Evidence for a Phase Separation in Metal-Rich Alkali-Halide Cluster Anions

P. Xia and L. A. Bloomfield
Department of Physics, University of Virginia, Charlottesville, Virgina 22901

(Received 21 December 1993)

We report photoelectron spectra of metal-rich alkali-halide cluster anions $(NaCl)_3Na_m^-$ and $(KI)_3K_m^-$ (m=0 to 5) which show evidence of phase separation within the clusters. The spectra are remarkably similar to those observed in pure alkali metal clusters and include such metal-like features as a highest-occupied–lowest-unoccupied molecular orbit gap that decreases with increasing m and an even-odd alternation in the electron vertical binding energies. These results suggest that the metal-rich alkali-halide clusters consist of metal anions, Na_m^- or K_m^-, weakly attached to neutral alkali halides, $(NaCl)_3$ or $(KI)_3$.

PACS numbers: 61.46.+w, 33.60.−q, 33.80.Eh, 78.50.−w

Metal-nonmetal transitions are fundamental issues in solids. These transitions can be induced by a variety of means, including changes in pressure, density, composition, temperature, and applied fields. One such metal-nonmetal transition should occur as the composition of an alkali-halide insulator is gradually changed to that of a pure alkali metal. Alkali halides and alkali metals are relatively simple materials, making metal-rich alkali-halide compounds attractive as systems in which to look for metal-nonmetal transitions.

Investigations of this sort have recently been carried out in small metal-rich alkali-halide clusters [1–6]. Earlier successes with alkali metal clusters [7,8] and alkali-halide clusters [9–12] provided a starting point from which to begin looking at that intermediate regime, in hopes of finding interesting transitions.

But early on, there were indications that the transition might not proceed smoothly and that a phase separation might occur instead. Photoionization studies of Na_2Cl by Peterson *et al.* [1] revealed that one valence electron is essentially delocalized. Subsequent studies of Na_mCl_j (j=1,2) clusters by Pollack *et al.* [3] showed that the valence electrons in $(NaCl)Na_8$, $(NaCl)_2Na_8$, $(NaCl)Na_9^+$, and $(NaCl)_2Na_9^+$ are also delocalized and form a closed shell structure, just as they do in pure Na_8 and Na_9^+ clusters. Rajagopal *et al.* [5] studied theoretically the addition of extra Na atoms to NaF clusters and predicted that $Na_{14}F_9$ should exhibit a segregated, metallized layer.

Most recently, Broyer and co-workers studied the optical absorptions and ionization potentials of Li_mH and Li_mH_2 clusters [13,14]. They found that each hydrogen atom localizes one electron from a nearby lithium atom. The remaining lithium atoms appear to be metallic. Thus a Li_mH cluster behaves much like a Li_{m-1} cluster and a Li_mH_2 cluster resembles a Li_{m-2} cluster.

In this paper, we report photoelectron spectra of the metal-rich alkali-halide cluster anions $(NaCl)_3Na_m^-$ and $(KI)_3K_m^-$ (m=0 to 5). The spectra of these two cluster sequences exhibit features that are very similar to those observed in the corresponding alkali metal anions Na_m^- and K_m^-. The metal-rich alkali-halide clusters exhibit such metal-like behaviors as a highest-occupied–lowest-unoccupied molecular orbit (HOMO-LUMO) gap that decreases as the number of metal atoms increases and an electron vertical binding energy that alternates in size between even and odd numbers of metal atoms. Based on all the evidence observed, it is likely that the metal-rich alkali-halide clusters are composed of two parts: a metallic part, Na_m^- or K_m^-, and a nonmetallic part, $(NaCl)_3$ or $(KI)_3$, that are only weakly interacting, analogous to the metal and nonmetal phase separation that has been found to occur in metal-rich alkali-halide melts [15].

The apparatus used in our experiment consists of a laser vaporization cluster source, a time-of-flight mass spectrometer, and a magnetic-bottle photoelectron spectrometer [16]. The cluster anions are produced directly in the source by vaporizing a NaCl or KI sample disk with the focused beam of a 193 nm ArF excimer laser (Lambda Physik EMG103MSC). The anions leave the source in a helium carrier gas and are steered toward the photoelectron spectrometer by the mass spectrometer. As clusters of the desired mass arrive in the photoelectron spectrometer, they are exposed to a 7 nsec pulse of 2.33 or 3.50 eV light from a Nd:YAG laser (Spectra Physics DCR-3D). Photoelectrons are guided along magnetic field lines in a drift tube and strike a dual-microchannel plate detector 2 m away.

We determine the kinetic energy of each photoelectron from its flight time through the electron spectrometer. This kinetic energy is converted to a binding energy (the energy used to remove that electron from the cluster) by subtracting it from the photon energy. We add many photodetachment events together to produce a photoelectron spectrum. Our photoelectron spectra are calibrated using the known electron affinities of the negative ions K^- and Na^- [17].

Figure 1 contains photoelectron spectra of $(NaCl)_3Na_m^-$ (m=0 to 4) taken with 3.50 eV light. Figure 2 contains photoelectron spectra of $(KI)_3K_m^-$ (m=0

0031-9007/94/72(16)/2577(4)$06.00

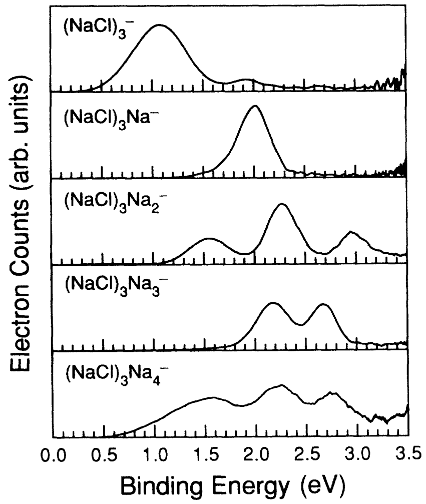

FIG. 1. Photoelectron spectra of $(NaCl)_nNa_m^-$ (m = 0–4) cluster anions using a 3.50 eV detachment photon energy.

to 5) taken with 2.33 eV light. Both spectra are remarkably similar to the corresponding pure metal spectra (Na_m^- or K_m^-) obtained by Bowen and co-workers [18]. The principal difference is that the metal-rich alkali-halide spectra are shifted to higher binding energies. Just such a blueshift should occur if a pure metal cluster is placed next to a dielectric material, such as an alkali-halide particle.

One example of this similarity is $(NaCl)_3Na_2^-$ and Na_2^-. Both cluster anions have three peaks in their photoelectron spectra. In $(NaCl)_3Na_2^-$, the peaks are centered at binding energies of 1.55 eV, 2.28 eV, and 2.98 eV. In Na_2^-, the peaks are centered at 0.54 eV, 1.25 eV, and 2.20 eV. The blueshift caused by adding $(NaCl)_3$ to the pure metal cluster is about 0.9 eV. Even the intensity ratios of the three peaks are the same.

Similar common features are found between all of the metal-rich alkali-halide clusters shown in Figs. 1 and 2 and their corresponding pure metal clusters [18]. In several cases, care must be taken when comparing the metal-rich alkali-halide and pure metal spectra because of our limited experimental resolution and artificial cutoffs that occur because of the photon energies. In $(NaCl)_3Na_4^-$, we were able to resolve the first broad peak seen in Fig. 1 into two peaks by using 2.33 eV light, so that the spectrum actually contains four peaks. The three least tightly bound peaks correspond to the three observed in Na_4^-. The fourth peak was not seen in Na_4^- because it lies beyond the 2.540 eV photon energy used in that work [18]. In $(KI)_3K_4^-$ and $(KI)_3K_5^-$, we are unable to resolve pairs of closely spaced peaks seen in K_4^- and K_5^-, respectively.

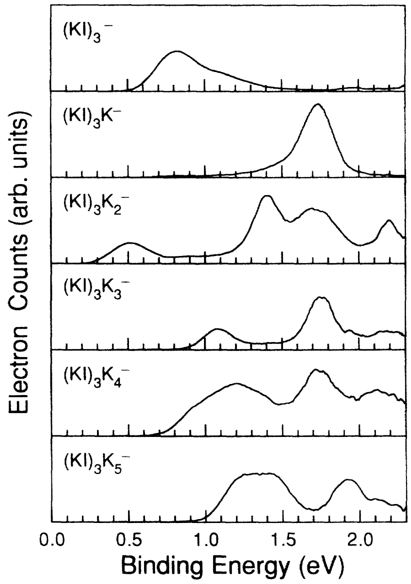

FIG. 2. Photoelectron spectra of $(KI)_3K_m^-$ (m = 0–5) cluster anions using a 2.336 eV detachment photon energy.

These similarities lead us to suspect that the metal-rich alkali-halide clusters in Figs. 1 and 2 are phase separated, with a pure metal anion component, Na_m^- or K_m^-, weakly attached to an alkali-halide component, $(NaCl)_3$ or $(KI)_3$. While we do not have definitive proof that such a phase separation occurs, it provides a very plausible explanation for the experimental results.

If a phase separation occurs, then the electrons that we observe in our experiment must be detached from the pure metal anion component of the clusters because those in the alkali-halide component are too tightly bound to be removed with 3.50 eV photons. The photodetachment process removes one of the electrons from the pure metal anion component in a vertical transition, leaving the remaining neutral cluster in one of many electronic and rovibrational levels. The different peaks we see in the spectra reflect different final electronic states, while the widths of the peaks reflect experimental resolution and rovibrational excitations in both the initial and final vibrational states.

Our first evidence for a phase separation comes from the spacing between energy levels. Let us assume that the most weakly bound electron in a metal-rich alkali-halide cluster anion is found in the lowest unoccupied molecular orbital of the neutral cluster. This assumption is not entirely justified because the electron distorts the neutral cluster to some extent and changes its energy levels. With this assumption, the most weakly bound electron that we observe in our spectra corresponds to the LUMO electron while the next most weakly bound electron corresponds to the highest occupied molecular orbital of the neutral cluster. The spacing between the two most weakly bound peaks is thus the HOMO-LUMO gap. In a bulk metal, the Fermi level falls in the middle of an electronic band so that the HOMO-LUMO gap is zero.

From the photoelectron spectra in Figs. 1 and 2, we obtain the HOMO-LUMO energy gap in the neutral $(NaCl)_3Na_m$ and $(KI)_3K_m$ clusters. The HOMO-LUMO gaps in these clusters are plotted in Fig. 3 as functions of the cluster size, together with the gaps in pure neutral Na_m and K_m clusters, derived from the spectra recorded by Bowen and co-workers [18]. The HOMO-LUMO gap in $(NaCl)_3Na_4$ was obtained from the photoelectron spectrum with 2.336 eV detachment photon energy [16]. The 1.7 eV HOMO-LUMO gap in $(KI)_3K^-$ was estimated from Ref. [19].

In all four cases, the HOMO-LUMO gap decreases rapidly as the metal atom component of the cluster becomes larger. The gaps in the Na_m and $(NaCl)_3Na_m$ clusters are almost identical while those in the K_m and $(KI)_3K_m$ are only slightly different. This tendency for the HOMO-LUMO gap to decrease as a metal cluster increases in size has also been seen and predicted in many metals [20,21].

More evidence that our clusters are phase separated comes from the measured electron vertical binding energies of clusters $(NaCl)_3Na_m^-$ $(m \geq 2)$. Metal clusters with delocalized electrons tend to have an even-odd alternation in their electron affinities. Since only two electrons can occupy each delocalized energy level, a cluster with an odd number of electrons must have one unpaired and relatively weakly bound electron. Recently, Landman and co-workers predicted such an even-odd alternation in the metallization sequence of Na_4F_m clusters $(0 \leq m \leq 4)$ [5].

In the cluster anions discussed in this paper, those with an odd number of atoms in the alkali metal part actually have an even number of delocalized electrons. There is one electron for each alkali metal atom and one extra electron that gives the cluster its negative charge. Figure 4 shows our measured values for metal-rich alkali-halide cluster electron vertical binding energies and those of Bowen *et al.* for pure alkali metal clusters [18]. The even-odd alternation is unmistakable, demonstrating the presence of electron pairing effects [6,22].

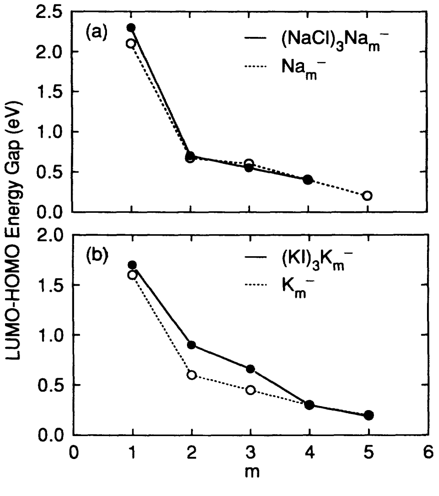

FIG. 3. HOMO-LUMO gap in neutral clusters obtained from the splittings between the two most weakly bound electrons, as observed by photodetachment of the cluster anions. Results for $(NaCl)_3Na_m^-$ $(m = 0\text{–}4)$ and $(KI)_3K_m^-$ $(m = 0\text{–}5)$ are the present work. Results for Na_m^- and K_m^- are from Ref. [20].

There are differences between the electron vertical binding energies in the metal-rich alkali-halide clusters and those in the pure alkali clusters. However, these differences can be explained almost entirely by the presence of a nearby dielectric in the metal-rich alkali-halide clusters. If our clusters are phase separated, then a tiny metal component sits atop a tiny dielectric component and localized electrons in the cluster's metal component polarize the dielectric component. As a result, the delocalized electrons become more tightly bound to the cluster. This polarization effect becomes less important as the metal component becomes larger. This behavior is clearly seen in the NaCl clusters [Fig. 4(a)] but is weaker in KI clusters [Fig. 4(b)].

The phase separation that appears to exist in these metal-rich alkali-halide clusters resembles a similar phase separation in the bulk. Alkali metals and alkali-halide salts generally do not wet one another. Furthermore, molten mixtures of alkali metals and alkali-halide salts are generally characterized by miscibility gaps. Although such mixtures can form homogeneous solutions at relatively high temperatures, the solutions tend to separate into a metallic phase and a nonmetallic phase as the metal concentration increases [15]. A possible physical mechanism driving such phase separations is Coulomb repulsion between the delocalized electrons and negative ions.

Although this paper focuses principally on

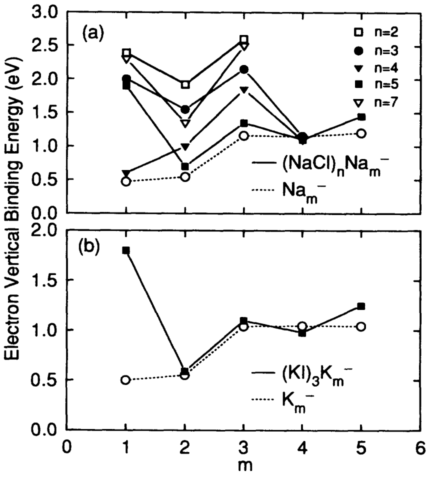

FIG. 4. Electron vertical binding energies of (a) $(NaCl)_nNa_m^-$ $(n = 2,3,4,5,7; m = 0\text{–}5)$ and (b) $(KI)_3K_m^-$ $(m = 0\text{–}5)$ cluster anions. Electron vertical binding energies for Na_m^- and K_m^- are from Ref. [20].

$(NaCl)_3Na_m^-$ and $(KI)_3K_m^-$ clusters, we have also studied the metal-rich alkali-halide cluster sequences $(NaCl)_2Na_m^-$ (m = 0–3), $(NaCl)_4Na_m^-$ (m = 0–4), $(NaCl)_5Na_m^-$ (m = 0–4), and $(NaCl)_7Na_m^-$ (m = 0–3) [16]. The electron vertical binding energies of the clusters also exhibit an alternation between the even and odd numbers of valence electrons [Fig. 4(a)]. However, their complete photoelectron spectra do not bear the same striking similarities to the pure Na_m^- spectra that we see when studying $(NaCl)_3Na_m^-$ clusters.

We attribute the high degree of similarity between the spectra of Na_m^- and $(NaCl)_3Na_m^-$ clusters to the inertness of the $(NaCl)_3$ cluster. $(NaCl)_3$ is a stable hexagonal ring and is very tightly bound [23]. It should offer a relatively large and smooth substrate on which to build an alkali metal component. In $(NaCl)_3Na_m^-$, the additional sodium atoms and the extra electron probably rest on the surface of this ring and form a fairly independent sodium cluster anion component. This metal component exhibits a photoelectron spectrum that is merely shifted from that of a truly independent sodium cluster anion. The same near independence should exist for the $(KI)_3$ and K_m^- components of $(KI)_3K_m^-$ clusters.

Since the photoelectron spectra of the other $(NaCl)_nNa_m^-$ clusters are less similar to those of Na_m^- clusters, these metal-rich alkali-halide clusters are either not phase separated or their phase separated components are distorted. Because these clusters still exhibit the even-odd alternation in electron vertical binding energy, we believe that the latter explanation is true. The interactions between the separate metal anion and nonmetal components probably deform each so that the photoelectron spectrum of the metal anion component is not identical to that of a free metal anion. The clusters $(NaCl)_2$ and $(NaCl)_4$, although stable, offer very tiny surfaces on which to build the metal anion component [23]. The clusters $(NaCl)_5$ and $(NaCl)_7$ are relatively unstable and deform in the presence of the metal anion component [23].

In summary, we have studied the photoelectron spectra of $(NaCl)_3Na_m^-$, and $(KI)_3K_m^-$ clusters, using a magnetic-bottle time-of-flight photoelectron spectrometer. The photoelectron spectra of these clusters exhibit features strikingly similar to those seen in spectra of pure alkali metal anions. They also exhibit a HOMO-LUMO gap that decreases as the number of metal atoms increases and an even-odd alternation in the electron vertical binding energies with the number of metal atoms. From the observed metal-like features, we suspect that the clusters are composed of metallic and ionic parts, weakly attached to one another. This situation is analogous to the metal and nonmetal phase separation in metal-rich alkali-halide melts. Unfortunately, this phase separation diminishes our hopes of observing a true metal-nonmetal transition in metal-rich alkali-halide clusters as a function of composition. However, studies of other metal-rich alkali-halide clusters are in progress.

The authors thank A.J. Cox and D.J. Fatemi for technical support. Acknowledgement is made to the Donors of The Petrolum Research Fund, administered by the American Chemical Society, for the support of this research.

---

[1] K. I. Peterson, P. D. Dao, and A. W. Castleman, J. Chem. Phys. **79**, 777 (1983).

[2] T. Bergmann, H. Limberger, and T. P. Matin, Phys. Rev. Lett. **60**, 1767 (1988).

[3] S. Pollack, C. R. C. Wang, and M. M. Kappes, Z. Phys. **12**, 241 (1989).

[4] H. Gohlich, T. Lange, T. Bergmann, and T. P. Martin, Phys. Rev. Lett. **65**, 748 (1990).

[5] G. Rajagopal, R. N. Barnett, and U. Landman, Phys. Rev. Lett. **67**, 727 (1991).

[6] Atsushi Nakajima, Tsuneyoshi Sugioka, Kunniyoshi Hoshino, and Koji Kaya, Chem. Phys. Lett. **189**, 455 (1992).

[7] W. D. Knight, Keith Clemenger, Walt A. de Heer, Winston A. Saunders, M. Y. Chou, and Marvin L. Cohen, Phys. Rev. Lett. **52**, 2141 (1984).

[8] M. Kappes, M. Schar, P. Radi, and E. Schumacher, J. Chem. Phys. **84**, 1863 (1986).

[9] T. P. Martin, Phys. Rep. **95**, 176 1983.

[10] C. Honea, M. L. Homer, P. Labastie, and R. L. Whetten, Phys. Rev. Lett. **63**, 394 (1989).

[11] G. Ragagopal, R. N. Barnett, A. Nitzan, U. Landman, E. Honea, P. Labastie, M. L. Homer, and R. L. Whetten, Phys. Rev. Lett. **64**, 2933 (1990).

[12] Y. J. Twu, C. W. S. Conover, Y. A. Yang, and L. A. Bloomfield, Phys. Rev. B **42**, 5306 (1990).

[13] B. Vezin, Ph. Dugourd, D. Rayane, R. Labastie, C. Bordas, and M. Broyer, Z. Phys. D **26**, 290 (1993).

[14] B. Vezin, Ph. Dugourd, D. Rayane, P. Labastie, J. Chevaleyre, and M. Broyer, Chem. Phys. Lett. **206**, 521 (1993).

[15] W. W. Warren, Jr., in *Metallic and Nonmetallic States of Matter*, edited by P. P. Edwards and C. N. R. Rao (Taylor & Francis, London, 1985).

[16] P. Xia and L. A. Bloomfield (unpublished).

[17] *Handbook of Chemistry and Physics*, edited by Robert C. Weast *et al.* (CRC Press Inc., London, 1987).

[18] K. M. McHugh, J. G. Eaton, G. H. Lee, H. W. Sarkas, L. H. Kidder, J. T. Snodgrass, M. R. Manea, and K. H. Bowen, J. Chem. Phys. **91**, 3792 (1989).

[19] Y. A. Yang, L. A. Bloomfield, C. Jin, L. S. Wang, and R. E. Smalley, J. Chem. Phys. **96**, 2453 (1992).

[20] D. G. Leopold, J. Ho, and W. C. Lineberger, J. Chem. Phys. **86**, 1715 (1987).

[21] Vlasta Bonacic-Koutecky, Piercarlo Fantucci, and Jaroslav Koutecky, J. Chem. Phys. **93**, 3802 (1990).

[22] D. R. Snider and R. S. Sorbello, Surf. Sci. **143**, 204 (1984).

[23] N.G. Phillips, C.W.S. Conover, and L.A. Bloomfield, J. Chem. Phys. **94**, 4980 (1991).