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Heteroepitaxial strain in alkali halide thin films: KCl on NaCl

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We have performed Monte Carlo simulations of the properties of a NaCl (001) surface covered by full or partial layers of KCl, for coverages up to 5 monolayers (ML). A wide variety of structures of the film is found. For integer ML coverages we find the continuous, so-called floating mode rumple structure, as was previously found in the KBr/NaCl system. However, for a coverage of ∼2.1 ML, we find a discrete structure of periodicity 3:4 of small regularly spaced KCl pyramids. It has the same scattering characteristics as the structure observed by Henzler *et al.* [Phys. Rev. B **52**, 17 060 (1995)], but it is two-dimensional modulated, rather than the rowlike stacking fault structure proposed by Henzler *et al*. Also, at a coverage of ∼0.8 ML there is a stable 3:4 structure. Other structures are found at intermediate coverages, corresponding to regular arrays of dislocation lines with periodicity 9:10. A further growth from such structures would give rise to growth of a ∼5° miscut KCl crystal relative to the NaCl lattice. The reciprocal space patterns corresponding to the continuous and the discrete film deformations are also calculated. [S0163-1829(99)00947-9]

I. INTRODUCTION

The relief of strain at epitaxial interfaces is of scientific and technological interest in many systems. In some cases, the consequences of strain are to be prevented (in heterostructure devices for example). In other cases, strain relief can result in desired properties (such as creating a self-organized mesostructure). In a recent review Mooney[1] discusses the problem for the technically relevant semiconductor interfaces with rather large misfits (∼4%). However, it is difficult to study even misfits of this size in atomistic detail using simulation methods, because it requires very large system sizes. An advantage is therefore to study model systems with very large misfits. These are found in the interlayers between different kinds of alkali halide salts.[2,3] Previously we made a simulation study of KBr/NaCl, which has a 17% misfit.[4] The general strain relief mechanism was by a ''floating''-mode rumpling mechanism. After a few rumpled layers perfect KBr could again be formed, with the same orientation as the substrate. These systems are experimental realizations of Frenkel-Kontorova models[5,6] in which unusual morphologies arise from relaxation of atomic positions or defect formation in order to accommodate a heteroepitaxial misfit. However, contrary to these models, which treat the substrate as a rigid corrugation potential, we find that the substrate undergoes as large deformations as the added film. This will probably be the case for most interfaces between elastically similar materials.

Henzler *et al.*[7] made the interesting observation that in the KCl/NaCl system, for which the misfit is ∼10%, both the floating mode and a ''discrete'' mode of strain relief could be found. He proposed the latter to be essentially of the type observed in the semiconductor case.[1] Accordingly, we set out to see if we could obtain the different modes in our simulation.

The alkali halides are ionic crystals for which the interaction is probably the best known of all substances. It is dominated (90%) by the exactly known Coulomb force. From that point of view they are ideal as model systems. However, the long-range nature of the Coulomb makes simulations very challenging technically. In this paper, we have tested the previously used and the presently used Monte Carlo calculations against exact Ewald calculations of the long-range potential.

The buildup of strain is presumably in several respects of similar nature for ionic crystals as for other systems with regard to the hard sphere properties of the ions. However, the ions are ideally spherical, contrary to those in more covalently bound crystals, and there is no screening of the Coulomb field as in metals. A further property of the ionic crystals is that any local unbalance in charge sets up long-ranging dipolar fields, similar to the elastic strain fields,[8] without possessing the crystal symmetry. This could be of importance especially for fractional coverages, which we shall study in the paper, since defect stabilized structures may interact directly via the Coulomb field. In a previous study, fractional coverage was studied in systems having Van der Waals interactions only, but without the Coulomb interaction.[9,10]

II. THE POTENTIAL AND COULOMB SUMMATION

At the interface of greatly mismatched layers, atomic displacements are likely to be outside the range of any harmonic potential approximations, such as are familiar in phonon lattice dynamical calculations. We therefore follow Gowda,[11] and use a phenomenological potential between ions i and j with charge p_i and p_j at a distance r. This is very well approximated by the following form

$$V_{ij}(r)=p_ip_je^2\left\{\frac{1}{r}+\frac{(\alpha_i+\alpha_j)}{2r^4}+\frac{2\alpha_i\alpha_j}{r^7}\right\}-\frac{C_{ij}}{r^6}+A_{ij}\exp\left(-\frac{r}{\rho_{ij}}\right). \tag{1}$$

In the study of KCl on NaCl, we need the interaction potential between all three kinds of ions. The polarizabilities

TABLE I. Potential parameters for alkali halide molecules.

ij	Parameters[b]			Expt. Values	
	C_{ij} [c] (eV-Å ^{6})	A_{ij} (eV)	ρ_{ij} (Å)	R_{eq} [d] (Å)	$-U_{eq}$ [e] (eV)
KK	9.06	3360	0.278		
NaNa	1.09	1622	0.240		
KNa	3.12	2335	0.258		
KCl	16.15	3067[a]	0.347	3.147	7.507
NaCl	5.43	1973	0.316	2.813	8.145
ClCl	29.94	2400	0.461		

[a] Modified to remove pressure in the film; for potential (2) we used the value 2840 from Ref. 12.

[b] Except where noted, from Ref. 12.

[c] Modified.

[d] From Ref. 13.

[d] From Ref. 11.

α_i, the Van der Waals coefficients C_{ij}, and the Born-Mayer repulsive parameters A_{ij} and ρ_{ij}, are basically from Celli and Urzúa,[12] with some modifications. We have tested the sensitivity of our results to modifications of the potential and found that the most crucial factor is to obtain the correct lattice spacings for the energy minima (for the perfect crystals), whereas other features of the potential are much less important. The raw Celli-Urzúa potential parameters do not yield the position of the minima sufficiently accurate and we have, therefore for simplicity, uniformly reduced the already small Van der Waals interaction, in order to reproduce the energy minima and the various lattice spacings as consistently as possible. Table I below lists the parameters for the potentials (1) and (2), which are used in the simulations. The form of potential (1) is shown in Fig. 1.

A long-standing problem in the calculation of the structural properties of the alkali halides has been how to treat the slowly converging Coulomb interactions. Several methods have been devised, which work well for perfect crystals,[14] in particular the Ewald method, which is a partial real and reciprocal space method,[15] but also various fractional charge box methods.[16] In our previous study[4] of KBr/NaCl we devised a simple method that works both for perfect and distorted crystals. The idea is simply to consider the ionic crystal as an assembly of formal dipoles. The Coulomb energy of an ion is found by summing its interaction with its formal partner and the surrounding neutral dipoles in a box size $x \times y \times z$. The method converges surprisingly rapidly to the exact Madelung result for the ideal NaCl structure. Partially as a test, we have in the present paper used a related but different method in which we do not form the formal dipole pairs, but simply account for ions inside a chosen box size, and follow these even if they do some movements. In more detail, ions surrounding the point of interest are recorded in a box extending horizontally 5 mesh spacings in the x and y directions, and to the surface and 5 mesh lattice spacings down in the z direction We find again the same good convergence, accuracy and speed for the perfect crystals as with the dipole method. Both schemes accomplish the charge neutrality necessary for convergence, without excess computational complexity.

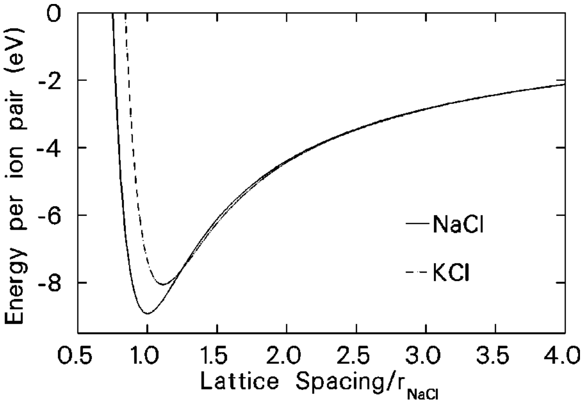

FIG. 1. The interaction potential for NaCl (full lines) and KCl (broken lines). The curves refer to potential (1) in Table I, giving exactly the bulk lattice constant for NaCl but a 0.7% reduced one for KCl.

Since it is more difficult to asses the accuracy for nonperfect crystals (for which the Madelung constant is not known) we have in the present work performed a number of tests using the Ewald method for the semi-infinite system.[17] This is able to correctly include the long-range part of the Coulomb interaction, but is somewhat time consuming. We have found that the above computer-efficient cut-off methods are accurate within 1–5 K for the *energy difference* between any two disordered structures having the same number of ions (periodically repeated). This is proved by calculating the corresponding energy difference using the Ewald method. This is important because in a Monte Carlo simulation, all we need is the energy difference between the initial and the presently simulated state. Hence, the approximate methods are valid and accurate for this use also for distorted crystals, as long as the individual ions remain close to the original position, as in the cases here studied. Clearly, if ions are allowed to migrate freely the above simple methods of *keeping track* of the ions must be modified, however the general idea of the approximation should still work as long as the charge neutrality principle can be maintained. The reason for the achieved accuracy and convergence is that in the dipole method, for example, calculating the energy difference amounts to calculating the energies of a dipole interacting with an effective quadropole, which is a rapidly converging problem.

On the other hand, not surprisingly, we find that the approximate methods are not very accurate in calculating the *absolute energy* of a single ion in the system. That may be off by ~15% corresponding to as much as ~1500 K per moving ion. The reason for this is essentially that the cut-off methods neglect the large Coulomb-tail extending from the about 5 cells to infinity, see Fig. 1. Consequently, we only compare energy differences and only for systems having the identical number of ions.

The Monte Carlo calculation is a further development of the continuous method used for studying adsorbed rare gases on graphite.[9,10] The atoms are formally recorded in a mesh, but are free to do any excursion in a small sphere from a given position. The energy of an atom is tested before and after a move, which is then accepted or rejected by the standard Metropolis rule,[18] which introduces the temperature by the Boltzmann factor. The continuous method has the advan-

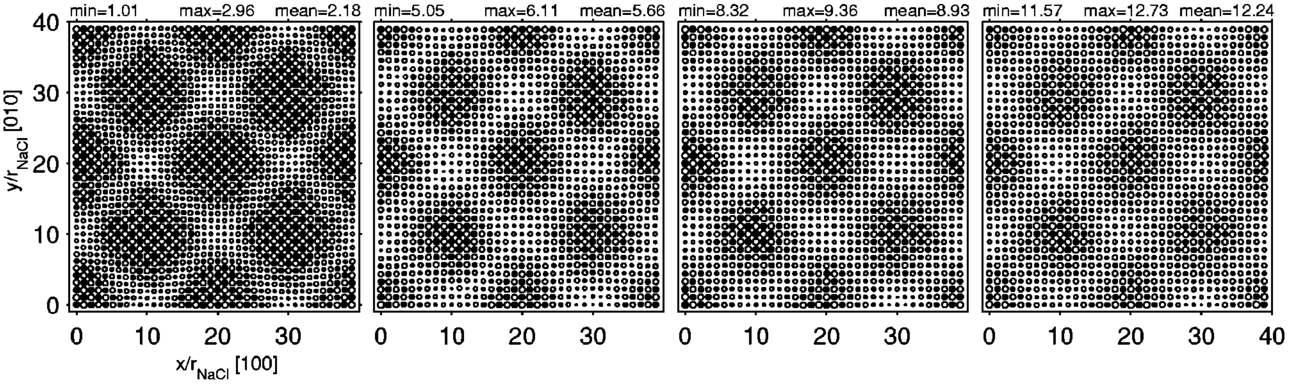

FIG. 2. The calculated ''rumpled'' structure for three ML coverage, {110} planes, showing the top substrate layer to the left, and consequently the added layers at full coverage. ● indicates cations, Na^+ and K^+, and ○ indicates the Cl^- ions. The magnitude of these signatures indicate the vertical displacements, such that the largest correspond to the maximum shown at the top in Å and the smallest the minimum, also shown at the top. We notice an almost regular ''rumple'' pattern of period 9:10 penetrates through all layers, weakening at the top layer. Also notice strong horizontal modulation of the top substrate (0) and first film (1) layers.

tage over lattice gas models in treating the strains set up by the lattice mismatch exactly. The advantage of Monte Carlo methods, and in particular the lattice gas models, is that they are very efficient on a computer, thus allowing principally interesting *statistical* phenomena to be studied.

Because KCl and NaCl nearest-neighbor distances fit nearly in a ratio of 9:10, simulations are performed with KCl films of $9n\times9n$ on top of NaCl substrates that are $10n\times10n$ atoms, where n is an even integer—because of the difference in the ionic charges. Excess strain caused by the inexactness of a fit to the 9:10 ratio is first minimized by using large n, and then altogether eliminated by periodic boundary conditions and adjusting the KCl optimum potential so as to yield a lattice constant of 3.125 Å, for which 36 KCl pairs exactly fit with 40 NaCl pairs, thus giving rise to no pressure, as discussed below.

III. RESULTS FOR INTEGER MONOLAYER COVERAGES

A. Full coverage

Since the lattice constants of KCl/NaCl relate as approximately 9:10, and there are cations and anions of opposite charges, the smallest substrate cell, which can be used has 20×20 substrate ions. However, in order to minimize effects from the periodic boundaries we have chosen to use the relatively large cell with 40×40 Na^+ and Cl^- ions. This can ideally be covered by layers of 36×36 K^+ and Cl^- ions. We start from a perfect substrate crystal covered by various numbers of perfect KCl monolayers (ML). The ions in the six top layers of the substrate and all ion positions in the films are allowed to relax in the Monte Carlo simulation. We find for all numbers (1, 2, 3, 4, and 5) of the added perfect KCl layers that the resulting structure is a rumpled one with an approximate periodicity 9:10 (more strictly the periodicity is 18:20 because of the two different kinds of ions with opposite charges). This is the expected structure in analogy with the structure found for KBr on NaCl experimentally[2] and in our previous Monte Carlo simulations.[4] The typical structure is shown in Fig. 2 for three film layers and the top substrate layer. Exactly similar rumples are found for the coverages with one and two layers only. The rumple amplitudes are shown in Fig. 3 for the different number of added mono layers. Notice the large deformation of the top substrate layer.

For one ML the simulated structure agrees with that experimentally found.[7] We return to the situation for higher coverages below. Since the KCl/NaCl and the KBr/NaCl are very similar physically it is apparently not surprising that the behavior is quite similar, and that we in both cases obtain the ''floating'' deformation mode.

B. Pressure effects

However, an effect was observed in our simulation for, in particular, the 1-ML coverage case. When using the potential (2), which gives the correct lattice spacing for bulk KCl we found that a few rows of KCl are pushed slightly out of the 1-ML film, as shown in Fig. 4, left (larger symbols indicate larger z coordinates). The reason for this is that 36 KCl lattice spacings = 113.3 Å is ≈1% larger than 40 NaCl lattice spacings = 112.5 Å to which the simulation box is matched. Accordingly, even with the rather large cell used, there is an effective pressure acting on the KCl film. This pressure is relieved by the outward relaxation of the rows of KCl. We notice that it occurs as rows of KCl electrical dipoles lined up in the ⟨100⟩ directions, and preferentially on top of the highest regions in the rumpled structures. To test the pressure hypothesis, we made simulations using a potential (3),

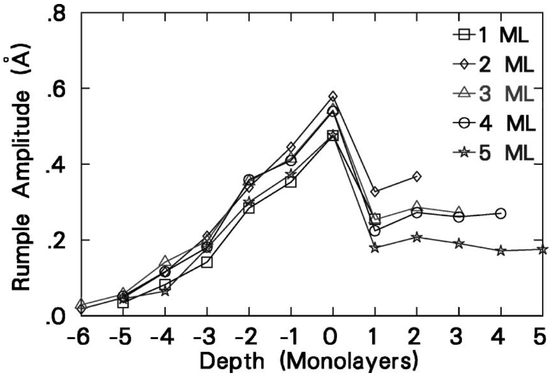

FIG. 3. The fitted rumple amplitudes for one to five added mono layers. The zero indicates the top substrate layer.

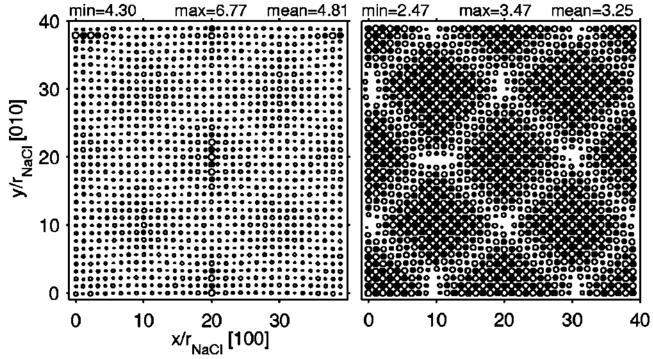

FIG. 4. Right, the first add-layer calculated using a potential (3) having a 2.5% too small KCl lattice constant, yielding a ''negative pressure'' in the film, and giving rise to ripples in the film oriented almost alternatively in the [100] and [010] directions. Left, similar for a potential (2) having a 1% too large lattice constant, and hence a positive pressure. Rows of dipoles are then protruded in the high density regions along [100] and [010] directions. The rumple amplitude is in both cases about the same.

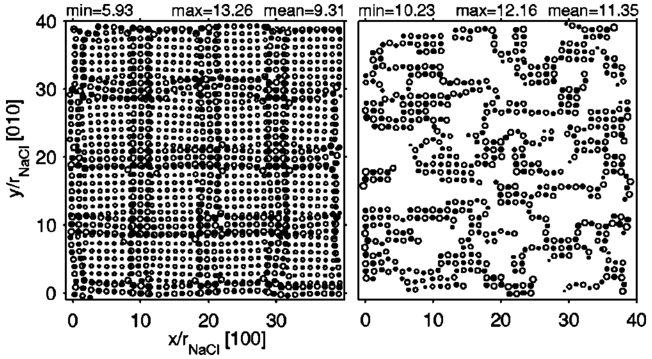

FIG. 5. Structures for 2.5-ML coverage. Right, top layer of relaxed, random 0.5-ML coverage over a 2-ML rumpled structure. Left, structure with regular dislocation lines along the ⟨100⟩ directions and spacing ~10 NaCl lattice spacings. They spontaneously all form with an additional add-layer in the same direction, corresponding to the onset of a growth of a uniformly miscut crystal in the [1,1,0] direction.

which is constructed to give a 2.5% smaller lattice constant and hence a negative pressure. Then, instead, narrow voids are formed in the rumple structure, again in the ⟨100⟩ directions, and in the regions where the misfit is largest, Fig. 4, right. To avoid the effect of pressure one either has to choose unmanageable large simulation cells (~4000×4000) or slightly adjust the KCl lattice constant by a reduction by 1%. We have chosen the latter solution, and have performed most of the simulations using potential (1), which has no pressure mismatch with the 40×40 NaCl cell. In a real crystal the slight additional 1% misfit is presumably relieved by inserting defects or dislocation lines at a larger mesoscopic scale.

IV. FRACTIONAL COVERAGE

A. High density structures

Henzler[7] pointed out that new surprising structures seemed to appear in the KCl/NaCl system at a nominal coverage of about 2.5 ML, characterized by having an approximate 3:4 periodicity. Hence, we have made extensive simulations for this coverage. Contrary to the case of physisorbed rare gases on graphite studied earlier,[9,10] where the added particles were able to diffuse over large distances on the surface, we find in the present case of chemisorbed KCl pairs that these are not able to diffuse further than a few lattice constants in the available computer time. The reason is the presence of deep local minima in the energy landscape. The present simulation is designed primarily to study the build up of strain in the substrate and the relaxation of the positions of the ions in the added film. The stability of these structures against relative small movements of the ions can be assessed, but a search for the global energy minimum must be done by trial and error, as it is usually the case in structure determination.

Hence, we shall test a number of likely relaxed structures. At first, the obvious choice for studying fractional coverage at 300 K is to randomly distribute the needed additional pairs of KCl on top of the closest fully covered and relaxed film, for example the 2 ML rumpled film. This configuration very easily falls into local minima in which the added ions form irregular voids and islands, which are often connected by strings of dipoles, preferentially in the ⟨100⟩ directions, Fig. 5, right. No major rearrangement of the 2-ML structure can, however, be expected to arise spontaneously from such a configuration. Instead it may be instructive to test with one pair of KCl ions where the optimum position of a single pair is on a rumpled 2-ML film. We have found that to be in a checker board pattern favoring islands of 8×8 ions centered on top of the maxima in the rumpled KCl 2-ML film (oriented with the side along the ⟨100⟩ directions).

As a first start structure (a) we have then chosen to fit 3200 ions, corresponding to a coverage of 2.47 ML in the form of 2 rumpled ML decorated with 512 ions in the square pattern described and in addition 96 ions uniformly surrounding these patterns, in all 608 additional ions. The resulting relaxed structure is a regular pattern of islands. It is found to be at least meta stable at a temperature of 300 K, however, the periodicity remains of course that of the rumpled structure 9:10. As an other choice (b), inspired by Henzlers suggestion of a structure with regular close rows of {111}-type stacking faults, we used as start configuration a coverage of two high density mono layers of 40×40, having again 3200 ions. Stacking-fault-like vertical relaxation was introduced by elevating by 1/3 lattice constant stripes of ions in a regular pattern along the ⟨110⟩ directions and with separation of 4 NaCl spacings, which was the modulation observed by Henzler. This structure was not stable, but instead deformed into a disordered structure where wedges of ions were protruded in the ⟨100⟩ directions having a spacing of about 10 NaCl lattice constants. The same happened if the separation at the outset was another than 4 NaCl spacings. The effect is similar to that found for the pressurized film.

Guided by this observation we tested a structure in which the two films were instead distorted by a regular pattern of elevated wedges in the ⟨100⟩ directions separated by 10 NaCl lattice distances. This structure relaxed into one that was at least meta stable at 300 K and is shown on Fig. 5, left. Again the periodicity is 9:10 as for the rumpled structure, but the misfit is in this case relieved by discrete dislocation lines in the ⟨100⟩ directions. Consequently, the modulated ''discrete'' pattern is rotated 45° form that of the ''floating''

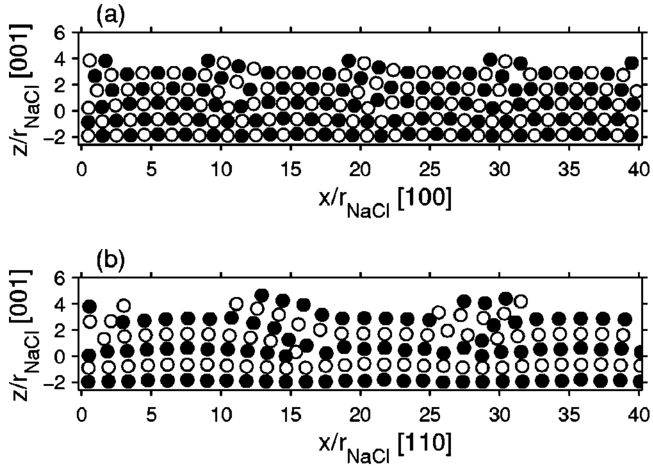

FIG. 6. (a) A vertical cut along a [010] direction through the regular $\langle 100\rangle$ dislocation structure, Fig. 5, left. It shows that the [100] dislocation line may originate in either layer 1, left, layer 0, middle, or the 2 layer, right. Clearly, a regularly stepped surface is the resulting structure. (b) A cut along the [110] direction along the diagonal.

rumpled structure. Figure 6(a) shows the ionic arrangement in this structure for cuts in the $\langle 010\rangle$ direction in the middle of the square pattern, Fig. 5, left. The $\langle 010\rangle$ cross section clearly shows that the induced wedge deformation has transformed into a single $\langle 100\rangle$ dislocation line, and a rumpled layer of KCl on NaCl in between the dislocations. Figure 6(b) shows a cut along the diagonal.

So although it is possible to find an at least meta stable structure at $\sim$2.5 coverage where the addions in addition to the 2 ML are placed as a regular pattern of dislocations, they are very different from those proposed by Henzler in two respects: (i) They are not fcc stacking faults, but dislocation lines running in the $\langle 100\rangle$ directions and (ii) the spacing is 10 NaCl lattice constants. This pattern provides steps on the surface at which further growth possibly could be highly favorable. After further growth a $\sim$4.5° skew or miscut, KCl crystal in the [110] direction will be formed.

B. The 3:4 modulated structure

The low-energy electron defraction (LEED) pattern observed by Henzler at nominally $\sim$2.5-ML coverage showed peaks indicating an unexpected 3:4 modulation. He suggested a corresponding real space picture consisting of regularly spaced *rows* of stacking faults, but without being very concerned with how to retain the two-dimensional (2D) symmetry. In an attempt to find and simulate this kind of structure, we used as a start configuration a choice of less dense overlayers: e.g., by covering the substrate with KCl monolayers having a uniform distribution of 30×30 ions. For coverages of 2 and 3 of these layers the simulation finds a structure that is at least meta stable at 300 K. This relaxed structure has indeed the 3:4 periodicity. It should be noticed that we have also tried to use other low-density coverages, for example using 32×32 ions. In all these cases, one finds rather disordered structures which appear not to be even meta stable, having small remaining, but fading, signs of the start periodicity, in case of the example 4:5. Among these, the simple 3:4 structure is found to be particularly stable and regular. This structure appears to be stabilized by defects, not only by regular stacking faults, but also by point vacancies and in particular by the rumple of the substrate. When starting with three of the 30×30 layers, the resulting structure is depicted in Fig. 7 showing to the left the top substrate layer and then the three additional KCl layers (for clarity for a small part only, corresponding to a 8×8 NaCl cell is shown). The resulting structure can be understood as three new, somewhat vertically distorted layers (indicated by the signature size for the ions). The first layer gives a coverage of 0.77 ML. Including the next layer gives a coverage of 1.38 ML and including the third layer yields a coverage of 2.08 ML. At very low temperatures it is possible to add an additional fourth layer, increasing the total coverage to 2.47 ML. However, this destabilizes the complete structure at 300 K, which reorganizes into rows of electric dipoles. In terms of number of ions in the 40×40 cell these layers have the simple number of ions: 1000, 800, 900 and 500 yielding a total of 3200 ions.

It is thus indeed possible to find an at least meta stable structure at fractional coverages between 2 and 3 ML, which shows the surprising 3:4 periodicity, as observed by Henzler.[7] It has an expected 2D symmetry and shows a regular square pattern of discrete dislocation lines running in the $\langle 110\rangle$ directions. Twice the unit cell is indicated by the drawn square in Fig. 7. In Fig. 8(a) we show a vertical cut in the $\langle 100\rangle$ direction along a diagonal of the square pattern.

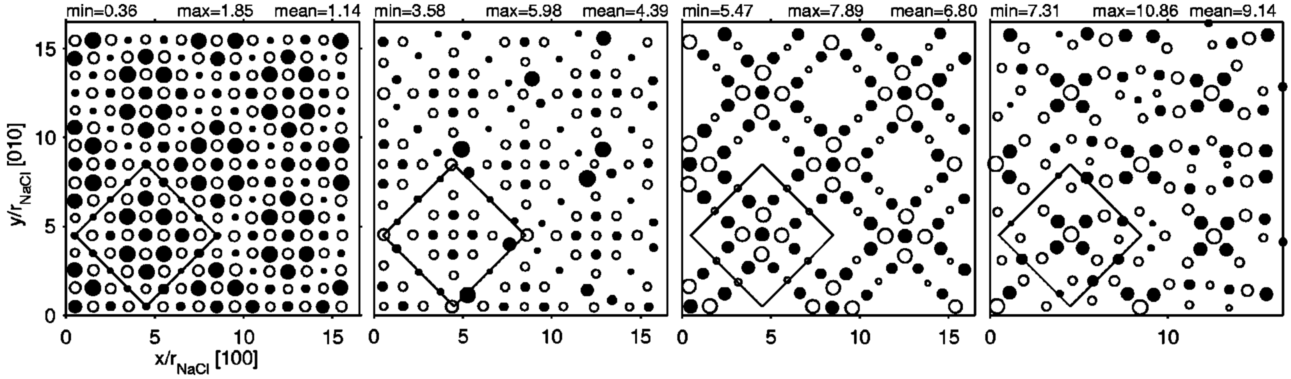

FIG. 7. The ''discrete'' structure for three low-density layers (nominal coverage 2.08 ML), showing top substrate layer to the left and consecutive add-layers to the right. The square shows twice the unit cell; the period is 3:4. Symbols are as in Fig. 2. The structure consists of a sequence with the indicated square as base, in between are some rather disordered ions, not forming a nice wedge.

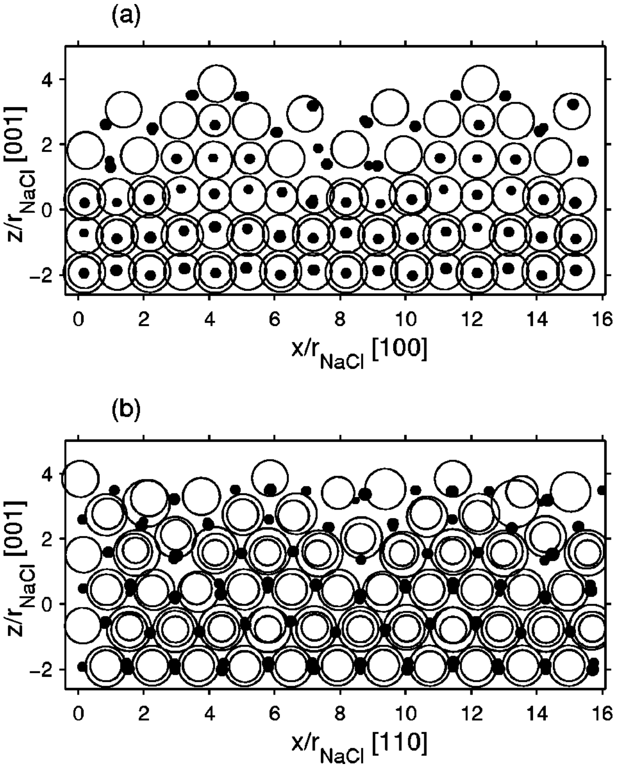

FIG. 8. (a) Vertical cut in the [100] direction along the diagonal of the square, Fig. 7. Recorded are ions in a strip within $\pm 1.1 r_{\mathrm{NaCl}}$. Shown are the top three substrate layers and above the highly structured film. Circles indicate Cl^- ions (these are in this figure made very large in order to facilitate comparison with the Henzler picture), largest symbols are closest to the observer. Diagonal cuts through perfect pyramids at 4 and 12 can be noticed. (b) shows the similar vertical cut along the [110] diagonal of the discrete structure, Fig. 7, in the middle of the square. The structure consists of small dense pyramids which are centered around 0, 6, and 12. One might alternatively view the structure as consisting of disordered ''wedge pieces'' depressed into the substrate at 3, 9, and 14. Ions within the strip $\pm 2.5 r_{\mathrm{NaCl}}$ from the [110] diagonal are recorded and plotted.

And Fig. 8(b) shows the vertical cut of the structure in the ⟨110⟩ direction in the middle of the square. This cut is identical to the cut depicted by Henzler, in the paper proposing the structure stabilized by stacking faults. Hence, we have plotted the Cl^- ions similarly as large circles to ease the comparison (largest indicates closest to the observer), we have in addition indicated the positions of the positive ions (●), which Henzler did not. Figure 8(b) shows all ions in a strip almost as wide as the indicated square. This and Henzlers picture are indeed quite similar. However, there are also significant differences. In the structure proposed by Henzler, regular wedges of ions (formed by a pair of {111} and {1-11} glides) are *protruded* in the ⟨110⟩ directions. In the simulated structure, the ''wedges'' are not the dominant feature, on the contrary rather open valleys *penetrate* into the substrate between small pyramidal formations. Further, the substrate is strongly corrugated with a periodicity of 4 NaCl lattice spacings. Clearly the locally strongly curved NaCl surface allows a better fit to the attached, slightly larger KCl pyramidal crystallites. For larger spacings it may be difficult to obtain a sufficient curvature for this to be energetically favorable. We believe the small scale rumple of the NaCl surface is playing an important role in stabilizing a 3:4 modulation. Henzler did not discuss how the stacking faults running in the (110) directions were to cross those running in the (1,−1,0) directions. Such are expected by the 2D symmetry, and also on the basis of the measured LEED pattern. We have found that the 2D symmetry is locally retained. In this situation the effect of the small energy of a {111} glide, which was proposed by Henzler to be the stabilizing mechanism, does not have a chance to play a significant role, since the extent of the stacking fault on the side of the pyramid is very small. For smaller misfits, where the sepation between the wedges is larger, the 60° {111} stacking fault mechanism is expected and often found.[1]

In the present simulation we find that the crossing is quite nontrivial, see the topview, Fig. 7. It gives rise to asymmetry in particular in the second layer for coverage with two layers. Here, around the central K^+ ion (●) in the pattern inside the indicated square a single apparently unpaired K^+ appears in place of one of the four pairs (●●). This ''odd'' ion is surprisingly needed to maintain charge neutrality, as discussed below. At 300 K a structure with this ''odd'' ion placed in a periodic pattern is stable, however also a pattern where it is randomly placed in the four symmetric positions in the neighboring square cells is stable in the simulations. We do not show this patters since it can be imagined from the similar second layer of the structure, shown on Fig. 7, which is spontaneously found when starting with the three perfect, uniformly stretched 30×30 layers. Although, the second layer is here more symmetric. For only two layer coverage one of the pairs is randomly replaced by a single ''odd'' K^+ ion, whereas the remaining structure of both first and second layer is almost as in Fig. 7.

It is interesting to study how it is possible to form small quite perfect pyramids of Cl^- ions and K^+ ions having different charge and ionic radii: $R_{\mathrm{Cl}^-} = 1.81$ Å and $R_{\mathrm{K}^+} = 1.33$ Å. The Cl^- ions form a perfect hard sphere pyramid with the number of ions per layers (bottom, middle, top) equal to (9,4,1). Inside, it is only partially charge compensated by a smaller K^+ pyramid with (4,1,0) ions. These pyramids are stabilized by the loosely packed ''wedges'' having (1,4,8) Cl^- and (6,8,8) K^+ ions. By adding the numbers one notices that there is total charge neutrality inside each square with 27+ and 27− ions. However layer two has a surplus of one +charge, whereas layer three has a surplus of one −charge, located at the top of the pyramid. (This explains the need for the ''odd'' K^+ if the third layer is removed.) The surface of the 3:4 structure is therefore polar with a large repeat distance.

Typically, the structures created in the above described start condition show on a larger scale in addition more disorder in which crystallites of almost perfect KCl crystals appear at random positions. An interesting observation is that close to these, occasionally an ion is pulled out of the substrate to participate in the film, thus creating a strain producing vacancy in the substrate. This is a well known effect in which an add layer creates defects in the substrate to accommodate the misfit.[1]

The conclusion is that a structure with a 3:4 periodicity can indeed be found at low-density coverages for KCl on NaCl, with properties compatible with the LEED observa-

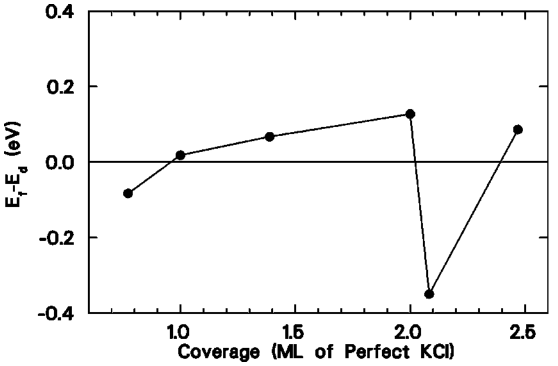

FIG. 9. The calculated energy difference for different structures having the same coverage. This shows that the ‘‘discrete’’ structure is favorable thermodynamically for coverages 0.77 and 2.08 ML, whereas for all other tested coverages and structures the fully covered rumpled structure with averagely filled fractional coverage is superior. At coverage 2.47 ML the ‘‘discrete’’ 9:10 ⟨100⟩-dislocation structure is furthermore the most stable structure found.

tions made by Henzler. Since it is not exactly that proposed by Henzler we shall call it a ‘‘discrete’’ dislocation structure in order to distinguish it from to the ‘‘floating’’ rumple structures.

V. STABILITY ANALYSES

The next question is which of the found, possibly only meta stable structures have the lowest energy, and hence should be thermodynamically stable at low temperatures. To study this we have on Fig. 9 compared the energy differences of structures having pairwise the same coverage. In this way we avoid the problem of comparing the absolute energies of structures having different number of ions. To obtain the needed coverages in addition to the closest number of perfect layers of the floating (f) or the discrete (d) structures we add the missing ions pairwise and randomly on the relaxed closest perfect layer(s) and equilibrate. Based on the structures obtained by the Monte Carlo simulations we evaluate the energies using the exact Ewald method. We find that the discrete structure is indeed most stable for the coverage of 2.08 ML corresponding to the 3 right layers in Fig. 7. At coverage of 2.47 ML we find, however, that the mentioned 2 ML + islands and any of the two structures, shown on Fig. 5, are more stable. Of these three possibilities we find that the structure with the regularly spaced 9:10 ⟨100⟩ dislocation lines is the most stable, Fig. 5, left and Fig. 6. As a result, we find that for less than full coverages, namely at the coverage of 0.77 ML a discrete, defect stabilized structure should be possible. It is essentially the same as that depicted as the first film layer in Fig. 7. This would indeed be very similar to such structures found in the simulations of mono layers of rare gases on graphite.[9,10] There it was found that such structures behaved quite distinct from the elastically deformed ‘‘floating’’ type structures, and in particular had a different epitaxial rotation. Summarizing, only for a coverage of ~2.1 and ~0.8 ML we have found that a structure with periodicity 3:4 is stable. It is only found when starting from a low-density distribution of the film layers.

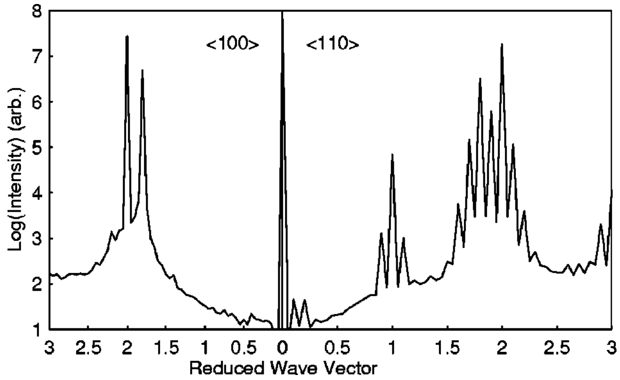

FIG. 10. Cross sections in reciprocal space for the full 2-ML rumpled case, showing the calculated x-ray intensity along the ⟨100⟩ and ⟨110⟩ directions. The major NaCl peaks are at [200], [220] and [110], similarly those for KCl at $\frac{9}{10}$ of these. Notice the additional satellites at the half spacings.

VI. RECIPROCAL SPACE

One of the big advantages of Monte Carlo simulation of structures is that it is possible to study both the real space and the reciprocal space. The reciprocal space measurements provided by x-ray scattering and He-scattering yield information on different aspects of the (average) structure of the outermost layers in the heteroepitaxial films and the substrate. More local information is provided by the LEED method and by real space methods as scanning tunneling microscopy.

In this section we shall present the reciprocal space signatures for the previously discussed relaxed structures. Figure 10 shows the predicted intensity along principal cuts through the horizontal q-space plane for the rumple structure with 2 ML. Characteristic are the film Bragg peaks at $\vec{\tau}_{\mathrm{KCl}}=[1.8,1.8,0]=[2,2,0]-2\vec{\delta}$, where $\vec{\delta}=[\frac{1}{10},\frac{1}{10},0]$ represents the misfit vector, and the associated additional satellite peaks in particular at $\pm N\times\vec{\delta}$ both around (1.8,1.8,0) and (1.8,0,0) peaks and equivalent peaks, where N is a small integer. Figure 11 shows the predicted q-space intensities for the ‘‘discrete’’ 3:4 structure at 2.08-ML coverage. The characteristic peak is at (1.5,1.5,0) and satellites as indicated. Henzler did find the main peaks in his LEED experiment, how-

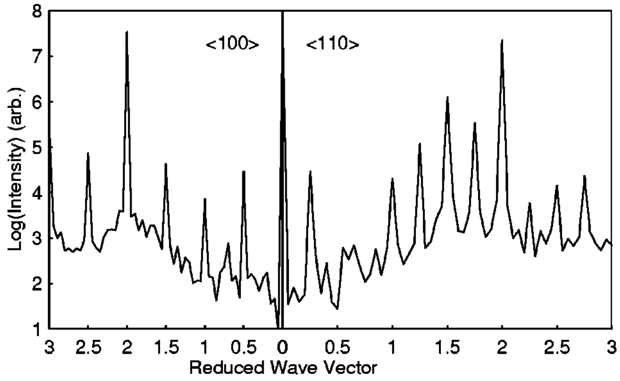

FIG. 11. Same as Fig. 10. for the ‘‘discrete’’ 3:4 structure with three effective layers, corresponding to a coverage of 2.08 full ML. Notice the dominant KCl peaks at [1.5,0,0] and [1.5, 1.5, 0] and the corresponding satellites.

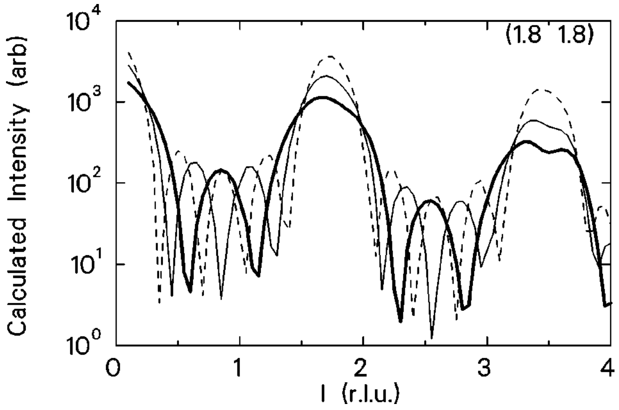

FIG. 12. The q_z variation of the calculated x-ray intensity of the [1.8, 1.8, 0] Bragg rod for the rumpled structure for coverages 1, 2, and 3 ML, heavy full, full and dashed lines, respectively.

ever no satellites are reported found, so a precise confirmation of the simulated structure awaits further experiments at this coverage. Henzler did measure the two-dimensional Bragg rods at a certain angle to the horizontal plane, therefore we have calculated the intensity profiles along the most characteristic rods. Figure 12 shows the Bragg-rod intensity for the rumple structure at $(1.8,1.8,q_z)$ for various number of coverages. Similarly, Fig. 13. shows the Bragg-rods for the 3:4 ''discrete'' structure at $(1.5,1.5,q_z)$. Measurement of these features would give information on the outward relaxation of the film layers, as well as the formation of the intermediate layers formed in the ''discrete'' structures.

VII. CONCLUSION

We have studied a model system of the problems arising at the (001) interface between mismatched cubic crystals. For the KCl/NaCl case the misfit is ~10% which makes it ideal for computer simulation, because it allows study of (periodic) samples much larger than the repeat distances. This is very important in order to realistically deal with statistical properties of and spontaneous defects at such interfaces, where it is not sufficient to consider the energetics of the minimum repeat units. In a previous paper[4] on KBr/NaCl (misfit ~17%) the experimentally observed rumpling behavior was simulated for coverages with a complete number of (unstrained) monolayers. Here, we have studied the influence of small remaining pressures in the films. A resulting mismatch between large repeating cells of just ~1% may lead to noticeable structural defects. For positive pressure within the surface layer rows of KBr pairs are protruded in the [100] directions at the top of the rumple pattern, as sharp wedges with intervals at about 10 NaCl spacings. At negative pressures on the other hand rifts in similar directions at the minima of the rumples are found. With uniformly covering films it was found that quite different relaxed structures could be found when starting from highly dense, zero pressure and low-density films on an uncorrugated NaCl surface. Starting with highly pressurized films perturbed by a variety of wedge protrusions, it was invariably found that the preferred structure was one with line dislocations in an approximate square 10×10 pattern in the [100] directions, which would make a start for further growth of KCl in the from of ''miscut'' crystals with the (001) axis tilted by ~5°. Starting form zero pressure add-layers we find for KCl/NaCl the rumpled structure with valleys in the [110] directions as in the KBr/NaCl case. Starting from low-density films it was on the other hand possible to find a quite unexpected structure with periodicity 3:4, signatures of which Henzler[7] had found in KCl/NaCl at fractional coverages. We are here able to provide a realistic real space picture. Although the structure is somewhat similar, it deviates considerably from the interpretation given by Henzler in particular by the having local 2D symmetry. We have studied a number of fractional coverages, between 0–1, 1–2, and 2–3 ML. The Hentzler-like structure was found to be energetically stable at 2.08 ML, which is somewhat lower than the nominal coverage 2.5 ML in Henzlers experiment.

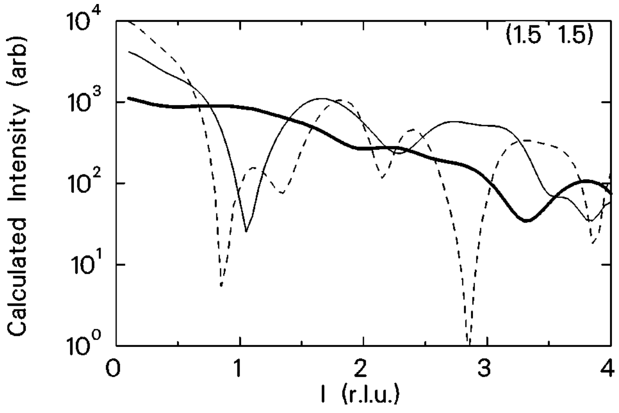

FIG. 13. Same as Fig. 12 for the ''discrete'' structure at the [1.5,1.5,0] Bragg rod for various effective number of layers corresponding to the coverages, 0.77, 1.38 and 2.08 ML, heavy full, full and dashed lines, respectively.

Because of our relatively large simulation cell we were able to find, that at low coverages it was often observed that the system had a tendency to develop nonuniform density and create regions in which rather unstrained, normal density KCl crystallites could be formed at random distances, leaving of course the remaining at even lower density than that at the start. This might be an explanation for the apparent discrepancy between the coverages in the experiment and in our simulation. The large cell also allowed us to observe cases of known defects at such interfaces: For example that a Na^+ ion can be pulled out of the perfect NaCl crystal and put into the surface layers, leaving a vacancy defect, the relaxation around which may help to relieve the interface strain.

The reason for why we find different structures depending on the start condition is that, by the method we use the system is not able to search for the absolute minimum in the energy landscape, but is bound to find only the optimum relaxation in a local minimum. The local minima are separated by large energy barriers. It is in fact likely that the same situation occurs in the experimental situation so that different structures may arise during different (nonequilibrium) growth conditions. Unfortunately, we can not directly relate the growth mode to our various surface layer structures, except to suggest that the effective density may play a very important role. In the simulations we can test the relative energies of the found local minima and thus point at the structures, which are thermodynamically stable (although only among the tested and found structures).

The alkali-halide case constitutes on the technical side a challenging problem in finding an efficient and accurate method of dealing with the long-ranged Coulomb forces. In this paper we have tested the previously used effective dipole method[4] as well as devised an other neutral cluster method and found that with respect to energy differences both methods are very accurate and much faster compared to an exact Ewald summation.

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[1] P. M. Mooney, Mater. Sci. Eng. **17**, 105 (1996).

[2] J. Duan, G. G. Bishop, E. S. Gillman, G. Chern, S. A. Safron, and J. G. Skofronick, Surf. Sci. **272**, 220 (1992).

[3] S. A. Safron, J. Duan, G. G. Bishop, E. S. Gillman, and J. G. Skofronick, J. Phys. Chem. **97**, 1749 (1993).

[4] J. Baker and P.-A. Lindgård, Phys. Rev. B **54**, R11 137 (1996); Jeff Baker and Per-Anker Lindgård, in *Stability of Matter*, edited by A. Gonis, P. E. A. Turchi, and J. Kudrnousky (Plenum Press, New York, 1996), p. 185.

[5] T. Kontorova and Y. I. Frenkel, Zh. Eksp. Teor. Fiz. **8**, 1340 (1938).

[6] F. C. Frank and J. H. v. d. Merwe, Proc. R. Soc. London **198**, 205 (1949).

[7] M. Henzler, C. Homann, and U. Malaske, Phys. Rev. B **52**, 17 060 (1995).

[8] P. Peyla, A. Vallat, C. Misbah, and H. Müller-Krumbaar, Phys. Rev. Lett. **82**, 787 (1999).

[9] E. Vives and P.-A. Lindgård, Surf. Sci. Lett. **284**, L449 (1993).

[10] E. Vives and P.-A. Lindgård, Phys. Rev. B **47**, 7431 (1993).

[11] B. T. Gowda and S. W. Benson, J. Phys. Chem. **86**, 847 (1982).

[12] V. Celli and G. Urzúa, J. Phys.: Condens. Matter **5**, B91 (1993).

[13] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders Company, New York, 1976).

[14] C. Kittel, *Introduction to Solid State Physics*, 2nd ed. (Wiley, London, 1960).

[15] P. P. Ewald, Ann. Phys. (Leipzig) **64**, 253 (1921).

[16] H. M. Evjen, Phys. Rev. **39**, 675 (1932).

[17] D. E. Parry, Surf. Sci. **49**, 433 (1975); **59**, 195 (1976).

[18] N. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).