Acc. Chem. Res. 1993, 26, 49–56

Alkali Halide Nanocrystals

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Received June 5, 1992

1. Introduction

Consider the cubic salt compound, with the chemical formula $Na_{14}Cl_{13}$, shown in Figure 1a. It presents a classic picture of ionic bonding, closely resembling textbook illustrations of the NaCl (rock salt) lattice structure. The small spheres represent Na^+ ions, and large spheres denote halide ions, Cl^-. The structure places three ions along each edge, and so consists of $3^3 = 27$ ions in total, $Na_{14}Cl_{13}^+$. These are arranged so that a Cl^- ion occupies the single interior site of the cubic lattice and each of the 12 edge sites. The Na^+ ions occupy the six face and eight vertex sites. Figure 1b shows its "negative", $Na_{13}Cl_{14}^-$, in which the anions and cations exchange sites. The overall dimension of these structures, specified by the length along an edge, is just under 1 nm; its diameter is $\approx$1.5 nm along the body diagonal.

Although the structures shown are based on computations, these compounds do exist,[1] and the recent elucidation of some of their important and remarkable properties is the subject of this Account. Because they are individual members of an infinite series of conceivable compounds [e.g., $(NaCl)_n$, $n = 1, 2, 3, \ldots$], they are often called *clusters*: specifically, alkali halide clusters. But if a cluster is sufficiently large that it adopts the essential structural aspects of the crystalline solid, as in Figure 1, then it is described more specifically as a nanometer-scale crystal, or *nanocrystal*.

In the past decade, the properties of nanocrystals have attracted steadily growing interest from chemists, physicists, and other materials scientists and engineers. They are simultaneously regarded as fundamental objects connecting the molecular and solid-state worlds and as a frontier area for applications. To recite three popular perspectives: First, nanocrystal structures represent the ultimate in miniaturization of solid-state materials and devices.[2] Second, many nanocrystal properties are dominated by their surfaces, because a large fraction of the atoms lie in the outermost layer. Third, the finite size and number of atoms in a nanocrystal, often $<10^3$, means that systems having the structures of bulk crystalline matter can be explored with a precision ordinarily reserved for atoms and molecules, using modern methods as described below.

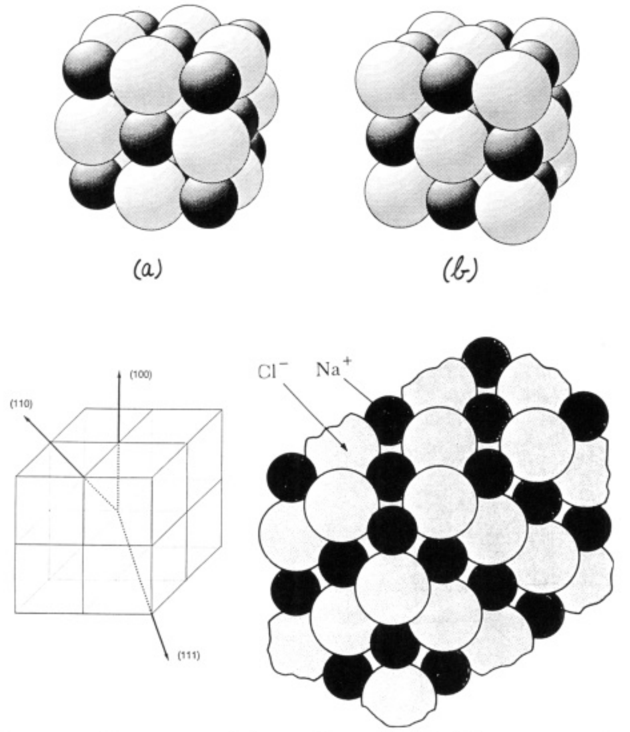

Figure 1. Structures of the smallest alkali halide nanocrystals, with 27 lattice sites (3 × 3 × 3). Dark spheres represent alkali ions M^+ (Na^+); light spheres represent the larger halide ions X^- (Cl^-). The nearest-neighbor distance is about 90% of the bulk lattice constant, $a = 2.79$ Å. (a) The $[M_{14}X_{13}]^+$ cubic nanocrystal composed of 14 M^+ ions and 13 X^- ions. As compared to the ideal cubic lattice, the surface is buckled in such a way that halide ions protrude out and the smaller alkali ions are recessed. (b) The $[M_{13}X_{14}]^-$ negative analog of structure a, with 13 M^+ ions and 14 X^- ions. Inset: The perfect rock salt lattice of "sodium chloride structure" and the corresponding low-index surfaces of alkali halide crystals, indicated by vectors and Miller indices.

This Account relates a few recent findings on alkali halide nanocrystals, including results on processes represented generically by the equations collected in Table I. Experiments on single nanocrystals now often extend into the thousands of atoms, with diameters of from 1 up to 5 or 10 nm, but here the focus, for simplicity, is on the smallest, like those shown in Figure 1. Alkali halides are not the only interesting nanometer structures—consider the astonishing range of carbon and silicon clusters[3]—but they are unique in providing fascinating insights into ionic-bonding structures. Some of these principles are also followed by more complex and valuable compounds, including certain IB–VII (photography), IIB–VI (photodetectors), and III–V (microelectronics, electrooptics) compounds,

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(1) For an excellent review of early work, see: Martin, T. P. *Phys. Rep.* **1983**, *95*, 167.

(2) For recent nonspecialized discussions, see: Ball, P.; Garwin, L. *Nature* **1992**, *355*, 761; *Science* **1991**, *254*, 1300–1311.

(3) Silicon: Jarrold, M. J. *Science* **1991**, *252*, 1085. Carbon: *Acc. Chem. Res.* **1992**, *25* (3).

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Table I. Generic Reactions of Alkali Halide Nanocrystals

1	adsorption	$M_nX_{n-1}^+ + NH_3 \rightleftharpoons M_nX_{n-1}^+\cdot NH_3$
2	halogen ejection	$M_{n\pm1}X_n^\pm + h\nu \rightarrow M_{n\pm1}X_{n-1}^\pm + X^0$
3	surface-fluoride transfer	$M_{n+1}F_n^+ + Si(s) \rightarrow M_{n+1}F_{n-1}^{2+} + Si(s)\text{–}F^-$
4	coulomb fission	$M_{n+1}X_{n-1}^{2+} \rightarrow M_nX_{n-1}^+ + M^+$
5	photoionization	$M_n^+X_{n-1}^-\cdot e^- \xrightarrow{h\nu} M_n^+X_{n-1}^- + e^-$
6	demetalization	$\xrightarrow{\Delta} (MX)_{n-1} + M^0$
7	evaporation	$(MX)_n \xrightarrow{\Delta} (MX)_{n-1} + MX \rightarrow (MX)_{n-2} + 2MX$
8	cleavage	$(MX)_n\ (n = jkl) \xrightarrow{\text{impact}} (MX)_m\ (m = j'k'l') + (MX)_p\ (p = j''k''l'')$

where the understanding of the nanocrystalline state is not yet so far advanced.

2. Ionic Bonding and Nanocrystal Structures, Formation, and Occurrence

The cohesion of alkali halide nanocrystals is provided by ionic bonding. Consequently, the energetic principles underlying their structures and dynamics are rather simple to express in terms of interactions between spherical ions. A quantitative description, which captures overwhelmingly the main contributions, includes a sum of coulomb attractions and repulsions (unlike and like charges) between all pairs of ions, along with short-range repulsions preventing overlap of the atomic cores.[4] Mathematically, and for computations, this is expressed through an interatomic potential, $\pm 1/R + A_\pm \exp(-R/\rho_\pm)$, where R is the distance between two ions, $\rho_\pm$ is related to the sum of their ionic radii, and A is an empirical constant. If the ions are fixed at cubic lattice sites, which is sometimes a good starting point, then the sum over the coulomb interactions takes the familiar form of a (finite) Madelung series. The relaxed structures of the nanocrystals are very stable; their cohesive energy per atom quickly approaches a large fraction of the energy of the perfect (infinite) crystalline solid.

The large cohesive energies can account for the abundance of alkali halide clusters in alkali halide vapors: small clusters, to $n = 3$ or higher, have long been detected along with diatomics in the equilibrium vapor of the molten salt.[5] Furthermore, nanocrystals of NaCl or NaBr are important in natural settings including marine atmospheric regions, where they crystallize from salt-water droplets that are swept up from ocean waves and dried. Their reactions with nitroxide pollutants provide one source of chlorine and bromine atoms for catalytic ozone depletion.[6] Aerosols composed almost entirely of alkali halide nanocrystals are also readily generated in cloud-chamber devices.[7]

The dominance of ionic bonding has important consequences for the structures of alkali halide nanocrystals. They are highly ordered, even at small sizes, in contrast to covalently bonded clusters, to metallic clusters, or to clusters held together by weak dispersion interactions. In 1981, researchers at the Naval Research Lab discovered that the most abundant (highly stable) of the alkali halide nanocrystals detected in a mass spectrometer are those with precisely the correct number of ions to fill the cubic lattice sites in a structure of cuboidal morphology.[8] These *perfect nanocrystals* minimize their surface energy by exposing (100) faces only, as in Figure 1 (inset). This criterion can be satisfied whenever the total number of ions, m, is a product of three integers, $m = jkl$, designating the number of ions along an edge. If m is even, then neutral clusters $(NaCl)_n$, where $n = m/2$, may satisfy this relation. If m is odd, as when (j,k,l) are *all* odd, then ionized clusters of the form $[Na_{n+1}Cl_n]^+$ or $[Na_{n-1}Cl_n]^-$ are appropriate (generally: $[Na_{n\pm1}Cl_n]^\pm$); these include the structures depicted in Figure 1, where $(j,k,l) = (3,3,3)$. Large clusters that do *not* have the requisite number of ions to satisfy this relation tend to form closely related structures in which the excess ions form *terraces* on the faces of the stable clusters.[9] An interesting consequence of the energetics of these structures is that newly formed hot clusters tend to cool by evaporating diatomic molecules [NaCl], until only perfect nanocrystals remain![10] Some other consequences of rigid ionic lattices are described below.

Ionic bonding in alkali halide nanocrystals also has subtle consequences connected with electron counting and charge. The chemical form $M_nX_m^{(n-m)} = (M^+)_n(X^-)_m$ implies a net charge $(n - m)$.[11] But the excess charge is not to be found in the structures, as charge in ionic compounds is well localized on individual atoms. Accordingly, charged alkali halides with $n - m = \pm 1$ ("singly charged") are not comparable to ordinary molecular cations or anions, which are much more reactive (better electron acceptors/donors) than the related neutral molecules. Instead, these entities are uniquely self-sufficient with regard to electrons (charge), implying that they are poor donors/acceptors and chemically inert. The evidence for this comes from separate experiments, described below, on neutral, negatively charged, positively charged, and doubly positively charged nanocrystals.

To study nanocrystals individually and in detail, special techniques are employed for their formation, separation, and detection. An approach that has proved very valuable encompasses the cluster-beam methods that incorporate pulsed lasers and mass spectrometers. In these experiments, nanocrystals are formed and annealed by vaporizing a portion of a solid salt, using an ultraviolet laser pulse focused onto the solid, under a dense flowing gas, typically helium or argon. The flowing gas facilitates the growth of the nanocrystals, both charged and neutral, and directs them into various sensitive measuring devices, including flow reactors for chemical kinetics and equilibrium studies, mass spectrometers for mass selection, and laser spectrometers for photochemistry and related measurements. No knowledge of these specialized methods is assumed in the following.[12]

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(4) Fumi, F. G.; Tosi, M. P. *J. Phys. Chem. Solids* **1964**, *25*, 31, 45.

(5) Davidovits, P., McFadden, D. L., Eds.; *Alkali Halide Vapors*; Academic Press: New York, 1979.

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(7) Armbruster, L., Technical report on "Kondensation-Aerosolgenerator".

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(9) Twu, Y. J.; Conover, C. W. S.; Yang, Y. A.; Bloomfield, L. A. *Phys. Rev.* **1988**, *B42*, 5306.

(10) Guang, S.; McIver, R. *Anal. Chem.* **1990**, *62*, 878.

(11) The normal or neutral state is $n - m = 0$, but writing the corresponding clusters as $(MX)_n$ should not be taken to imply that they are composed of diatomics, as would, e.g., $(HCl)_n$.

(12) Zheng, L. S.; Brucat, P. J.; Pettiette, C. L.; Yang, S.; Smalley, R. E. *J. Chem. Phys.* **1985**, *83*, 4273. Honea, E. C.; Homer, M. L.; Whetten, R. L. *Int. J. Mass Spectrom. Ion Processes* **1990**, *102*, 213.

3. Cleaving and Melting by Impact

A remarkable consequence of the structural rigidity of single alkali halide nanocrystals is the cleavage process discovered by Beck et al.[13] They used beams of various alkali halide clusters, charged either positively or negatively and accelerated to a desired energy in vacuum, and found that the collision of a perfect nanocrystal against a solid surface "wall" shatters it into two pieces which are themselves perfect nanocrystals (Table I, line 8). When the nanocrystal is sufficiently large, e.g., the $Na_{38}F_{37}^+$ (3,5,5) cluster, such that several cleavage channels are possible, then each is observed. Microscopically, the impact evidently stresses the tiny crystal so that it cleaves along the favorable cleavage planes, much as a brittle crystal shatters upon impact to give fragments that have crystalline facets. (A shear stress is particularly effective, because a "slip" of only half the lattice constant will negate the attraction between the fragments.) In the experiments, cleaving occurs much more readily on stiff materials, such as the diamond-hard surfaces of silicon, than on highly elastic materials like the mattress-soft surface of oriented graphite. One example of this process is shown in Figure 2, by experimental traces of scattered fragment mass spectra. The nanocrystal–solid impact event is illustrated by high-level computer simulations of Landman and co-workers.[15]

Cleaving or other fission-type processes only occur beyond a certain cluster size, corresponding to the onset of three-dimensional nanocrystal structures, i.e., the (3,3,3) structures of Figure 1. Impact or other heating of smaller clusters generates the loss of a series of diatomics or small fragments. Beyond the onset size, it is the imperfect nanocrystals that are easiest to fragment, through shearing off a terrace.[14]

When a nanocrystal is heated, e.g., by absorption of a sufficiently large energy, it melts and thereby becomes a finite molten salt (Figure 2 inset). A severe shock that transfers sufficient energy to melt leads *not* to cleavage but rather to a cascade of "evaporation" events in which individual NaCl units are lost. This is expressed in Table I, line 7. This transformation occurs at a temperature somewhat lower than the melting point of the macroscopic material.[16]

4. Reactions of Alkali Halide Nanocrystals with Molecules and Surfaces

A. Adsorption of Polar Molecules on Nanocrystals. The chemical inertness of alkali halide nanocrystals, based on their composition of closed-shell atomic ions, contrasts sharply to the reactivity of metal or semiconductor clusters which have unsaturated, or "dangling", bonds at their surfaces. Of course, alkali halide surfaces are reactive toward their own vapor, i.e., they *grow* readily if unprotected, in contrast to the case of the separable fullerene molecules like C_{60} and C_{70}, which were also originally discovered in cluster beams.[3]

An important elementary chemical process that alkali halide nanocrystals do undergo at moderate temperatures is *adsorption* of polar molecules like NH_3 or H_2O, process 1 in Table I. This process has been studied by Homer et al.[17] using a flow reactor, where reactants and nanocrystals are diluted in flowing helium. At ambient temperature, the n-dependence of the adsorption reactivity, k_n, corresponding to the chemical process $Na_{n+1}F_n^+ + NH_3 \rightarrow [Na_{n+1}F_n]^+\cdot NH_3$, is very strong, Figure 3. The perfect nanocrystals, (3,3,3) and (3,3,5) and higher, are nonadsorptive under these conditions, reflecting their ideal, defect-free surface structure. The others show some tendency to adsorb ammonia. The same pattern is observed for KF and NaCl clusters also. Particularly reactive are those nanocrystals that are related to the perfect ones by the loss of a single NaF unit. The two smallest of these have the optimized structures illustrated in Figure 3, with a basket-like defect large enough for the polar molecule to substitute structurally for the missing diatomic. The nanocrystal structure should not be much altered by the adsorption, given weak interaction between nanocrystal and adsorbed molecule. At lower temperatures all alkali halide clusters, including the perfect nanocrystals, adsorb polar molecules, with little variation with cluster size. This is consistent with a reaction limited only by the frequency of reactant–nanocrystal encounters.

B. Reactivity of Alkali Fluorides toward Silicon Surfaces. Aside from molecular adsorption, alkali halide nanocrystals are probably inert in most chemical environments, although they would dissolve into solvated ions in a great excess of water. The alkali *fluorides* are exceptional: their bulk solids are *not* very hydroscopic. However, fluorine atoms are special in that they can also form very strong bonds with a number of elements (H, C, S, Si), particularly silicon.

A remarkable example of the selective reactivity of alkali fluoride nanocrystals is provided by their halide-transfer reactions in single low-energy collisions with solid surfaces, as found by St. John et al.[18] Nanocrystal–surface reactions occur only when the surface is silicon and the nanocrystal is a fluoride (NaF or KF). In this case, the cluster–surface encounter causes a single F^- ion to be transferred from the nanocrystal, process 3 in Table I. This process occurs with very high probability even at impact velocities below 2 km/s, where the F atom's speed equals its mean speed at 600 K. It occurs in up to half the collision events for larger nanocrystals like $Na_{53}F_{52}^+$, the (3,5,7) perfect nanocrystal, Figure 4, colliding with the Si(111) surface. However, when the surface is passivated with hydrogen, so that all the surface Si atoms are tetravalent, there is no reaction, only cleavage. The reaction's high efficiency at low impact speed indicates that the driving force is formation of a Si–F bond that is as strong as the Na^+–F^- bond. The reaction probability increases very strongly with size, indicating that the impact dynamics involve a collective motion of all the atoms in the nanocrystal, as they "pile up" behind the impact front.

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[13] Beck, R. D.; St. John, P. M.; Homer, M. L.; Whetten, R. L. *Science* 1991, *253*, 879; *Mater. Res. Soc. Symp. Proc.* 1991, *206*, 351–360.

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[15] Kaukonen, H.-P.; Landman, U. Unpublished.

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[17] Homer, M. L.; Livingston, F.; Whetten, R. L. *J. Am. Chem. Soc.* 1992, *114*, 6558; *Z. Phys. D.*, in press.

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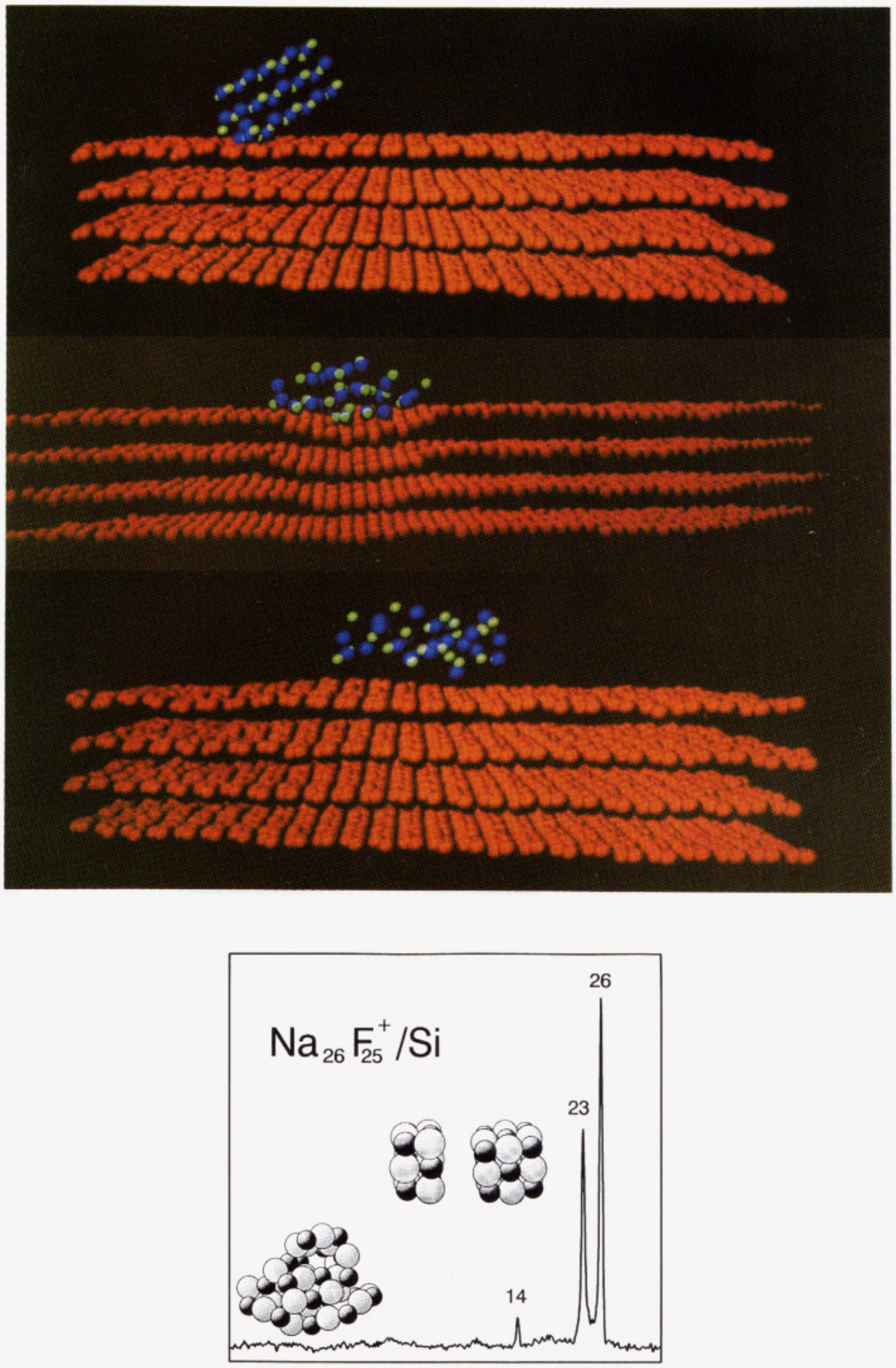

Figure 2. Bottom: Processes induced in alkali halide nanocrystals by impact against a solid surface,[10] including a time-of-flight mass spectrum showing how $Na_{26}F_{25}^+$ splits after impact against silicon. The structures illustrate the cleaving and melting of the (3,3,5) nanocrystal. Top: Snapshot from the computer simulation of a molten-salt cluster $Na_{25}F_{24}^+$ formed by energetic impact on graphite; from ref 15, with permission.

5. Substitution of "Excess" Electrons for Halide Ions

A. Excess Electrons and Surface Color–Center Spectroscopy. The ionic nature of alkali halide nanocrystals makes possible another type of substitution, involving an "excess" electron. In 1985, Landman et al.[19] predicted that an electron can play the role of a "missing" halide ion in an alkali halide cluster. Figures 5, 7, and 8 show such structures, including the (3,3,3) nanocrystal $Na_{14}F_{12}^+ = (Na^+)_{14}(F^-)_{12}\cdot e^-$ (Figure 8). [Its negative analog is $(NaF)_{13}^-$.] Such clusters can be generated by ultraviolet irradiation of alkali halide nanocrystals (section 6) or by condensation in excess metal vapor at low temperatures. The electron, represented by a probability distribution (dot cloud), spreads over the site where an F^- ion would normally

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[19] Landman, U.; Scharf, D.; Jortner, J. *Phys. Rev. Lett.* **1985**, *54*, 1860.

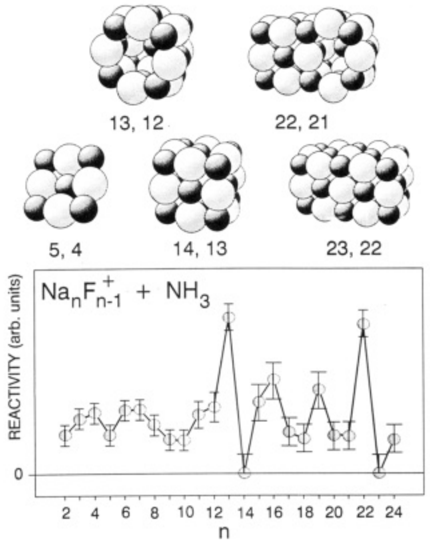

Figure 3. Relative reactivity of sodium fluoride clusters toward adsorption of NH_3, with the most (above) and least (below) reactive structures shown.[13]

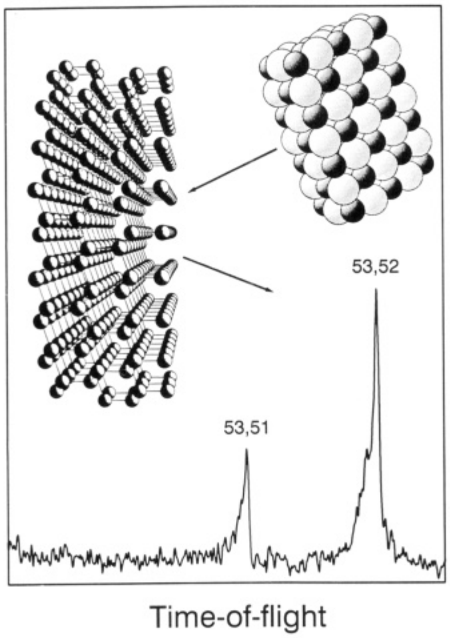

Figure 4. Reactive transfer of an F^- ion during collision of a sodium fluoride cluster with the diamond-like structure of Si(111).[14] The time-of-flight mass spectrum shows the partial conversion of $[Na_{53}F_{52}]^+$ (structure shown above) to the doubly charged $[Na_{53}F_{51}]^{2+}$ cluster at an impact energy of 30 eV, or 0.28 eV per atom.

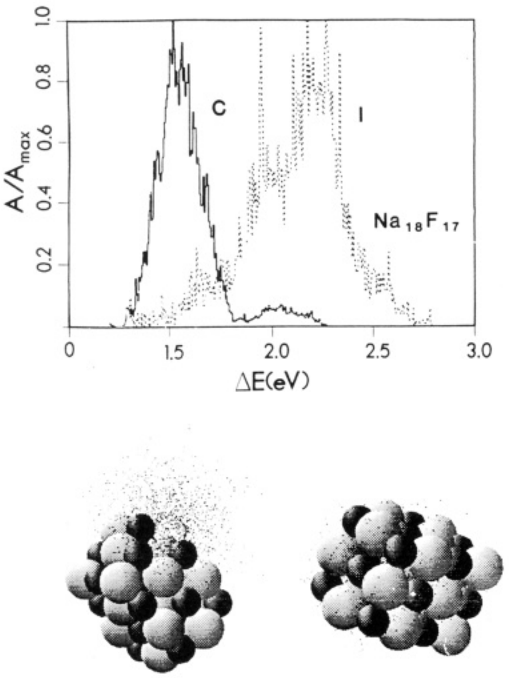

Figure 5. Optical absorption bands computed for two isomeric forms of the (4,3,3) solvated-electron cluster $M_{18}X_{17}$. There are 18 M^+ ions, 17 X^- ions, and an excess electron cloud in either an internal site (I) or the more favorable corner site (C).[18] The observed spectrum shows the very strong near-infrared band, in agreement with the corner site.[18,19]

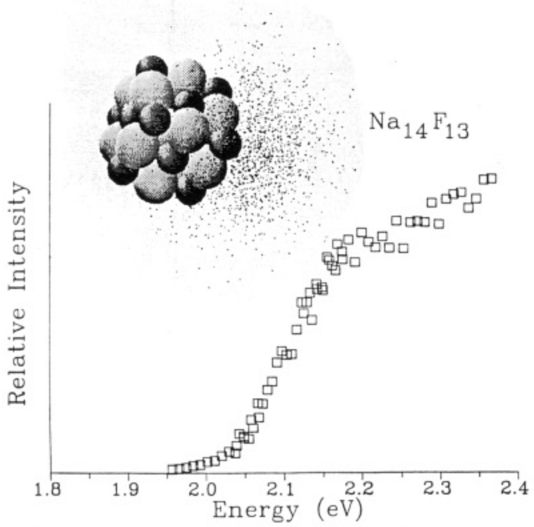

Figure 6. The photoionization threshold (photoelectric effect) for $Na_{14}F_{13}$, showing a threshold near 1.9 eV.[21] The structure is computed $M_{14}X_{13}$, composed of 14 M^+ ions, 13 X^- ions, and an excess electron in a diffuse surface state.[19]

reside (cf. Figure 1a) and contributes to the electrostatic energy of the nanocrystal in much the same way as a halide ion would. But it is not quite as stable, because of the large (positive) zero-point energy associated with *localization* of a light quantum particle.[20] This is manifested in an energy to eject the electron (ionization potential or electron affinity; Table I, line 5) that is about 2 eV lower than the energy required to remove a halide ion from the analogous alkali halide nanocrystal. The experiments of Honea et al.[21] on the neutral excess-electron series like $(Na^+)_n(F^-)_{n-1}{\cdot}e^-$ indeed found such very low values, near 3 eV. The more recent measurements of Li et al.[22] on charged CsI and KBr clusters showed that the ionization potentials of the small nanocrystals $(Cs^+)_{14}(I^-)_{12}{\cdot}e^-$ and $(Cs^+)_{13}(I^-)_{11}{\cdot}e^-$ are near or below 5 eV, which would be the lowest reported values for creating a small, *doubly* charged compound. Another view of these values is that they reflect the stability of the fully ionic clusters, which have no need for the neutralizing electron.

A second, related consequence of electron substitution is the creation of a low-energy dissociation path, namely, the loss of a neutral metal atom, or "demetalization" (Table I, line 6). To visualize this, imagine that at high

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(20) Barnett, R. N.; Landman, U.; Scharf, D.; Jortner, J. *Acc. Chem. Res.* **1989**, *22*, 350.

(21) Honea, E. C.; Homer, M. L.; Labastie, P.; Whetten, R. L. *Phys. Rev. Lett.* **1989**, *63*, 394. Honea, E. C. Ph.D. Thesis, UCLA, 1990.

(22) Li, X.; Whetten, R. L. *Chem. Phys. Lett.* **1992**, *196*, 535.

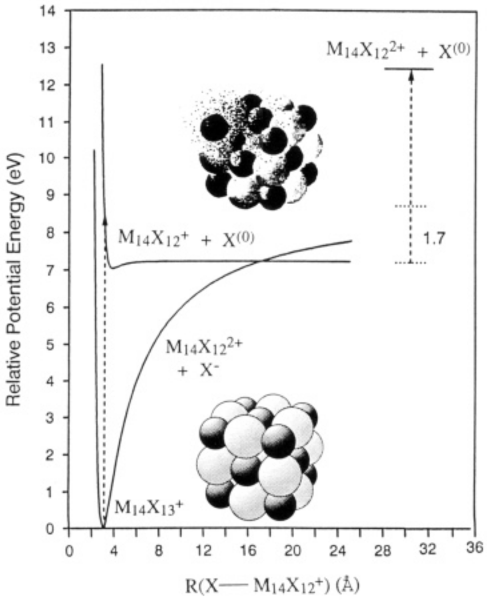

Figure 7. Potential-energy curves for the excitation (vertical arrow) and photoejection of a neutral halogen atom from the (3,3,3) nanocrystal, to leave behind the solvated-electron state.[22,24]

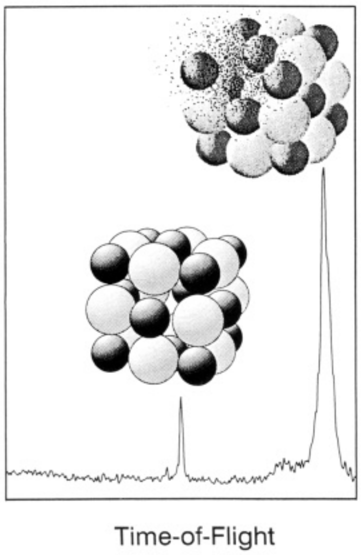

Figure 8. Generation of doubly charged nanocrystal, $[Cs_{14}I_{12}]^{2+}$, by absorption of an ultraviolet photon ($h\nu = 6.4$ eV).[25] The time-of-flight mass spectrum shows the partial conversion of the solvated-electron cluster at right to the doubly charged cluster, $[M_{14}X_{12}]^{2+}$, a (3,3,3) nanocrystal "cage" with 14 M^+ ions and 12 X^- ions.

temperature the electron wanders onto a metal ion, M^+, momentarily neutralizing it, and thereby negating its source of strong interaction with the remaining cluster.[19] This process was confirmed experimentally by Beck et al.,[23] who used low-energy cluster–surface collisions of the $Na_{14}F_{12}^+$ cluster (Figure 7 structure) to generate exclusively $Na_{13}F_{12}^+ + Na^0$.

A third consequence of this kind of electron substitution and localization is the introduction of *color* into alkali halide nanocrystals, which otherwise are transparent in the visible region. Looking again at the quasi-spherical electron cloud in Figure 5, resembling an atomic S orbital, it is easy to imagine the strong transitions to P-type orbitals at energies of only 1.2–2.0 eV (the red and near-infrared regions of the spectrum), as found by Rajagopal et al.[24] Just such optical absorption bands are found in the predicted regions, as described by Honea et al.[25]

B. The Surface-Electron State. What if there is no lattice site available for electron substitution, as in the case of a perfect, charged nanocrystal like the one depicted in Figure 1? The electron cannot displace a halide ion from its lattice site. Instead it resides in a weakly bound surface state, because of the zero-point energy associated with confinement.[19,20] Such states and the slight symmetry-breaking that drives their localization are of great interest in surface physics. From accurate microscopic calculations, Rajagopal et al.[24] predicted that the addition of an electron to the (3,3,3) perfect nanocrystal $Na_{14}F_{13}^+$ results in a slight distortion of the structure accompanied by localization of the electron in a cloud like that shown in Figure 6. The resulting structure is an overall neutral nanocrystal, $Na_{14}F_{13} = (Na^+)_{14}(F^-)_{13}{\cdot}e^-$, and is predicted to have an ionization potential of only 2.0 eV. The experiment[24,25] (Figure 6) gives a photoionization threshold at 1.89 eV, which appears to be *the lowest ionization potential ever measured*! For the next higher perfect nanocrystal (3,3,5), the value is slightly lower, at 1.80 eV. The values suggest that these neutral nanocrystals would be extremely good electron donors in liquid or solid solutions, and so would exist preferentially in the charged (oxidized) state.

The extraordinarily low energies required to remove excess electrons from alkali halide nanocrystals should not be confused with the energy required to eject the tightly bound electrons in the halide ions. For example, the electron affinity of clusters like $K_{13}Br_{14}^-$ (cf. Figure 1b) are greater than 5 eV,[26] placing them among the very highest reported electron affinities.

6. Electronic Excitations, Photochemistry, and Charging

A. Excitations and Spectroscopy in the Ultraviolet Region. To this point, the alkali halide nanocrystals have been described as being composed of alkali ions (M^+), halide ions (X^-), and (sometimes) excess electrons, e^-. However, the valence electrons (p^6) in the halide ions are not so strongly bound and can be excited by ultraviolet radiation.[27] In the case of the heavier halides (bromides and iodides), the minimum photon energy required to excite the electron lies in the normal ultraviolet region of the spectrum, and the excited electron is transferred from the halide ion only to the nearest alkali ions, so that both the halide and alkali ions are neutralized, $M^+X^- \rightarrow M^0X^0$. These charge-transfer transitions—the reverse of ionic bond formation from neutral alkali and halogen atoms—give rise to very strong (bright) absorption bands that are well-known for diatomic molecules and for macroscopic crystals.

The electronic absorption bands and photochemistry of alkali halide nanocrystals, particularly KBr and CsI,

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have been explored by tunable-laser excitation of a mass-selected beam of ionized clusters.[26,28] Li et al.[28] found that the bands lie at much higher energy than the diatomic, reflecting the increasing expense of neutralization with increased coordination, yet still below the bulk, emphasizing the role of excitations in the outermost layer, where the coordination is incomplete.[29] For example, the CsI diatomic has its charge-transfer band maximum at 3.8 eV, the bulk crystal has its first absorption maximum at 5.7 eV, and the (3,3,3) nanocrystal $Cs_{14}I_{13}^+$ (Figure 1a structure) has an absorption onset at 5.2 eV and first maximum near 5.5 eV. The theoretical picture of the nanocrystal is that an electron from an edge I^- ion is transferred to a neighboring vertex Cs^+ ion. Generally, the nanocrystals with the highest threshold energy for electronic excitation are the perfect nanocrystals: (3,3,3) positive and negative and (3,3,5) positive.[30] The band intensities are indeed found to be extremely strong. They may also turn out to be much sharper as well, because of the discreteness of the electronic levels of finite-size systems.

B. Photochemistry: Ejection of Halogen Atoms. The electron-transfer transition just described leads to the neutralization of two ions. This is highly destabilizing because it negates the ionic bonding that is responsible for cohesion. When diatomic MX molecules are excited, they dissociate into neutral atoms, within a few vibrational periods. Electronic excitation of bulk crystals has the remarkable consequence that neutral halogen atoms are ejected from their surfaces, with high directionality. Analogous to this result, Li et al.[26] found that the exclusive consequence of electronic excitation of the alkali halide nanocrystals, including CsI, KI, KBr, and NaI, is *ejection of a single neutral halogen atom*, process 2 in Table I.[26] This process occurs with a very high efficiency, suggesting that alternative relaxation channels, such as fluorescence or decay into heat, are not competitive. Figure 7 illustrates how the excitation and ejection processes might appear for the (3,3,3) nanocrystals, e.g., $Cs_{14}I_{13}^+ \rightarrow Cs_{14}I_{12}^+ + I^0$. By further excitation of the product of this reaction, it was verified that the product behaves like a substituted excess-electron nanocrystal. From the potential energy curves in Figure 7 and other calculations, it is clear that neutralization of a halide ion leaves it prone to desorption; in fact, a high ejection velocity is indicated from the loss of electrostatic attractions to counterbalance the short-range repulsions. Neutral alkali atoms are not lost in the primary step, because the transferred electron is more delocalized.[26]

C. Doubly Charged Clusters: Limits to Stability. The electrostatic coulomb force, as balanced by core repulsions to prevent collapse, is responsible for the cohesion of the ionic nanocrystals. It may seem paradoxical that this same force could also destabilize them. However, imagine that several halide ions are removed from a nanocrystal structure; now the repulsions among the alkali ions are no longer fully compensated by attraction to halides, and the system can become unstable toward alkali ion emission, process 4 in Table I. Similar considerations are well-known in the fission of atomic nuclei. Just such a limit to stability is found in nanocrystals that are doubly ionized by deep ultraviolet radiation, as observed by Li et al.[22] Figure 8 shows the formation of a very stable doubly charged cluster corresponding to another version of the (3,3,3) nanocrystal, e.g., $[Cs_{14}I_{12}]^{2+}$. Here the central anion (I^-) is missing, giving it a hollow cage appearance. In fact, the locations of the ion centers describe a somewhat spherical surface. Although the repulsive coulomb energy is very large, the stable, symmetrical form gives this cluster an especially high stability against ion emission.

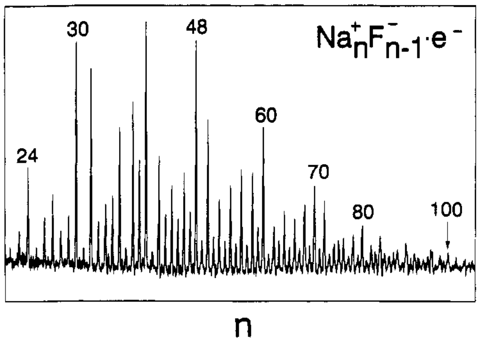

Figure 9. Mass spectrum obtained by photoionization ($h\nu$ = 4.0 eV) of a beam of clusters Na_nF_{n-1}, reflecting the abundances of the neutral clusters.[16,26] The preferential stability of even-n clusters is discussed in the text.

7. More on Cohesion and Stability: Dipole Pairing

As a final result, consider the abundances of Na_nF_{n-1} reflected in the photoionization mass spectrum of Honea et al., Figure 9.[21] A very similar pattern is obtained for the LiF series. As described in section 2, the abundances reflect the stability of the clusters with respect to evaporation; in this case a neutral Na atom would be lost, process 6 in Table I. There is a strong pattern of even–odd alternations at large n. Recalling that the electron simply plays the role of an F^- ion (section 5), much of the pattern (local maxima) can be explained in terms of perfect nanocrystals through the rule $2n = jkl$. The pattern of odd–even intensity alternations is beyond this explanation, however, and terraced structures also provide no explanation for such a persistent regularity. While the answer is not yet established, there is at least one idea that can account for it: In the summation over ion–ion interactions on a cubic lattice (Madelung series), there is a slight favoritism shown toward structures with an even number of MX diatomics, which can be analyzed by representing neighboring diatomics by electric dipoles, $M^+–X^-$, of finite length.[31] This argument can be precisely quantified in the hypothetical case of a linear chain of diatomic alkali halide units, showing that the magnitude of the energetic preference is simply the dipole–dipole interaction evaluated at a distance equal to the length of the chain.

By analogy, this dipole-pairing effect in three-dimensional structures may have a magnitude given

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(30) Li, X.; Whetten, R. L. Excited States and Photochemistry of Alkali-Halide Nanocrystals. *J. Phys. Chem.*, submitted.

(31) Honea, E. C.; et al. Stability of Larger Alkali-Halide Nanocrystals. Unpublished.

approximately by the dipole–dipole interaction evaluated at the diameter of the cluster. It is interesting that for an infinite ionic solid there is no additional insight, only mathematic convenience, gained by changing the order of summation of the coulomb interactions. By contrast, in ionic nanocrystals, it seems that insight is gained by summation over interactions between ion pairs (diatomics), the main component of the vapor, rather than between individual ions as suggested by the form of the potential given in section 2.

8. Nanocrystal Structures and Materials

This account of the recent exploration of alkali halide nanocrystals has included results on the cohesion, bonding, and structures; crystallinity phenomena including cleaving and melting; molecular adsorption reactions; halide-transfer reactions; electron substitution, solvation, and spectroscopy; surface electron states; electronic excitations and photochemistry; multiple charging; and other subtle effects in nanolattices. With the exception of the first topic, essentially all this has been learned in the past four years.

Some major issues remain untouched. First, the reliability of structural calculations, whether based on first-principles methods or simple pair potentials like those described above, has meant that most experimental results have been interpretable using calculated structures[32] like those shown in the figures herein. In fact, excellent agreement has been obtained between experiment and high-level theoretical simulations on every important property, supporting this structural picture. However, direct experimental evaluation of precise structures would be of great value. Approaches to accomplish this include electron diffraction, atomic (force) microscopy, and high-resolution spectroscopy.[33] Any of these will require improvements in the quality and selection of nanocrystal samples, but can be expected in the coming years.

Second, it is interesting to consider the prospects for the preparation of macroscopic quantities of specific-size ionic nanocrystals. Favoring this development is their inertness toward many substances. However, they will grow if allowed to come into contact, so that a protective layer is required, as is done in the colloidal methods used to prepare nanocrystalline CdSe and GaAs particles in narrow size distributions.[34] Motivating this development are the interesting optical and other properties likely to be found: just think of the properties found since macroscopic quantities of certain fullerenes were isolated.[3] At the same time, enough interesting chemistry and physics has been learned, at a fundamental level, from the study of nanocrystals, that it will all be worth it even if the immediate impact on materials applications is small.

It is a pleasure here to recognize the assistance and direction given to nanocrystal exploration in Los Angeles by former and continuing students Eric C. Honea, Margie L. Homer, Xiuling Li, Pamela M. St. John, and Frank Livingston and by postdoctoral associates Dr. Pierre Labastie and Dr. Rainer D. Beck, and also to acknowledge the impetus given to this work by Prof. Uzi Landman (Georgia Tech) and his student Gunaretnam Rajagopal. Funding has been provided by the Office of Naval Research through its Accelerated Research Initiative on Clusters, from the National Science Foundation through its Presidential Young Investigator program, and from a fellowship awarded by the David and Lucille Packard Foundation. The author also acknowledges the hospitality of the Institut für Molekülphysik, Freie-Universität-Berlin, during the period of writing the manuscript.

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(34) Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183. Wang, Y.; Herron, N. *J. Phys. Chem.* **1991**, *95*, 525. For an example of surface passivation, see: Colvin, V. L.; Alivisatos, A. P.; Tobin, J. G. *Phys. Rev. Lett.* **1991**, *66*, 2786.