text{NaI})_n\text{Na}_m^-$ systems exhibit clear indications of phase-separated metallic and ionic components for all n that we studied. In contrast, the evidence for phase separation in cesium-rich cesium chloride clusters is either much weaker or absent altogether.

Previous experimental and theoretical work on metal-insulator transitions in alkali-rich alkali halide clusters focused on sodium- and potassium-halide clusters, and found metal-nonmetal phase separation to be their dominant characteristic. Our results suggest that work involving cesium-rich cesium halide clusters can provide opportunities for studying systems in which excess metal atoms mix into the overall structure instead of remaining phase separated. Examination of such mixtures would provide an excellent probe of the features involved in metal-insulator transitions in finite systems.

ACKNOWLEDGMENT

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