I. INTRODUCTION

Rayane et al.\textsuperscript{1} have pioneered the experimental study of dipole moments and polarizabilities of NaF clusters, focusing on systems such as Na\textsubscript{N}F\textsubscript{N−1} with one electron outside a closed shell. However, even the closed shell systems Na\textsubscript{N}F\textsubscript{N} have dielectric properties of considerable interest. A study of this can illuminate such issues as how ferroelectric dipolar order of the bulk evolves up from nanocrystals. Our main focus is the quantity $\alpha_N$, defined as the polarizability per molecular unit of a cluster of $N$ molecular units,

$$\alpha_{N,\alpha\beta} \equiv \frac{1}{N} \frac{\partial \mu_{\alpha}}{\partial F_{\beta}}$$

where $\mu$ is the total dipole moment of a cluster or crystal and $F$ is the external electric field. The Clausius-Mossotti relation

$$\alpha_\infty = \lim_{N \to \infty} \alpha_N = \frac{\alpha_1}{1 - (4\pi n/3)\alpha_1}$$

is often used to relate the crystal polarizability per molecule $\alpha_\infty = (\epsilon - 1)/4\pi n$ to the molecular polarizability $\alpha_1$ and the molecular density $n$. This equation is exact for a bulk crystalline solid where point-polarizable and isotropic molecules sit at sites of cubic symmetry. It takes into account the local electric fields of all other induced dipoles which enhance the applied field at the cubic sites. This provides the simplest model for a ferroelectric instability when $\alpha_1$ is large enough. Numerical linear algebra allows the formula to be extended to less symmetric systems of point-polarizable molecules. However, no solid sequesters all polarizable entities accurately into point objects, or has only dipolar interactions, so the applicability of the formula to real ionic crystals, while traditional, can be regarded as largely wrong\textsuperscript{3}, or alternately as basically right but only after the ions are altered by crystal field and confinement effects\textsuperscript{4}. Here we use electronic structure theory (density functional theory, or DFT) to provide “data” on the evolution of polarizability\textsuperscript{5}.

Semiconductors like Si\textsuperscript{6} and CdSe\textsuperscript{7} have received a large amount of attention. The alkali halides, however, provide simpler model systems. Hudgins et al.\textsuperscript{8} have documented experimentally the stability of simple cuboidal fragment structures in NaCl. Much modeling has been done, mostly using classical models such as the shell model\textsuperscript{9–14}. Electronic structure methods have been applied to diatomic alkali halide molecules\textsuperscript{15–17} and various alkali halide clusters\textsuperscript{18–20}.

We choose NaF as a model system for studying the evolution toward bulk properties as well as the idiosyncrasies of individual nanoparticles. The bulk\textsuperscript{21} and surface\textsuperscript{22} vibrational properties are both known. Foremost among idiosyncrasies of nanophases is the fact that non-zero equilibrium electrical dipoles $\mu$ are necessary, just for reasons of cluster geometry and symmetry. This is well known\textsuperscript{23,24} in materials like CdSe whose bulk phase lacks inversion symmetry. It is less well known that dipoles must occur even in rather symmetrical cuboid rocksalt fragments, unless they have high enough symmetry ($T_d$ or symmetries which include inversion) to forbid a dipole.

Concerning electrical polarity of nanoclusters, there is a large literature of experimental and theoretical studies for metal clusters, especially simple metals\textsuperscript{25,26} (e.g. Na). There are also studies of polarity in semiconducting nanoclusters\textsuperscript{27}. Microscopic dielectric screening theory has been developed and implemented for semiconductors\textsuperscript{28,29}. In ionic nanophase materials no systematic study of polarity using full electronic structure theory is known to us. One new feature in ionic materials, not seen in metals or homopolar semiconductors, is a large contribution to polarity coming from nuclear displacements. We call this contribution the “vibrational” part $\alpha_{\text{vib}}$. Heteronuclear materials with partially ionic nature, such as the rocksalt crystal GeTe, can have ferroelectric instabilities driven partly by vibrational polarization\textsuperscript{30}.

NaF is a good choice for a first study for two rea-
TABLE I: Experimental and theoretical properties of the NaF diatomic molecule.

| Property | Present calc. | NRLMOL ref.33 | SCF ref.34 | ACPF ref.16 | Ref.17,19,20 |
|----------|--------------|---------------|------------|-------------|--------------|
| d (Å)    | 3.69         | 3.64          | 3.64       | 3.6         | 3.6          |
| μ (µB)   | 3.07         | 3.21          | 3.22       | 3.2         | 3.2          |
| ω (cm⁻¹) | 510          | 536           | 536        | 540         |              |
| α₁,∥ (Å³) | 2.39        | 1.82          |            |             |              |
| α₁,⊥ (Å³) | 3.33        | 1.95          |            |             |              |
| α₂,∥ (Å³) | 0.86        | 1.04          |            |             |              |

The NaF diatomic molecule or “monomer” allows a study of classical pictures for a future paper, and present here are the results of a quantum study using DFT. This paper is based largely on the results of the MA thesis of C. Schmidt.

II. DIATOMIC MOLECULE

The NaF diatomic molecule or “monomer” allows a good comparison between our calculations and both previous33–35 and experimental16,19,20,36,37 work. We use the package NRLMOL37 which allows accurate and versatile DFT calculations for molecules. We choose the PBE38 version of the generalized gradient approximation (GGA), and include a spin density functional for systems with uncompensated spins (i.e., the Na and F atoms and Na₁₃F₁₃.) Results are shown in Table I. We also show in Fig. 1 the total energy from DFT relative to isolated atoms. The experimental dissociation energy of 5.3 eV39 is quite accurately reproduced, as are the bond-length, dipole moment, and vibrational frequency.

Can the diatomic results be related to atomic, ionic, or bulk properties? Computed atomic and ionic polarizabilities are shown in Table II. The sum of DFT polarizabilities of the Na⁺ and F⁻ ions is 1.37 Å³. This is close to the polarizability α∞ = 1.45 per formula unit of the solid. However, Clausius-Mossotti theory gives the value α₁=1.16 Å³ from the crystal data. It is difficult to know how to interpret these numbers. Fowler and Madden4 make three relevant observations. (1) Correlation corrections greatly enhance the polarizability of the larger F⁻ ion, doing little for the isoelectronic but smaller Na⁺ ion. (2) Putting the ion in a crystalline environment makes the F⁻ ion shrink, both because of the attractive crystal field of the surrounding ions and because of the repulsion of the surrounding electrons. The resulting smaller ion has a polarizability which is much less altered by correlation. (3) The resulting smaller polarizability estimated for the “ion-in-a-crystal” is perhaps quite consistent with Clausius-Mossotti. It is unfortunate that there are no direct experimental data for the polarizability of the ions Na⁺ or F⁻. A long list of highly diverse values for the F⁻ polarizability is tabulated by Iwadate and Fukushima4⁰. None are direct measurements.

It is difficult to know how to relate these ideas and numbers to our calculated polarizability of the diatomic. In zeroth approximation the equilibrium dipole of the diatomic is ed and the electronic polarizability is the sum of the ionic polarizabilities, or 1.37Å³. The computed dipole is smaller by 17%, but the computed polarizability is far larger than the zeroth order estimate. Using the average \( \bar{\alpha} = (\alpha_\text{x-x} + \alpha_\text{y-y} + \alpha_\text{z-z})/3 \), the diatomic has \( \bar{\alpha}_{1,\text{ed}}=2.70 \), larger by 2 than the sum of free ions. Also the diatomic has anisotropy \( \Delta\alpha/\bar{\alpha}=34\% \), where \( \Delta\alpha^2 = [(\alpha_{\text{x-x}} - \alpha_{\text{y-y}})^2 + (\alpha_{\text{y-y}} - \alpha_{\text{z-z}})^2 + (\alpha_{\text{z-z}} - \alpha_{\text{x-x}})^2]/2 \). In an attempt to account for these discrepancies, three corrections were tested. (1) Each ion polarizes in the self-consistent field of the other, and these local field corrections are accounted for by solving two coupled linear equations for the moments \( \mu_1 \) and \( \mu_2 \). Unlike Fowler and Madden, we did not correct the polarizability of the ions for their altered environments. The corrections depend on the ratios \( \phi_{\perp} = \alpha_{\perp}/d^2 \) for the two ionic species, where \( d \) is the internuclear separation. For Na⁺ \( \phi_{\perp} = 0.0193 \), and for F⁻ \( \phi_{\perp} = 0.1652 \). The reduced ratio \( \phi_{\text{red}} = \phi_{\perp}/(\phi_{\perp} + \phi_{\text{+}}) \) is 0.0173. The corrected values of the permanent dipole4¹ and polarizability tensor1⁵ are

\[
\mu = ed \left[ 1 - \phi_+ - \phi_- + 8\phi_+\phi_- \right] = 0.80ed
\]

\[
\alpha_{\perp} = (\alpha_+ + \alpha_- \left[ 1 + 4\phi_{\text{red}} \right] = 0.08(\alpha_+ + \alpha_-)
\]

\[
\alpha_{\parallel} = (\alpha_+ + \alpha_- \left[ 1 - 2\phi_{\text{red}} \right] = 0.97(\alpha_+ + \alpha_-)
\]

The result of simple screening of the naive dipole ed by point ionic polarizability agrees closely with the computed total dipole (Table I), but the enhancement of α
parallel to the molecular axis, and smaller enhancement perpendicular, while in the right direction, are much too small. It appears that when higher-order multipoles are included, they make corrections comparable to the dipolar ones, so the agreement with the total dipole moment is partly accidental. (2.) Nonlinear corrections are not negligible since the local fields are large. Since the ions are inversion-symmetric, the leading correction is \( \mu = (\alpha + \beta F^2/2)F \). Using NRLMOL we computed \( \beta = 7.9 \) and 0.06 for \( F^- \) and \( Na^+ \), in atomic units \( (a_0^2/e^2) \). The ions sit in fields \( F = e/r^2 \) which are large, and the non-linear correction is estimated to be +12% for the polarizability of the F part of NaF, and +1% for the Na part; again the direction is right but the effect is much too small. (3.) There is incomplete charge transfer between Na and F in the diatomic. Using the computed zero-field dipole as a measure, the static charge \( \mu/d \) is \( \pm 0.85e \), which suggests that the Na could be treated as 83% Na\(^+\) and 17% Na. Because of the giant polarizability of neutral Na (see Table II), it is easy to rationalize a large correction, but less easy to make a simple classical model for both tensor components of the electronic polarizability.

The vibrational part of the polarizability is a new effect that occurs in the diatomic and has no counterpart in atoms or ions. We compute it from the formula:

\[
\alpha_{\text{vib},\alpha\beta} = \sum_{ij,ij'} Z_{\alpha,ij}(K^{-1})_{ij,j'i} Z_{ij',\beta}^T
\]

(4)

where \( Z_{\alpha,ij} \) is the dynamic effective charge tensor \( \partial\mu_{\alpha}/\partial u_{ij} \), \( u_{ij} \) is the \( \mu \)-th Cartesian component of the displacement of the \( i \)-th atom, and \( K \) is the force constant tensor.

Since atoms and ions have no vibrational polarizability, we look instead to the bulk solid for guidance, and here a surprise occurs. The static \( \epsilon_{\text{tot}} = \epsilon_{\text{dc}} \) and optical \( \epsilon_{\text{el}} = \epsilon_{\text{opt}} \) dielectric constants of NaF are 5.1 and 1.74\(^{45}\); the effective polarizabilities \( \alpha = (\epsilon - 1)/4\pi n \) are 8.04 \( \text{Å}^3 \) (electronic plus vibrational) and 1.45 \( \text{Å}^3 \) (electronic only). Thus the vibrational contribution is 5 times the electronic contribution to the bulk polarizability, whereas in the diatomic molecule according to Table I the ratio is 0.29/2.70, 50 times smaller (this uses the average of the diagonal elements of the \( \alpha \) tensor.) An alternate analysis of the bulk is to extract “molecular” polarizabilities from the Clausius-Mossotti formula. These are 1.16 \( \text{Å}^3 \) (electronic) and 2.29 \( \text{Å}^3 \) (vibrational). The ratio is reduced from 5 to 2 but is still 20 times larger than in the diatomic molecule. This remarkable difference comes partly because the electronic polarizability is reduced (per molecule) in the bulk, but mostly because the vibrational part is increased.

III. CLUSTERS

We have studied Na\(_N\)F\(_N\) for \( N = 2, 4, 6, 9, 18, \) and 32. For contrast, we also studied the system Na\(_4\)F\(_3\) which is a symmetric \( 3 \times 3 \times 3 \) cuboid of \( \text{O}_h \) symmetry. Except for \( N = 2 \), and the ring structure of \( N = 4 \), these are all cuboids, shown in Fig. 2. Vibrational frequencies and infrared activities used to compute \( \alpha_{\text{vib}} \) are summarized in Fig. 3. Polarizabilities are summarized in Figs. 4 and 5, and polarizabilities, formation energies, and permanent dipole moments are summarized in Table III.

A. \( \text{Na}_2\text{F}_2 \)

This cluster is not a cuboid, but is included because it has previously been studied experimentally\(^{46–49}\) and theoretically\(^{9,19,20}\). Our DFT gives a binding energy relative to two separated diatomics of 2.4eV. Previous calculations by Dickey et al.\(^{19}\) gave 2.6eV, which agrees well with the experiment of Eisenstadt\(^{46}\). The geometry is a rhombus with Na-F-Na angle 94.7° and Na-F bond length 3.96 \( a_0 \), agreeing with Dickey et al. and with experiments by Hartley and Fink\(^{47}\) and Lapshina et al.\(^{48}\).

The DFT prediction of polarizabilities is given in Table III. The electronic contribution is surprisingly isotropic. Per ion pair, the polarizability \( \alpha_{\text{el},2} \), plotted on Fig. 4 is significantly reduced compared with the diatomic molecule, and closer to the bulk limit. The vibrational polarizability has a large anisotropy dominated by out of plane motions, and per ion pair, \( \alpha_{\text{vib},2} \) is much larger than the diatomic and out-of-line with the results for larger clusters, already close to the bulk value. The 6 vibrational normal modes consist of three even, Raman active modes (\( A_g \) at 205 cm\(^{-1}\), \( B_{1g} \) at 326, and another \( A_g \) at 377) and three odd, infrared active modes, roughly equally intense (\( B_{1u} \) at 149 cm\(^{-1}\), \( B_{2u} \) at 362, and \( B_{2u} \) at 373). In assigning these symmetries, we used a co-
FIG. 2: Structures of NaF rocksalt fragments (cuboids, except for Na$_2$F$_2$) given by DFT. The Na$_4$F$_4$ ring structure and O$_4$ 4 × 4 × 4 cuboid Na$_{32}$F$_{32}$ are not shown. The Na$_4$F$_4$, Na$_4$F$_{16}$, C$_{4v}$ structures have even numbers of 3 × 3 planes; planes are charged alternately + or -, so the fragments are polar. The Na$_4$F$_{13}$ O$_h$ cuboid has an odd number of 3 × 3 planes and is non-polar. It consists of a closed shell positively charged cluster plus a compensating electron distributed mainly on corner Na$^+$ ions.

ordinate system where the x-axis passes through the Na atoms and the y axis through the F atoms. These numbers can be read from Fig. 3, which also shows the relative infrared intensities of the active modes. Our frequencies agree to better than 10% with unrestricted Hartree-Fock calculations and somewhat less well with shell model calculations. A matrix-isolation experiment has reported two Na$_2$F$_2$ infrared active vibrations above a spectrometer cutoff at 190 cm$^{-1}$. The experimental numbers 360 and 363 cm$^{-1}$ are close to our values. It is the low frequency B$_{1u}$ mode, polarized out of plane, which is responsible, because of its low frequency, for the large z$z$-component of vibrational polarizability in our calculation.

B. Na$_4$F$_4$

This cluster has a relatively low-lying structural isomer with a D$_{4h}$ ring geometry which has been studied theoretically. We find the T$_d$ cuboid geometry to be lower in energy than the ring by $\Delta$=0.75 eV, twice as much as the figure 0.37 eV mentioned by Calvo. The vibrations of the ring have a wider range of frequencies than any of the cuboids, with many low-frequency modes. We estimate the temperature of isomerization to be 1000 K in the following way. If only two isomers need consider-

ation and if harmonic approximation is sufficient, and if we ignore rotations, then statistical mechanics says that the fraction of rings $f_R$ should be given by

$$1/f_R = 1 + e^{\beta \Delta} \prod_i \frac{\sinh(\beta \omega_{i}^R / 2)}{\sinh(\beta \omega_{i}^C / 2)}$$

where $\omega_{i}^R$ is the i-th vibrational mode of the ring and $\omega_{i}^C$ is the i-th vibrational mode of the cuboid. At low $T = 1/\beta k_B$, the ring population is exponentially small, but as $T$ increases, the lower vibrational frequencies give an entropic stabilization of the rings. In the classical limit $\beta \hbar \omega / 2 \ll 1$, the temperature $T_R$ at which the ring population is 1/2 is

$$k_B T_R = \Delta / \sum_i \log(\omega_{i}^C / \omega_{i}^R)$$

Our computed vibrational spectra, shown in Fig. 3, give the logarithmic denominator to be 8.5, greatly reducing the temperature of isomerization. This reduction factor should be slightly increased to take into account the higher rotational moments of inertia, and thus higher rotational entropy, of the rings.

The polarizabilities, shown in Table III, are surprisingly isotropic for the ring. Electronic parts are surprisingly similar for the ring and cube geometries, while the vibrational polarizability is bigger by a factor 4 in the ring because of the low frequency infrared activity shown in Fig. 3.

An interesting property of the Na$_4$F$_4$ T$_d$ structure is that the ground state has an octupole $(xyz)$ moment, but no quadrupole moment. In the point group T$_d$, a vector $(x, y, z)$ and an off-diagonal second-rank symmetric tensor $(yz, zx, xy)$ have the same symmetry. This means that an applied electric field $F_z \hat{z}$ induces both a dipole moment $\mu_z$ and a quadrupole moment $\Theta_{xy}$. We calculated the octupole moment, which is equivalent to static point charges of $\pm 0.866 e$ on the ions. This can be compared with the static charge $\pm 0.83 e$ deduced from the dipole of the monomer NaF. The induced quadrupole was computed to be

$$\Theta_{xy} = \frac{3}{2} \int d^3 x y p(\vec{r}) = (-8.2 a_B^4) F_z.$$  

C. Larger Stoichiometric Cuboids

The vibrational eigenfrequencies are shown in Fig. 3. The polarizabilities are shown in Fig. 4, and contrasted with crystalline compounds in Fig. 5. We see a non-monotonic but fairly smooth evolution of both vibrational and electronic polarizabilities with linear dimension of the cluster, provided we ignore the planar species Na$_2$F$_2$ and D$_{4h}$ Na$_4$F$_4$. The Na$_4$F$_4$ and Na$_{32}$F$_{32}$ T$_d$ structures are the first two in the series of T$_d$ structures of $2n \times 2n \times 2n$ atoms with isotropic polarizabilities whose properties should scale smoothly and perhaps rapidly to
the bulk limit. The electronic polarizability does approach the bulk limit rapidly, but the vibrational part does not. There is a subtlety in the vibrational polarizability of the bulk. The Lyddane-Sachs-Teller relation shows that the splitting of TO and LO optical phonon frequencies is tied to the splitting $\epsilon_{dc} - \epsilon_{opt}$. In point group $T_d$ or $O_h$, the infrared optic modes belong to triply degenerate representations – there is no distinction between LO and TO. The bulk crystal violates this symmetry only because the distance of spatial variation of the probing electric field is smaller than the sample size. Therefore the bulk limit for $\alpha_{\text{vib}}$ may not be reached until the sample size exceeds the wavelength of the radiation used to measure $\epsilon_{dc}$.

We have done three clusters with uniaxial anisotropy. NaF$_6$ is first in a sequence of long skinny cuboids of $2 \times 2 \times (2n + 1)$ structures with $D_{2h}$ symmetry or of $2 \times 2 \times (2n + 2)$ structures with $D_{4h}$ symmetry. Actually the former group is not strictly uniaxial, but has weak splitting of the equatorial two-fold axes, which accounts for a very weak splitting of the $xx$ and $yy$ parts of the $\alpha$ tensors. NaF$_9$ and NaF$_{13}$ are the first two of the $C_{4v}$ sequence of $3 \times 3 \times 2n$ structures. The polarizability is relatively isotropic, except that the vibrational polarizability of NaF$_{13}$ is 20% enhanced along its long axis. The clusters with dimensions $3 \times 3 \times (2n + 1)$ have an odd atom count and are thus non-stoichiometric. The $O_h$ $3 \times 3 \times 3$ cluster NaF$_{13}$ is discussed below; the higher clusters have $D_{4h}$ symmetry.

### D. Permanent Dipole Moments

The two cuboids of $C_{4v}$ symmetry, NaF$_9$ and NaF$_{13}$, have permanent dipole moments just of structural necessity. Naively, if the cuboid were an exact sodium chloride structure fragment, with the NaF bulk lattice constant of 4.62 Å, and the charge of $+e$ were assigned to the ions, then the dipole moments would be 2.31 eÅ and 4.62 eÅ for the smaller and larger cuboids. However, the ions have somewhat distorted positions, and the structural dipoles are reduced to 1.34 eÅ and 3.16 eÅ respectively, assuming unit quantized charges. The actual DFT values, shown in Table III are 1.06 eÅ and 2.71 eÅ, respectively. These numbers show that the total dipole is reduced by screening, both “vibrational” and electronic. Vibrational screening is larger than electronic, in line with the fact that vibrational polarizabilities are roughly twice electronic polarizabilities. The slab-shaped NaF$_9$ is more affected by screening than the needle-shaped NaF$_{13}$, as one expects from the well-known depolarization effects in slab vs. needle shaped samples. The dipole of NaF$_{13}$ was previously calculated by Rayane et al.$^3$ to be 7.5 D = 1.84 eÅ, significantly smaller than our value. Their calculation was part of an investigation of non-stoichiometric Na$_N$F$_{N-1}$ species such as NaF$_{17}$. Only the outer electron was treated by quantum mechanics. The stoichiometric species has no outer electron, so apparently their number is based on a classical polarizable ion model, which apparently overscreens.

### E. Non-stoichiometric $O_h$ NaF$_{13}$

This is such an interesting cuboid that we could not resist departing from our main theme of polarizability evolution in stoichiometric cuboids. The last electron resides outside the closed shell of NaF$_{13}$. Alkali halides with one electron outside a closed shell have attracted attention$^{1,51}$ since the prediction by Landman et al. that such clusters might have a second-order Jahn-Teller instability. This, and the subsequent studies by Durand et al.$^{53,54}$ kept only a single electron in the quantum part of the dynamics, while Ochsenfeld and Ahrlich$^{55}$ have studied several alkali halides using all-electron theory.

The single outer electron gives rise to a giant electronic polarizability shown in Table III. On a per molecule basis, the total polarizability of 313 Å$^3$, shared by 13.5 molecules, is larger by 15 than the interpolated value $\sim 1.5$ seen in Fig. 4. On an absolute basis, it is larger by

---

**TABLE III: Polarizabilities (in Å$^3$), formation energy $E_f$ (in eV), and permanent dipole moment $\mu$ (in atomic units $e\alpha_B$) for NaF molecules and nanocrystals.**

| Point group | $\alpha_{dl}$ | $\alpha_{vib}$ | $E_f$ | Permanent dipole $\mu$ |
|-------------|--------------|---------------|------|------------------------|
| NaF | | | | |
| NaF$_2$ | | | | |
| NaF$_4$ | | | | |
| NaF$_6$ | | | | |
| NaF$_9$ | | | | |
| NaF$_{13}$ | | | | |
| NaF$_{18}$ | | | | |
| NaF$_{32}$ | | | | |

$a$Ref. 39  
$b$Ref. 46
FIG. 3: Integrated vibrational densities of states for various clusters of NaF. The degeneracy of each mode is coded in the step increase, as the spectrum steps upward to the final mode $3N - 6$. Vertical bars are the relative infrared activities of the various modes; the absolute scale is not given.

13.5 than the polarizability of the neutral Na atom. On a per molecule basis, the vibrational polarizability of 24.7 is smaller by 0.6 than the interpolated value of the stoichiometric clusters. Apparently the loose last electron is exceedingly polarizable, and partly screens the change in dipole per unit displacement that causes vibrational polarizability according to Eq. (4).

The large polarizability gives one a right to expect that Na$_{14}$F$_{13}$ might distort to a lower symmetry polar structure such as $C_{3v}$, as was discovered theoretically in a restricted model by Landman et al.\textsuperscript{52} in the Na$_{14}$Cl$_{13}$ cuboid. In a naive view, point-polarizable ions have a density-dependent critical $\alpha_{el,c}$ beyond which ions polarize spontaneously. In cubic crystals it is $3/4\pi n$ which equals 5.88 Å$^3$ for the density $n$ in bulk NaF. In fragments $\alpha_c$ approaches the bulk limit rapidly\textsuperscript{2}. The per molecule electronic polarizability of Na$_{14}$F$_{13}$ is way beyond that limit, and thus unstable in this model. However, the giant polarizability is almost all associated with the delocalized last electron, making the Clausius-Mossotti analysis inappropriate.

The highest occupied molecular orbital (HOMO) is non-degenerate but lies not far below other levels with which it is forbidden by symmetry to mix. The second-order Jahn-Teller effect is a distortion motivated by the “desire” for such a mixture in order to lower (quadratically in distortion amplitude) the HOMO energy. Kristoffel and Konsin\textsuperscript{56} argue that such a mechanism is at work in the ferroelectric distortion of GeTe crystals, involving the mixing between states just below and just above the narrow gap of this IV-VI semiconductor with two more electrons than are needed to fill the usual $s-p$ shell. The instability of Landman et al.\textsuperscript{52} is a nanocrystalline analog.

We find that this instability does not happen in Na$_{14}$F$_{13}$. This contradicts other theories and the interpretation by Rayane et al.\textsuperscript{1} of their experiment. Theories which keep only the extra outer electron are not reliable enough if the energy balance is delicate. Rayane et al.\textsuperscript{1}
found a very large deflection of neutral Na$_{14}$F$_{13}$ particles in electric field gradients. There was a moderate $T$-dependence, but not the full $1/T$ of the usual Debye-Langevin polarizability $\mu^2/3k_BT$ of a molecule with a permanent dipole $\mu$. Nevertheless, the authors believe their data to be consistent with a permanent dipole, although they do not claim that their analysis is firm. Our finding is that the electronic polarizability is indeed extremely large and will give large deflections, but there is no symmetry-breaking or permanent dipole moment. We believe the data may be consistent with this alternate interpretation.

IV. DISCUSSION

A. Formation energy

We define the formation energy $E_f$ as the energy per ion pair relative to the energy of separated neutral atoms. Values of $E_f$ are given in Table III. The increasing formation energy with cluster size can be organized phenomenologically according to the numbers of ions with various geometric sites. We distinguish corner, edge, face, and interior ions. In the Na$_N$F$_M$ cuboids these sites occur as pairs of oppositely charged ions. For example, Na$_4$F$_4$ has 4 corner pairs, Na$_6$F$_6$ has 4 corners and 2 edges, Na$_8$F$_9$ has 4 corners, 4 edges, and one face, and Na$_{18}$F$_{18}$ has 4 corners, 8 edges, 5 faces, and 1 interior ion pair. The values of $E_f$ then correspond to the assignment $7.01$ eV for corner pairs, $7.53$ eV for edge pairs, $7.63$ eV for face pairs, and $9.11$ eV for interior pairs. This last is close to the experimental bulk value of $9.30$ eV. These assignments then predict $E_f$ for larger cuboids. Na$_{32}$F$_{32}$ has 4 corners, 12 edges, 12 faces, and 4 interior pairs, so is predicted to have $E_f=7.70$ eV, very close to the computed DFT value of $7.6$ eV.

B. Trends of Polarizability

The trend to smaller electronic polarizability as size increases should certainly be attributed to enhanced stabilization of the filled $p$ shell as the ion acquires larger numbers of neighboring counterions. The HOMO and LUMO states of a finite cluster are located mostly at the surface. The HOMO-LUMO gap is reduced in clusters relative to bulk, corresponding to a cluster analog of surface localized states on a bulk surface. As the cluster size increases, electronic spectral weight gets pushed upward toward the bulk band gap of $11\text{eV}$.$^{58}$ In bulk alkali halides, an excess electron is a delocalized carrier, but an excess hole self-traps on a dimerized anion pair (V$_K$ center). On clusters, one would expect the trapped hole to lie on surface anions. The excess electron, after migrating to the surface, might also self-trap. This would be a “pseudo-Jahn-Teller polaron”. The fact that the second-order Jahn-Teller effect does not occur in Na$_{18}$F$_{17}$ (according to us) suggests that the surface electron might not trap but remain delocalized. We note that localization of the excess electron could be enhanced within a formalism where the electronic self-interaction (SI) is fully corrected.$^{59}$ Further investigation of this effect within an SI-free framework would be necessary to rule out the possibility of surface trapping.

The enhanced vibrational polarization of larger clusters is harder to explain. Large electronic polarizability should diminish vibrational polarizability by screening. The dynamical effective charge matrix (change of electrical dipole per unit displacement) is reduced by the polarizability of the ions which are displacing (see Eq. 3.) We find little support for this idea in the trends of dielectric constants of other alkali halides, shown in Fig. 5. Here the value of $\alpha$ per molecule is $(\epsilon - 1)/4\pi n$, with the optical dielectric constant giving the $\alpha_{el}$ as before. The vibrational polarizability seems roughly independent of the electronic polarizability.

Acknowledgments

We thank Y.-R. Chen and D. O. Welch for helpful discussions, and Y.-R. Chen for help with the manuscript. Work at Stony Brook was supported in part by NSF Grant DMR0089492. C. S. was supported by a student fellowship from the German government. T. B. and M. P. were supported in part by the ONR and the HPCMO and CHSSI initiatives.
N. Kristoffel and P. Konsin, Phys. Stat. Sol. 21, K39 (1967).

NIST chemistry webbook.

K. Kameswara Rao, T. J. Moravec, J. C. Rife, and R. N. Dexter, Phys. Rev. B 12, 5937 (1975).

J.P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).