Effects of Lattice Polarity on Interfacial Space Charges and Defect Disorder in Ionically Conducting AgI Heterostructures

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Heterostructured (β/γ)-AgI exhibits a spontaneous lattice polarization not accounted for in standard space-charge models. This polarization field dominates the positional variation of energies of isolated defects, and Ag^+ vacancies and interstitials are stabilized at alternate [β/γ] interfaces. This suggests enhanced Frenkel pair separation, analogous to electronic charge separation in polar semiconductor heterostructures. Stoichiometric systems are, however, characterized by associated Frenkel pairs due to strong V_{Ag}-Ag_i interactions and show no enhancement of defect numbers. In nonstoichiometric systems, lattice polarization does direct the distribution of the excess defect species, and defect-defect interactions enhance local Frenkel pair concentrations at interfaces, suggesting that nonstoichiometry is critical to the extreme room-temperature ionic conductivities observed in heterostructured AgI nanoplates.

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Nanostructured solid-ionic materials often exhibit ionic conductivities considerably larger than their homogeneous, bulk counterparts [1]. This opens the possibility of improved, tailored electrolytes in batteries, fuel cells, etc., if the effect of sample morphology on the behavior of ionic charge carriers can be understood. A generic explanation of this ‘‘nanoionic’’ behavior has been offered by Maier [2], who noted that a local departure from electrical neutrality may occur at an interface. Of particular interest for engineering high performance electrolytes are layered heterostructures, such as CaF_2/BaF_2 [3–5], in which the defect chemistry is dominated by Frenkel disorder. If the intrinsic chemical potentials of vacancies or interstitials change across the interface, then Frenkel pair separation is predicted to be enhanced, with vacancies stabilized on one side of the interface and interstitials on the other. These oppositely charged defects are confined by their mutual interaction to space-charge layers close to the interface, where they promote a large increase in net ionic mobility. The analysis that leads to this proposal is similar to the textbook treatment of the distribution of electrons and holes at semiconductor *p-n* junctions. Within this model the interaction between vacancies and interstitials is purely Coulombic, and defects are treated as residing in a continuous medium, without reference to the atomistic structure [1,2].

For CaF_2/BaF_2, both components crystallize in the fluorite structure, and planar heterostructures demonstrate shared (111) surfaces that are equivalent due to the nonpolar lattice symmetry. In general, however, crystal lattices in layered heterostructures may have an asymmetric polarity perpendicular to the interfacial plane. In this case, internal interfaces are nonequivalent, since their characterization depends on both the identity and relative orientation of the proximate crystalline layers. The standard formulation of the space-charge model neglects the role of atomic structure, specifically crystal symmetry, and hence may not be appropriate for describing the defect distribution in these polar systems.

Polar heterostructures constructed from alternating wurtzite and zinc blende regions are well known in semiconductor physics, e.g., in III–V nitrides [6,7]. In these materials, differences in spontaneous and piezoelectric polarization between heterolayers produce opposing potential gradients [6,8], resulting in spatial localization of electronic states, enhanced electron-hole pair separation, and phenomena such as quantum wells and quasi-2D electron and hole gases [9–11]. Equivalent polarization potentials in *ionic* polar heterostructures might be expected to cause vacancies and interstitials, formed as Frenkel pairs, to behave similarly to electrons and holes in these semiconductors. This would manifest as enhanced Frenkel pair separation and a corresponding increase in ion mobility.

In this Letter, we describe a theoretical examination of AgI heterostructures, constructed from alternating polar wurtzite and zinc blende domains, in order to understand the relationship between defect distribution and lattice geometry. This model system allows us to assess deviations from the predictions of the standard space-charge model and the extent to which this can be explained by simple electrostatic considerations. Besides studying stoichiometric samples, where the point defects arise from Frenkel pair formation, we also examine nonstoichiometric systems containing an excess or deficiency of Ag^+ ions, which allows the behavior of vacancies and interstitials in isolation to be analyzed.

Understanding the defect distribution in heterostructured AgI is also of practical interest. AgI nanoplates synthesized as two-dimensional layered heterostructures exhibit a conductivity enhancement of $\times 10^4$ at room temperature relative to conventional bulk samples [12–15]. The utility of this behavior has been demonstrated by the use of heterostructured AgI as the electrolyte in an all-solid-state Ag^+ rechargeable battery [15].

Under ambient conditions, bulk AgI typically adopts the wurtzite structured β phase. All ions have tetrahedral coordination, and the structure can be considered as two interpenetrating hexagonally close-packed sublattices. Each ionic species occupies half the vacant tetrahedral sites in the conjugate sublattice, to give the characteristic $[AB]$ stacking sequence. The alternative cubic stacking sequence $[ABC]$ gives zinc blende structured γ-AgI. The highly conducting AgI nanoplates described by Maier and co-workers have been identified as specific "7H" and "9R" polytypes that can be considered as heterostructures constructed from alternating β-AgI and γ-AgI layers [12–14]. It has been proposed that the high conductivity exhibited by these samples arises from space-charge effects at the numerous $[\beta|\gamma]$ interfaces [5]. Ag^+ ions are thought to redistribute from β- to γ-AgI, producing a high degree of defect disorder throughout the sample [1]. Hence the experimentally observed high room-temperature conductivities have been proposed to be an intrinsic property of these 7H and 9R AgI polytypes [14,15].

We modeled a 19-layer heterostructure containing 2128 ions with stacking sequence $[(\mathrm{BCA})_3(\mathrm{BA})_5]$: nine layers with cubic γ-like stacking and ten layers with hexagonal β-like stacking [Fig. 1(a)]. This construction gives an inequivalent pair of $[\gamma \rightarrow \beta]$ and $[\beta \rightarrow \gamma]$ interfaces in the xy plane, where $\rightarrow$ indicates $+z$. Calculations were performed by using the rigid-ion pair potential of Parrinello, Rahman, and Vashishta [16], which uses an empirical $1/r^4$ term to describe polarization-mediated interactions [17] has been used to model defect behavior in both β- and high-T α-AgI [18–20], and reproduces well the known phase diagram across a broad range of temperatures and pressures [21]. Geometry optimizations for static energies used conjugate gradient minimization with a convergence criterion of 2.7×10^{-5} eV in total energy. Calculations were performed at the volume and c/a ratio obtained from fully optimizing bulk β-AgI at zero temperature and pressure [20]. Molecular dynamics (MD) calculations were run at constant NVT at 500 K for 300 000 steps of 200 a.u., equivalent to 1.45 ns, following thermal equilibration. MD simulation of nonstoichiometric conditions was achieved by adding or removing two Ag^+ ions [22].

The defect chemistry of β- and γ-AgI comprises native Frenkel pair formation, $\mathrm{Ag}_{\mathrm{Ag}}^{\times} + V_i^{\times} \rightleftharpoons V'_{\mathrm{Ag}} + \mathrm{Ag}_i^{\bullet}$ [23], and extrinsic contributions to nonstoichiometry, typically divalent cation dopants with charge compensating V'_{Ag}. Both polytypes have tetrahedral and octahedral interstitial sites, $\{\mathrm{Ag}_{i(T)}, \mathrm{Ag}_{i(\mathrm{O})}\}$, whose relative energy depends on the local stacking and whether the interstitial is associated with a neighboring vacancy [24]. The iodide ions vibrate about fixed lattice points and can be used to identify the two sets of tetrahedral sites available to the mobile Ag^+ ions, one set corresponding to the nondefective lattice and the second the set of tetrahedral interstitials. Within close-packed structures the set of all tetrahedra and octahedra are space filling, and any Ag^+ not occupying a tetrahedral site (perfect crystal or interstitial) is assigned as $\mathrm{Ag}_{i(\mathrm{O})}$. The same analysis allows instantaneous vacancy positions to be assigned to the centers of unoccupied tetrahedra.

Figure 1 shows the profile along z of the mean electrostatic potential, calculated by integrating Poisson's equation $\nabla^2 = -\frac{\rho}{\epsilon_0}$, where ρ is the mean charge density from the stoichiometric MD simulation and ϵ_0 is the permittivity of free space. The sharp oscillations along z are due to oppositely charged planes of I^- and Ag^+. Of greater relevance to the distribution of defects is a superimposed $\wedge$-shaped profile with the same 19-layer repeat distance as the simulation cell. This is associated with small differences between β and γ regions in the relative positions of the planes of ions along z. In the β region, average layer-layer spacings are 3.740 Å, and the average z offset between I^- and Ag^+ is 1.274 Å, compared to 3.747 (+ 0.18%) and 1.295 Å (+ 0.16%), respectively, in the γ phase. This variation in the distribution of charge corresponds to the β and γ domains being oppositely polarized and is a consequence of the breaking of translational symmetry introduced by heterostructuring.

The effect of this polarization potential on the energy of independent defects was assessed by comparing energies for optimized cells containing a single defect. The relative energies for an isolated excess Ag^+ interstitial in both tetrahedral and octahedral sites are shown in Fig. 2(a). In the β-AgI regions, the tetrahedral interstitials are higher in

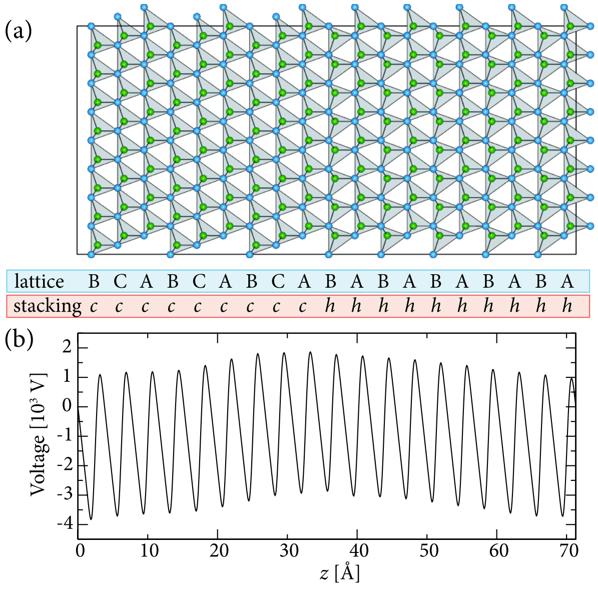

FIG. 1 (color online). (a) A schematic of the close-packed iodine tetrahedra occupied by silver ions in the 19L $[\gamma|\beta]$ cell. (b) The Poisson potential calculated from this cell from MD simulation.

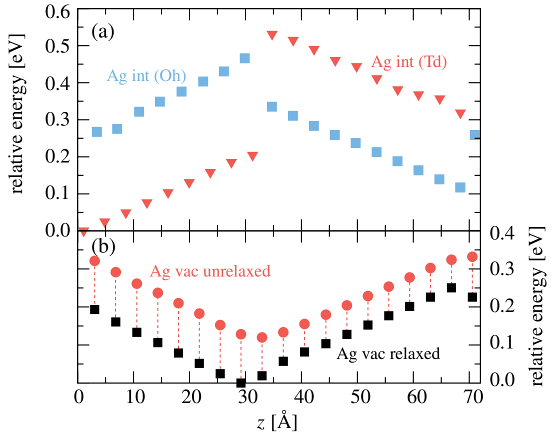

FIG. 2 (color online). Relative energies as a function of defect position for isolated defect species in nonstoichiometric AgI. (a) $\mathrm{Ag}_i^{\bullet}$ (Ag-excess): blue squares (Ag int Oh) show interstitials at octahedral sites, and red triangles (Ag int Td) show interstitials at tetrahedral sites. (b) V'_{Ag} (Ag-deficient): black squares (Ag vac relaxed) are for fully relaxed geometries, and red circles (Ag vac unrelaxed) are for vacancies in the otherwise perfect lattice. The vertical dashed lines indicate the relaxation energy.

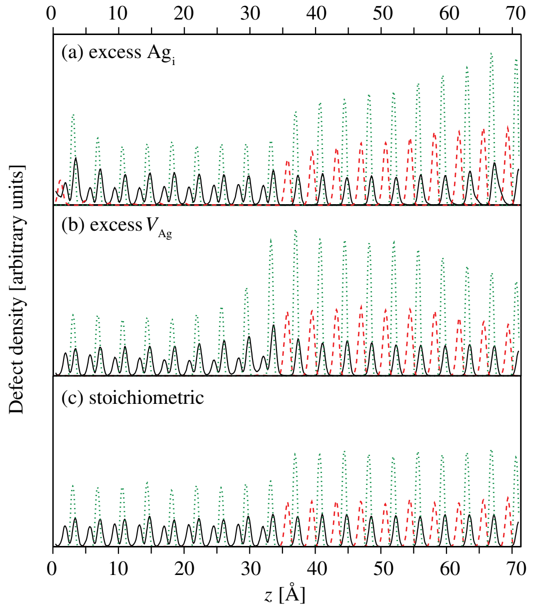

FIG. 3 (color online). Time-averaged defect distributions from molecular dynamics simulations at 500 K. $\mathrm{Ag}_{i(\mathrm{O})}$ are shown with solid black lines, $\mathrm{Ag}_{i(T)}$ are shown with dashed red lines, and V_{Ag} are shown with dotted green lines.

energy than the octahedral, since they correspond to doubly occupied tetrahedral pairs, with a small Ag-Ag separation [24]. In γ-AgI, this order is reversed, again due to the interaction with neighboring occupied Ag^+ sites. The interstitial energies follow the $\wedge$ profile of the polarization potential, with the most stable position at the $[\beta \longrightarrow \gamma]$ interface and the least stable at the $[\gamma \longrightarrow \beta]$ interface. This is consistent with the interstitial energy varying as for an infinitesimal point charge in a polarized medium.

The z dependence of relative energy for excess vacancies shows an approximate negative correlation with the Poisson potential [Fig. 2(b)]. Here the most stable position is approximately at the $[\gamma \longrightarrow \beta]$ interface and the least stable at the $[\beta \longrightarrow \gamma]$ interface. The minimum energy is not precisely at the $[\gamma \longrightarrow \beta]$ interface and as such does not precisely follow the Poisson potential, since relaxation energies vary with the local geometry around the vacancy (see [25]).

Figure 3 shows time-averaged defect distributions along z, obtained from MD simulations, that reveal the behaviors of thermally generated populations of Frenkel pairs and of the extrinsic defect species under conditions of excess Ag_i or V_{Ag}. These profiles are strikingly different from those predicted by simply considering the energies of isolated defect in otherwise perfect lattices. For example, in all three cases the relative proportions of $\mathrm{Ag}_{i(\mathrm{O})}$ and $\mathrm{Ag}_{i(T)}$ are the opposite of those suggested by Fig. 2, since these interstitials are now able to coexist with neighboring vacancies as Frenkel pairs or extended defect complexes.

Under nonstoichiometric conditions [Figs. 3(a) and 3(b)], the behavior of the excess defect species is, however, as anticipated by considering the isolated defect energies. For excess Ag_i the interstitial density is greatest at the $[\beta \longrightarrow \gamma]$ boundary, and for excess V_{Ag} there is an enhancement of V_{Ag} density at the $[\gamma \longrightarrow \beta]$ boundary. Interestingly, in both cases the counterdefects arising from intrinsic Frenkel pair formation, and having opposite effective charges, are also enhanced in the same regions: Ag_i concentrations are enhanced at the $[\gamma \longrightarrow \beta]$ interface under Ag-deficient conditions, and V_{Ag} segregates to the $[\beta \longrightarrow \gamma]$ boundary under Ag-excess conditions. This local increase in minority defect numbers can arise only if Frenkel pairs are able to form more easily in the vicinity of the *excess* defect species, corresponding to an associated reduction of the Frenkel pair formation energy.

If thermally formed Frenkel pairs in a stoichiometric sample could be considered as composed of noninteracting defects, then enhanced defect separation might be expected, with interstitials segregating to the $[\beta \longrightarrow \gamma]$ interface and vacancies to the $[\gamma \longrightarrow \beta]$ interface. The resultant overall reduction in defect energy would lead to an increase in the number of Frenkel pairs formed relative to either bulk phase and a net charging at each interface. The defect profile in Fig. 3(c) for the stoichiometric MD simulation is roughly constant within each of the β and γ regions, and the interfaces show no difference relative to the bulklike regions. This supports the $\wedge$ potential in Fig. 1 being an intrinsic property of the heterostructure lattice and not due to a particular defect disorder at either interface. Since this profile is not simply a superposition of those in Figs. 3(a) and 3(b), it is clear that these Frenkel pairs do not respond to the lattice polarization as do excess defect species and vacancy-interstitial interactions are playing a substantial role.

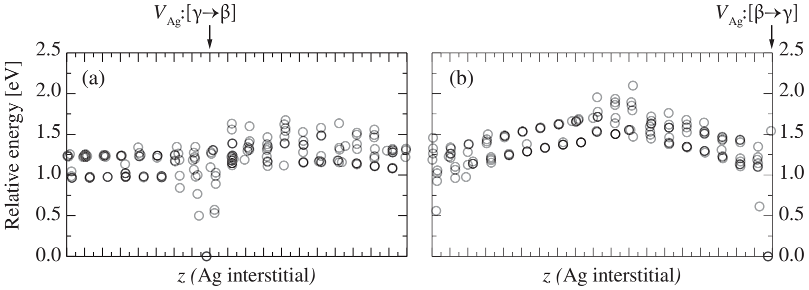

FIG. 4. Potential energies for minimized structures of [$\mathrm{Ag}_i^\bullet + V'_{\mathrm{Ag}}$] Frenkel pairs, for an Ag vacancy at each [$\beta|\gamma$] interface and with each data point giving the z coordinate of the interstitial and the total energy relative to the perfect lattice.

The vacancy-interstitial interaction may be examined by creating a single Frenkel pair with the interstitial and vacancy initially placed at specific sites in the simulation cell and calculating the energy, after lattice relaxation, as a function of these positions. Figures 4(a) and 4(b) show results obtained when the vacancy is placed at each interface and the position of the interstitial is varied: one for V_{Ag} at the [$\gamma \rightarrow \beta$] interface, expected to be the most favorable vacancy position, and one for V_{Ag} at the [$\beta \rightarrow \gamma$] interface, expected to be the least stable. For each set the data lie in two bands, corresponding to tetrahedral and octahedral interstitials. For both V_{Ag} positions there are a small number of low energy configurations with the interstitial close to the vacancy corresponding to associated Frenkel pairs, with a formation energy of ~0.5 eV. For separations beyond neighboring sites, the defect formation energy becomes roughly independent of the separation (V_{Ag}:[$\gamma \rightarrow \beta$]) or increases with separation (V_{Ag}:[$\beta \rightarrow \gamma$]). Two effects contribute to this energy profile: the Ag_i interacting as a point charge with the lattice polarization potential, which depends only on the absolute position in the lattice, and a Ag_i-V_{Ag} attraction that is independent of the absolute lattice position. These two effects are of very similar magnitude. For V_{Ag}:[$\beta \rightarrow \gamma$], the expected unfavorable vacancy location, they both act to prevent defect separation. For V_{Ag}:[$\gamma \rightarrow \beta$], where the preference for separation is strongest, the effects cancel to give a flat defect energy profile at moderate separations. Hence the absence of enhanced Frenkel pair dissociation for the stoichiometric MD simulation, anticipated from the *isolated* defect energies and the putative analogy with the III–V semiconductor heterostructures, is a consequence of the long-ranged V_{Ag}-Ag_i attraction, which prevents the defects from acting as independent species.

Vacancy-interstitial radial distribution functions $g(r_{ij})$ for occupied interstitial positions relative to vacant Ag-lattice sites provide further evidence for strong defect association in the thermally equilibrated simulations. When compared with the radial distribution functions for the interstitials relative to *any* Ag-lattice site, these show major differences, as seen in Fig. 5. In the stoichiometric system, 90% of the considered pairs are at separations within the position of the first minimum of the radial distribution functions, corresponding to associated Frenkel pairs with defects on neighboring sites, and $g(r)$ falls away to a very low value after a small second peak. The $g(r)$ for nonstoichiometric systems show similar large first peaks, indicating strong association between the extrinsic defect species and spontaneously formed Frenkel pairs to produce defect complexes [26]. This explains the enhancement of the *minority* defect species at interfacial regions in Fig. 3 under nonstoichiometric conditions: Because of the lattice polarization potential, extrinsic defects segregate to the appropriate interface, where Frenkel pair formation is promoted at neighboring sites to reduce the local strain.

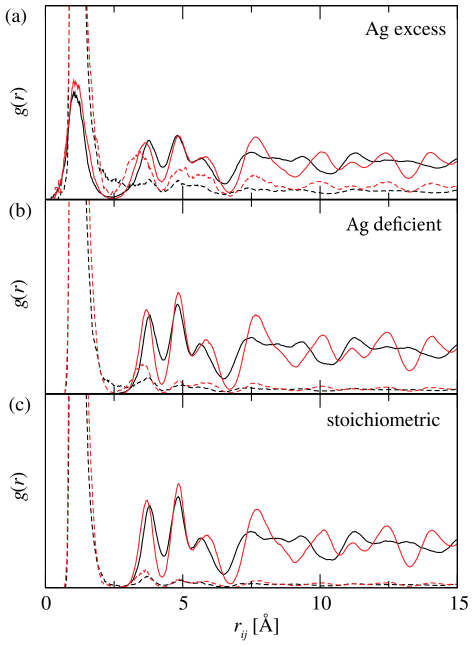

FIG. 5 (color online). Radial distribution functions (normalized so that all curves cover the same area for $r \leq 15$ Å) between octahedral (black) or tetrahedral (red) interstitials and the centers of the normally occupied tetrahedra, considering either all such tetrahedra (solid lines) or vacant tetrahedra (dotted lines).

In ionic heterostructures with polar constituent layers, as in AgI, spatial variations in individual defect energies are dominated by the interaction with a spontaneous lattice polarization. This interaction is absent in the standard space-charge model, which neglects atomistic structure but which could be extended to include appropriate continuum polarization fields. For weakly interacting defect species, this polarization suggests enhanced Frenkel pair separation as an analogue to electron-hole redistribution in III–V semiconductor heterostructures. In stoichiometric simulations, however, the mutual interaction between defects outweighs the tendency of Frenkel pairs to dissociate towards opposite interfaces. We can speculate that the difference compared to the electron-hole case is that the defects here are highly localized charge centers and strongly locally polarize the lattice through both Coulombic and excluded volume interactions. Electrons and holes, in contrast, are more delocalized as quantum particles and interact relatively weakly with the lattice. Strong defect association is also demonstrated in nonstoichiometric systems, where this results in the formation of charged defect complexes, and explains the increase in concentrations of *both* defect species at the appropriate interface.

These results also provide insight into the extreme conductivity enhancement in experimental AgI heterostructures. Since *stoichiometric* heterostructured AgI displays no increased disorder at $[\beta|\gamma]$ interfaces, the results presented here contradict the suggestion that the high room-temperature ionic conductivity observed in experiments for the 7H and 9R polytypes is an *intrinsic* property of these heterostructures [14,15]. Increased defect disorder is predicted only for nonstoichiometric AgI, suggesting that nonstoichiometry is a necessary condition for AgI heterostructures to exhibit high room-temperature conductivities. The strong defect interactions described here, however, indicate that it is likely a nontrivial relationship exists between defect numbers and ionic conductivities. One candidate for the introduction of effective nonstoichiometry in heterostructured AgI nanoparticles is the local charge non-neutrality that characterizes surface space charges. Further insight into this behavior then is likely to require a detailed understanding of the defect chemistry of surface and near-surface regions.

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