

## Computation of the energetics of surface vacancy and interstitial generation in silver halide

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We have considered alternative mechanisms through which flat, stepped, or kinked surfaces of silver halide may participate in the generation of interstitial or vacancy silver ions. In the energetically favored mechanism, the surface sites ionize to generate an adsorbed silver ion and a vacancy. The former has a smaller energy requirement for exchange into the bulk than the latter, as deduced from our calculations. Positive kink sites require the smallest overall energy for this generation step compared to flat {100} or stepped {105} surfaces. The nature of the space-charge layer involving surface negative charge and subsurface silver ions agrees well with the accepted experimental picture. Computed energies of these processes are presented along with a preliminary estimate of the entropy of formation of point defects from the AgBr surface. A calibration of our procedure for NaCl surfaces is made by comparison of our calculated energies of formation to experimental enthalpy values for vacancies and shows excellent agreement.

### I. INTRODUCTION

The surface can exert a dominating effect on the physical properties of materials. This is particularly true of the silver halide microcrystals used in photography, where the surface-to-volume ratio is large. In order to understand the role of the surface, we need to know whether it is just acting as a source or sink for ions or whether the particular geometric arrangement of surface ions imparts some specific properties. Characterization of the surface of microcrystals is difficult, and much of the present level of understanding comes from recourse to information available from single crystals, or geometric reasoning based upon the bulk structure. Much of the conceptual thinking has ascribed a special role to surface kink sites involved in point defect generation of electronic carrier trapping. Some experiments that are interpreted on this basis include dielectric loss,<sup>1,2</sup> radiotracer measurements of surface potential,<sup>3</sup> photoconductivity measurements of electron lifetimes,<sup>4</sup> and photographic measurements of chemically produced silver centers,<sup>5</sup> to name a few.

Ionic point defects can be generated at a surface individually, as compared to the bulk, where they must be generated in pairs of opposite charge. This feature is known to be responsible for the generation of a space-charge layer<sup>6-10</sup> because each component of the defect pair will, except for the isoelectric temperature, have different free energies of formation. In silver halide, the space charge is generally thought to consist of a negatively charged surface compensated for by an enhanced subsurface concentration of interstitial silver ions near room temperature. Experiments on thin films,<sup>11-13</sup> emulsion grains<sup>1,2</sup> and single crystals<sup>10,14,15</sup> have been analyzed in terms of this type of space-charge layer model. The extraction of thermodynamic parameters characterizing the formation of point defects requires a quantitative theory. The equations derived by Kliever<sup>7</sup> for a pure or impurity-containing crystal of sufficient thickness that

the interior of the crystal achieves bulk properties contains no limitations on the density of surface defect sites. These are generally used to analyze experimental data. While such a model does contain simplifications and does not specify particular surface sites, it is realistic for many systems. Recent experiments<sup>3,14</sup> measuring the concentration gradients of radioactive divalent cation impurities in silver halide and sodium chloride single crystals have made use of this model to determine the free energies of formation of point defects as a function of temperature. Thus the model remains of importance.

Surface kink sites have played an important role in the conceptual development and thinking about electronic and ionic processes in silver halide. This is due, in part, to the latent image formation models<sup>16</sup> of Hamilton that incorporate the proposal of Seitz,<sup>17</sup> that key surface defects are kinks which possess a partial charge that can be reversed upon carrier trapping. Such models also view the charged kink sites as shallow potential wells for electron trapping, and that act as sites for the photolytic growth of silver atom clusters through alternate electronic and ionic steps. In addition to the role involving electronic carriers, kink sites have been invoked in descriptions involving the generation of ionic point defects. The models of Blakely and co-workers<sup>18,19</sup> have shown that if the surface concentration of kink sites is limited, there will be modifications in the normally expected space-charge picture.

The purpose of this work is to begin a computational treatment of the ionic defect formation processes at various surface sites of crystals. We would like to examine the energetics of various mechanisms of defect formation using methodologies that have been widely used to treat bulk ionic defects. We propose to begin with the most straightforward model of silver bromide or chloride, which is that of an ionic solid whose surface ions possess charges like the bulk ions. The ionic model has been shown in many studies<sup>20</sup> to be capable of explaining defect formation energetics in the bulk and surface of crystals.

## II. METHOD

The atomistic simulation procedure<sup>20</sup> has been documented in application to silver halide.<sup>21-24</sup> Ions possessing an integer net charge are represented by a harmonically coupled core and shell of different charges. The force constant is determined by a relationship involving the ion polarizability.<sup>25</sup> These charged core and shell species interact over long ranges. The short-range interactions between the shells of ions are a result of the overlap of electron clouds from the ions. In this work, we employ two-body short-range functions for AgCl and AgBr from Ref. 23. The values for the Frenkel energies determined from these interatomic potentials agree well with experiment, and have the correct temperature dependence. Their principal shortcoming is a failure to reproduce the Cauchy violation, known for the elastic constants in silver halide. Three-body<sup>24</sup> short-range interactions are required to produce this effect. We do not expect that this is a serious shortcoming for defect energetics, but future work will study this point.

These calculations employ the HADES (Ref. 26) code to determine bulk defect energies. We employ a lattice constant appropriate to a particular temperature to enable us to determine temperature-dependent properties. The surface defect energy calculations employ the MIDAS and CHAOS (Ref. 27) codes that operate for surfaces, much like the HADES code operates for the bulk. A relaxed equilibrium surface structure is computed for a two-dimensional film of varying thickness that is attached to a block of ions fixed at their appropriate bulk positions. These relaxed coordinates are used as a starting point for calculations of properties of isolated defects. These procedures have been employed and are described in an earlier study of silver bromide surfaces.<sup>28</sup>

## III. RESULTS

### A. Surface models

We have considered point defect formation at four distinct surface sites that are shown in Fig. 1. One is just the flat {100} close-packed surface of the sodium chloride structure. This nonpolar surface contains equal numbers of anions and cations upon which vacancies are generated by removing a surface ion, while interstitials are generated by placing the ion upon the perfect surface. The second site considered is a step on this flat surface that is periodically repeated across the surface. We considered the {105} surface where the steps are spaced every fifth row, although other surfaces of differing step densities could have been considered. We note that the step edge consists of alternating anions and cations next to one another. Finally, we considered a kink site prepared by removing pairs of ions along a step of the {105} surface. This creates positive and negative kinks, separated in this case by 12 nearest-neighbor spacings. Thus an interstitial ion at the kink is created by ion placement next to the kink of opposite charge, and a vacancy is created by removing an ion right at the kink site. One possible deficiency of this kink model is the proximity of the positive and negative kink sites, which is forced

in this model by the size of the system that we can accurately treat in our calculation. We examined models with differing separations from four to ten spacings, and the calculated surface defect energies varied by only a few percent. Thus we report only values at the eight-layer spacing that is considered reliable for these calculations.

### B. Mechanism of Frenkel defect formation at kink sites

We would like to consider various means by which surfaces or surface sites are involved in the creation of point defects. Frenkel<sup>29</sup> and Lehovcic<sup>6</sup> considered processes by which ions or vacancies could be transported from the surface to the bulk, but did not consider specific types of surface sites or the detailed steps that might be involved in these processes. Since silver halides are the topic of this work, we restrict our attention to the formation of cationic Frenkel pairs. There are two alternative routes by which the surface can participate in the formation of point defects, such as interstitial and vacancy species. In

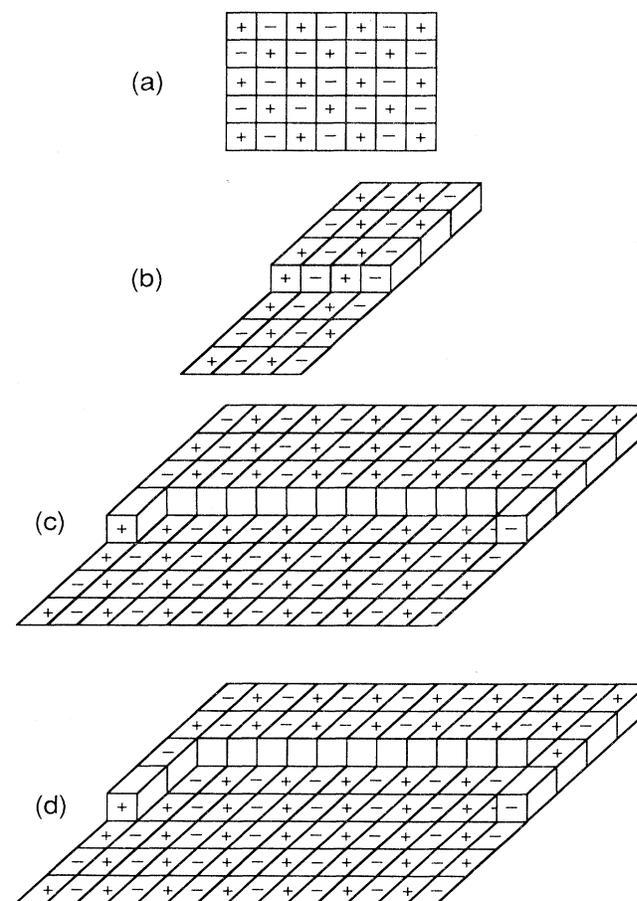


FIG. 1. Sketches of the surfaces and defects considered in this work are shown. In (a) we show the {100} surface, in (b) we show a portion of the stepped {105} surface, in (c) we show a region of a single kink site generated from the stepped surface, and in (d) we show the double kink site.

the initiation step of the first mechanism, the surface ionizes to create a silver ion and a vacancy at the surface. For silver halide we can write



where  $\text{Ag}_s^+$  is the silver ion on the surface, and  $V_s$  is the corresponding surface vacancy. After this first step, both of the surface species are free to form bulk point defects independently. The bulk interstitial ( $\text{Ag}_i^+$ ) is formed by



while the bulk vacancy ( $V_B$ ) is formed by the movement of a lattice silver ion to the surface vacancy, creating a bulk vacancy



In both reactions 2 and 3, we may imagine a chainlike sequence of ion jumps that accomplishes the transport of ions between surface and bulk. For example, in reaction 3, a cation one layer beneath the surface may move into the surface vacancy, creating a vacancy at its former position. Repetition of this process involving ions at successively deeper levels accomplishes the net transport represented in reaction 3. We emphasize that in this mechanism a surface initiation step occurs without the participation of any bulk defects. Then the surface vacancy and adsorbed silver ion partition into the bulk separately, where the competition between reactions 2 and 3 will determine the sign of the surface charge and the composition of the space-charge layer.

The second possible mechanism for creating bulk point defects involves adsorption of ions from the bulk ( $\text{Ag}_B^+$ ) lattice sites to create bound surface ions ( $\text{Ag}_s^+$ ). We write the first step of this path as



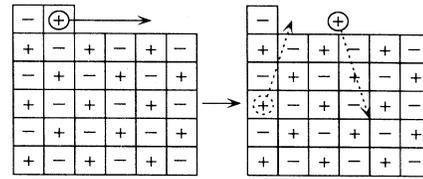
We consider that the extra surface ion is bound at the surface site of greatest stability. For kink sites, this would correspond to binding the surface silver ion next to a negative kink site, as contrasted to a positive kink site where reaction 1 proceeds. The complementary reaction for bulk interstitial formation is



In order to evaluate which mechanism predominates, we will perform some energy calculations. First, let us point out that the sum of energies required for reactions 1, 2, and 3 equals the sum for reactions 4 and 5, which is just the bulk Frenkel defect formation energy.

The distinction between the two mechanisms for the generation of point defects can also be stated in terms of the relative reactivities of the surface sites. Consider kink sites, where, in reaction 1, a positive kink is converted to a negative kink with the formation of a silver ion. In the second mechanism, initiated by reaction 4, a negative kink is converted to a positive kink by silver ion adsorption accompanied by the formation of a bulk silver ion vacancy. These two possibilities are sketched in Fig. 2. The mechanisms just discussed apply equally well to

Mechanism I.



Mechanism II.

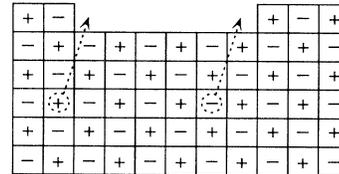


FIG. 2. We consider the two mechanisms of initiating the surface generation of point defects. The single kink surface in side view is considered. Mechanism I includes reactions 1, 2, and 3, and mechanism II includes reaction 4.

flat or step surfaces. At the flat  $\{100\}$  surface, we are comparing mechanisms where a vacancy in the surface or an interstitial on the surface is first formed. Likewise, the same considerations apply to the step site on the  $\{105\}$  surface, where a vacancy forms by removal of a step ion and an interstitial forms by adsorption of an ion next to the step.

### C. Calculation of surface defect energies

We have calculated the energy change accompanying formation of vacancies or interstitials individually at defect surface sites. Table I contains results for AgCl and AgBr at 0 and 298 K, where the latter values are deter-

TABLE I. Calculated energy (eV) of formation at constant volume for cation vacancies and interstitials.

Site <sup>a</sup>	0 K			
	AgCl	<i>I</i>	<i>V</i>	AgBr
Flat	5.554	-2.300	5.209	-2.649
Step	5.267	-3.983	4.958	-3.371
Kink	4.722	-4.469	4.431	-4.402
Bulk	5.799	-4.127	5.442	-4.309
			298 K	
Flat	5.503	-3.430	5.174	-2.685
Step	5.202	-3.975	4.895	-3.406
Kink	4.709	-4.455	4.415	-4.196
Bulk	5.739	-4.162	5.406	-4.273

<sup>a</sup>The site designation is explained in the text.

<sup>b</sup>*V* and *I* refer to the energy of formation of vacancy or interstitial from infinity, respectively.

mined with the quasiharmonic approximation.<sup>30</sup> These values represent constant volume energy terms,<sup>31</sup> as opposed to constant pressure terms that are generally measured experimentally. As pointed out by Jacobs,<sup>32</sup> the correction needed to convert the values at constant volume to values at constant pressure is small, and we shall use the constant volume values in comparison to experimental enthalpy values for the low temperatures used in this study. The energy of formation refers to the removal of an ion to infinity to form a vacancy with a corresponding interstitial formation in the reverse process. Thus positive values indicate that energy is required for the process. Many of these processes can be conveniently visualized through the energy diagrams in Fig. 3. Here we compare the energy of a silver ion at various sites in the crystal referenced to vacuum. The adsorbed ion as well as lattice ions are considered in these plots. Lattice ions are the most strongly bound, and adsorbed ions on the flat {100} surface the most weakly bound. From the data in Table I we note that vacancies are formed with the most difficulty in the bulk, and become progressively easier to form as we move from flat to step to kink surfaces. Interstitial silver ions are most stable in the bulk or at the negative kink site, and least stable on the {100} surface where they bind over the center of four ions. There are small variations caused by temperature. The calculated Frenkel energy is just the sum of the interstitial and vacancy formation energies in the bulk shown in Table I, and gives 1.58 eV for AgCl and 1.13 eV for AgBr at 298 K. Experimental enthalpy values summarized by Friauf<sup>33</sup> are 1.45–1.49 eV for AgCl and 1.07–1.16 eV for AgBr from several different measurements. Our calculations reproduce these values well.

#### D. Evaluation of surface mechanisms

We consider the energies of reactions 1–5 in terms of the values reported in Table I. We write the energy change of each reaction as

$$E_1 = V + I, \quad (6)$$

$$E_2 = I(\text{bulk}) - I, \quad (7)$$

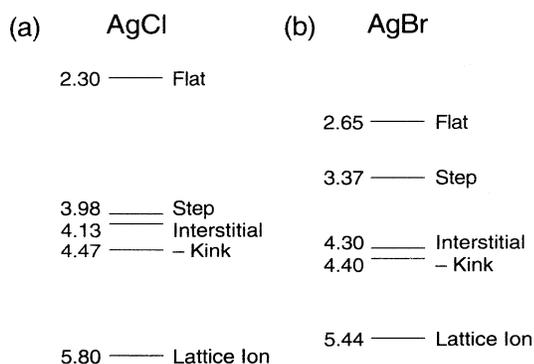


FIG. 3. The energy (eV) of a silver ion at various surface sites and the normal lattice sites is shown at 0 K for AgCl in (a) and AgBr in (b).

$$E_3 = V(\text{bulk}) - V, \quad (8)$$

$$E_4 = V(\text{bulk}) + I, \quad (9)$$

$$E_5 = I(\text{bulk}) - I, \quad (10)$$

where we shall recall that  $V$  and  $I$  refer to surface or bulk vacancy or interstitial formation energies, respectively, with reference to infinity. These values are calculated and presented in Table II for reactions 1–5, where we note that reactions 2 and 5 have the same value. In order to determine which of the two possible mechanisms is most favorable, we compare  $E_1$  with  $E_4$ , since these are the energy changes for the first steps in either mechanism. The path with the smallest energy should predominate. The data shown in Table II clearly indicate that reaction 1, involving surface ionization, should predominate over reaction 4, involving ionization of bulk lattice ions at all three of the sites considered. Perhaps this is not surprising in retrospect, since surface ions have fewer bonds (nearest neighbors) to break than the corresponding ion in the bulk. When we compare results for the different types of surface sites, we see that the energetic requirements are smallest at the kink sites for reaction 1. This result is also consistent with the general expectations noted above. Thus bulk interstitial formation is concluded to form most easily from ionization of sites on the surface.

We can now consider the nature of the space-charge layer as dictated by the competition between reactions 2 and 3. The data in Table II support interstitial silver ion formation relative to bulk vacancy formation for all three sites considered. In many cases, reaction 2 proceeds with a decrease in energy. This means that the surface will acquire a net negative charge due to the excess of surface vacancies relative to surface silver ions. Likewise the bulk will acquire an excess of interstitial silver ions. This

TABLE II. Computed reaction energy (eV) for various defect mechanisms.

Site	0 K		298 K	
	AgCl	AgBr	AgCl	AgBr
	$E_1 = V + I$			
Flat	3.25	2.56	2.07	2.49
Step	1.28	1.59	1.23	1.49
Kink	0.25	0.03	0.25	0.22
	$E_2 = I(\text{bulk}) - I$			
Flat	-1.83	-1.66	-0.73	-1.59
Step	-0.14	-0.94	-0.19	-0.87
Kink	0.34	0.10	0.29	-0.08
	$E_3 = V(\text{bulk}) - V$			
Flat	0.25	0.23	0.24	0.23
Step	0.53	0.48	0.54	0.51
Kink	1.08	1.01	1.03	0.99
	$E_4 = V(\text{bulk}) + I$			
Flat	3.50	2.79	2.31	2.72
Step	1.82	2.07	1.76	2.00
Kink	1.33	1.24	1.28	1.21

picture is entirely consistent with the accepted structure of the space-charge layer in silver halide.

### E. Double-kink model

A double-kink model was prepared by removing two adjacent rows, each consisting of four pairs of ions in a fashion similar to the kink models described above. A sketch of this model is shown in Fig. 1. The double-kink model is thought to represent a neutral kink site<sup>5</sup> because it consists of adjacent and oppositely charged ions right at the kink sites. We consider the loss of a silver ion from the most exposed edge of the double kink, and the adsorption of a silver ion at the inner edge of the kink near halide ions. The energetics of defect formation at this site is like that step sites, but unlike that at the charged kink sites. Table III contains the data calculated for this kink site. We observe that the most favorable pathway is by ionization of the surface defect sites ( $E_1$  less than  $E_4$ ), which is like that for charged kink sites. The bulk interstitial formation is more favorable than the bulk vacancy formation, in line with the results for the other surface sites. Still, reaction 1 proceeds with a much higher energy on the double-kink than the single-kink sites, and is more in line with the behavior we report for step and flat surfaces. Apparently, the effective charge of the surface defect site plays an important role in determining the energy required for the initiation step.

### F. Surface defect energies in NaCl

We examined point defect formation at NaCl surfaces in order to analyze our computed data better, and to facilitate comparison with experiment. In NaCl, the elastic constants do not exhibit the large Cauchy violation mentioned in silver bromide and chloride. Thus we can employ the two-body form of interatomic potential<sup>34</sup> with greater confidence in NaCl. A second point is that substantial experimental data<sup>14,35</sup> exist for comparison for NaCl. A complicating factor, as far as our analysis is concerned, is that Schottky defects predominate in NaCl. This means that in terms of the mechanisms in Eqs. (1) and (4), only reaction 4 need be considered, since interstitial formation is not significant in NaCl. Thus we consider reaction 4 for the formation of bulk vacancies of sodi-

TABLE III. Calculated energy (eV) of point defect formation at double kinks.

0 K		298 K	
AgCl	AgBr	AgCl	AgBr
$E_1 = V + I$			
1.22	1.28	1.15	1.25
$E_2 = I(\text{bulk}) - I$			
0.00	-0.55	-0.02	-0.52
$E_3 = V(\text{bulk}) - V$			
0.46	0.41	0.45	0.41
$E_4 = V(\text{bulk}) + I$			
1.67	1.68	1.60	1.66

um and chlorine ions at negative and positive kink sites, respectively.

The calculated energies of formation for vacancies is shown in Table IV for NaCl. First, the vacancy energies are computed with respect to infinity. These energy terms are rather similar for the anion and cation vacancies. There is one important contrast, however, with the results determined for the silver halides. We find that interstitial ions are more stable in the bulk of silver halide as compared to any surface site. This is opposite to the behavior for anion or cation interstitials in NaCl, and consistent with the virtual absence of Frenkel defects in this material. The energy values computed for reaction 4 are also shown in the table. The data indicate that vacancy generation at kinks is predominant, and that the energies are rather similar for the anion and cation vacancies. We will see below that this result is very consistent with experiment.

### G. Entropy of point defect formation in AgBr

The entropy of formation of individual point defects in the bulk of silver halide can be computed from the vibrational frequencies of the crystal in the presence of a defect. Catlow *et al.*<sup>23</sup> computed the Frenkel defect entropy in silver halide using the high-temperature harmonic approximation

$$\frac{S_v}{k_B} = -\ln \left[ \frac{\prod_{i=1}^{3N'} W'_i}{\prod_{i=1}^{3N} W_i} \right] + 3(N' - N) \left[ 1 - \ln \left[ \frac{\hbar}{k_B T} \right] \right], \quad (11)$$

where  $N$  and  $N'$  are the numbers of ions, and  $W_i$  and  $W'_i$  are the vibrational frequencies in the initial and final states of the crystal, respectively. The formation entropy is at constant volume,  $\hbar$  is Planck's constant,  $k_B$  is Boltzmann's constant, and  $T$  is the temperature. This method of calculation is programmed in the SHEOL code.<sup>36</sup>

TABLE IV. Energy of defect formation (eV) at various NaCl surface sites at 0 K.

Site	$V_{\text{Na}}$	$V_{\text{Cl}}$	$I_{\text{Na}}$	$I_{\text{Cl}}$
A. Vacancy and interstitial energies relative to infinity				
Flat	5.14	5.22	-2.23	-2.24
Step	4.86	5.01	-2.44	-1.86
Kink	3.99	4.40	-3.93	-4.11
Bulk	5.14	5.11	-1.58	-1.21
B. Vacancy energies relative to surface sites				
	Na		Cl	
	$V(\text{bulk}) + I$		$V(\text{bulk}) + I$	
Flat	2.91		2.87	
Step	2.70		3.25	
Kink	1.21		1.00	

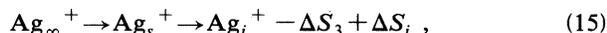
TABLE V. Calculated entropies of formation in AgBr at 298 K at constant volume (eu).

A. Relative to infinity	
$\Delta S_1$	$\Delta S_2$
-4.8	8.9
B. Relative to surface	
$\Delta S_v$	$\Delta S_i$
-0.4	5.0

We follow the procedure above to calculate the entropy of formation values in the bulk crystal. It will be necessary to make an approximation to convert these data to values appropriate to the surface. We compute the entropy change at constant volume for



where the subscripts refer to the cation at infinity, on the surface site or interstitial site. The computed values are given in Table V, where we note that interstitial formation has a positive value, and vacancy formation has a negative value. Now we consider an approximation to separate out the surface term. These reactions can be written to proceed through a site on the surface:



where we have written the corresponding entropy changes next to each reaction. We note that the step involving the exchange of a surface cation with infinity is common to reactions 14 and 15. This term ( $\Delta S_3$ ) cannot now be calculated, but will be approximated. We consider that the entropy change for movement of the silver ion from infinity to the surface site will be roughly half that for movement from infinity to the bulk interstitial site. At the surface site there are roughly half the number of nearest neighbors of the interstitial site. Employing this approximation, and using values calculated for  $\Delta S_1$  and  $\Delta S_2$ , we arrive at the values in Table V for the vacancy and interstitial formation entropies from a surface site. The result of our analysis indicates that the majority of the entropy of formation is associated with interstitial formation rather than vacancy formation from the surface. Clearly, this result is dependent upon the approximation we employed, and is preliminary.

#### IV. DISCUSSION

The mechanism of silver ion interstitial and vacancy formation in silver bromide and silver chloride involves a first step in which a positive kink site ionizes to form a bulk interstitial ion and a vacancy bound at the kink. The latter corresponds to a negative kink site. This overall mechanism operates in preference to one in which a bulk silver ion leaves its site and becomes bound to the surface negative kink site. Since it is thought<sup>17</sup> that these kink

sites bear a half-unit charge from a long-range perspective, this preferred mechanism will result in a net negative surface charge through the consumption of positive kinks and the generation of negative kinks.

The kink site models that we employ are hypothetical, but reasonable based upon the geometric structure of the surfaces considered. Experiment has not yet been able to define the microscopic surface structure of active sites on ionic surfaces. Of course, other types of sites might be imagined on the {100} or {111} surfaces. On the latter surface, sites resulting from the octopolar stacking of cubes have been proposed in recent fractal models.<sup>37</sup> Whatever the sites present, they must share important properties with those considered in this work since each should have partial charge and contain ions of lower than bulk coordination. Thus it is believed that the sites considered in this work are realistic representations for sites on various surfaces of silver halide.

A direct comparison of the experimental and calculated energies of vacancy formation is possible in NaCl. Formation enthalpy values have been reported<sup>14</sup> as 1.24 and 1.17 eV for sodium and chlorine vacancies, respectively. Our calculated values at the positive and negative kink sites are 1.21 and 1.00 eV for sodium and chlorine vacancies, respectively; this agrees very well with experiment. This result predicts a slightly positive charged surface apart from entropy considerations. The excellent agreement we observe is good support for the overall analysis procedure we are using to analyze formation energies in ionic solids. It also points to the fact that the positive and negative kink site models that we employ are

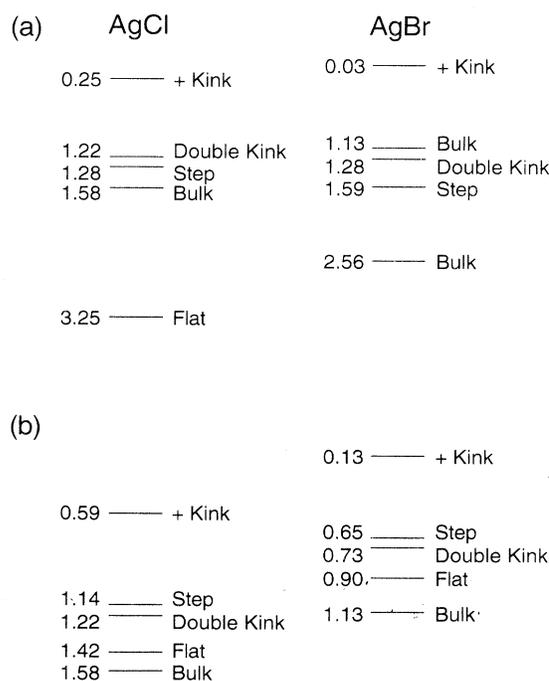


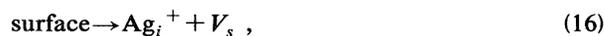
FIG. 4. The energy (eV) for reaction 1 is shown in (a) for AgCl and AgBr. The corresponding energy for reactions 1 and 2 is shown in (b) for AgCl and AgBr.

realistic. Of course, NaCl behaves more according to the Born model of central forces than silver halide, and the possible effect of deviations from this behavior will be examined in the future. Our expectations are that this will result in perturbations of the formation energy values, but not major changes in their values.

Qualitative comparisons between calculation and experimental information about the space-charge layer for silver halide surfaces reveal similarities. For example, ionic conductivity experiments in the presence of divalent cation impurities in microcrystals<sup>1,38</sup> or thin films<sup>11,12</sup> reveal a negative surface charge near room temperature. Other measurements in single crystals<sup>15</sup> are consistent with this feature. This behavior is exactly what would be expected from the point defect generation at each of the surface sites considered in Tables II and III. In each case the energy for reaction 2 is less than for reaction 3. Thus we would expect predominant interstitial formation in the subsurface that would leave a negatively charged surface. Of course, it is the free energies that are involved in this experiment, and for this we must calculate the entropy of formation of the point defects. The entropy values that we calculated would not be expected to lead to free-energy values at room temperature significantly different than the energy values that we calculated.

The energy required for the key surface processes that we have determined for silver halide is sketched in Fig. 4. First consider reaction 1, in which a silver ion and a corresponding vacancy are generated at various possible sites in AgCl or AgBr. The energy required for these processes is shown in Fig. 4(a) at different sites. This sketch shows the relative ease with which kink sites participate in the reaction relative to other sites including the bulk. A reaction leading to the formation of interstitial silver ions may be constructed from the sum of reactions

1 and 2. Here the overall reaction is



where the energy required is just  $E_1$  plus  $E_2$ . This energy is compared at various sites in Fig. 4(b) with the Frenkel energy. This energy for formation of the interstitial silver ion and corresponding vacancy is smallest at the positive kink site, and increases as we move to the bulk.

The attempt to extract quantitative thermodynamic values from these calculations for comparison to experiment is more complicated for silver halide than sodium chloride. Two factors are responsible for this. One is the nature of the surface equilibrium represented in reaction 1. For generation of subsurface interstitial silver ions, the equilibrium is strongly dependent upon the surface vacancy concentration. We estimate that, for the generation of subsurface interstitials, the activation energy for formation is given by the sum  $E_1 + E_2$  which is plotted in Fig. 4.

The second complicating factor for silver halide surfaces is that apparently multiple sites contribute to the generation of point defects. If only the predominant positive kink sites were contributing for AgBr surfaces, the activation energy for formation of interstitials would be rather lower than expected from considerations of the space-charge layer.<sup>9</sup> While single kinks are expected to be the low-energy site for the reaction, other sites have higher concentrations and, thus, could be expected to contribute to interstitial formation even though their energetic requirements may be greater. Thus it may be that in any given experiment the observed energy of interstitial formation will depend upon the relative surface concentrations of different sites. Further analysis of this mechanism in order to allow comparison to experiment is not undertaken at this time.

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