The possibility of a split interstitial silver ion in AgCl

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Abstract. Hartree–Fock calculations treating the normal and split interstitial geometries for
the interstitial silver ion at low temperature in AgCl have been performed. Several different
embedded cluster models having different sizes, basis sets, and treatments of lattice polarization
and electron correlation were studied. We found that the split interstitial geometry was favoured
by up to a few tenths of an electronvolt, with the greatest relative stability occurring with the
most extensive basis sets and with treatment of electron correlation. This species has a calculated
bond length of 2.36 Å and is not a deep electron trap in AgCl.

1. Introduction

Silver chloride is known to contain large concentrations of ionic defects that range up to
0.7% of the lattice ions near the melting temperature. Reviews [1, 2] of various experimental
data have indicated the predominant Frenkel defect nature of AgCl, consisting of a silver
ion interstitial and vacancy. Ionic conductivity measurements and analyses [3–6] have
given the enthalpy of formation of 1.46–1.49 eV and a corresponding entropy of formation
of 9.4–11.1 eu. These measurements also indicate that the interstitial silver ion has the
dominant mobility in AgCl with an activation energy for motion of 0.02–0.04 eV. The
reasons for the low activation energy for mobility are thought to be related to the quadrupolar
deformability of the silver ion in this lattice. This is demonstrated in the modelling studies
of silver ion mobility in AgCl by Jacobs and coworkers [7]. Only with the inclusion of
quadrupolar deformations of the silver ion from spherical symmetry could the low activation
energy for mobility be explained. Likewise, studies of the phonon dispersion required the
inclusion of this deformability to reproduce experimental dispersions [8, 9]. These studies
clearly indicate the complicated behaviour of silver ions in AgCl and point to the possible
importance of quantum mechanical approaches in the modelling of this system.

The mechanism of diffusion of silver ions in AgCl has been studied extensively by Friauf
[1, 2]. Comparisons of diffusion and ionic conductivity experiments have given evidence for
the correlated motion of ions. One of the modes of motion possesses a saddle point closely
related to the topic of this work involving the split interstitial structure for the interstitial ion.
A collinear interstitialcy mechanism in which a silver ion interacts with a second silver ion
and pushes it along the {111} direction has been deduced from the analysis of experimental
data. The saddle point for this motion has two silver ions lying along the {111} axis with
their midpoint on a normal silver ion lattice site and is sketched in figure 1.

Recent pulsed ENDOR experiments [10] conducted on AgCl single crystals at 1.2 K
have given evidence for a shallowly trapped electron species which has as its core the
split interstitial silver ion. While electrons in AgCl shallowly trapped by interstitial silver
ions at low temperature have been assigned [11–13] in various experiments for some time,
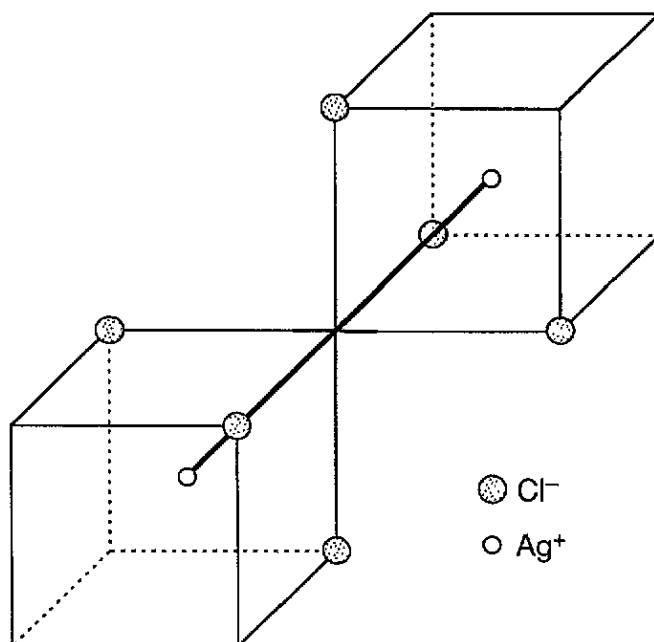
Figure 1. A sketch of the ion positions at the saddle point for the collinear interstitialcy mechanism of silver ion diffusion.

evidence that the core is the split interstitial has only come from the pulsed ENDOR studies. It is not clear how this shallowly trapped species forms. Two possible mechanisms have been discussed [10]. In one, the electron is trapped on an interstitial silver ion that is converted to a split interstitial species. In the second mechanism, the species is formed by a Frenkel pair process on the silver sublattice. Since this shallowly trapped electron has a radius of 17.2 Å, it is not likely that the electron contributes to any substantial extent to the binding of the two silver ions to favour the split interstitial structure.

The equilibrium concentration of interstitial silver ions becomes negligible at low temperatures in pure AgCl. Of course, this fact does not preclude the presence of such species frozen into the lattice by cooling and whose concentration would be dependent upon experimental conditions. Indeed, the detection of interstitial silver ions at low temperature by several different experimental techniques [10–12] supports the possibility of its non-equilibrium state. The split interstitial structure is different from the normally assumed structure of an interstitial silver ion occupying a cube centre and having four silver ion and four chloride ion nearest neighbours. It is possible that at low temperature the favoured structure is different from that at room temperature because of changes in lattice properties, or details of the freezing in process. One possibility, not investigated here, is that the high-temperature form of the interstitial is a dynamical species with average position at the centre of a cube, but which is moving between the four possible split interstitial sites. At the same time, we cannot rule out the formation of this structure during a Frenkel pair process at low temperature.

The purpose of this work is to examine by *ab initio* calculation the possible stability of the split interstitial species. The diffusion studies suggest that such a species is close in energy to the normally assumed interstitial structure where the silver ion occupies the centre of a cube position. In any case, there are no experiments or calculations that give

the energy of this split interstitial structure. Treatment of this problem requires an accurate quantum mechanical method and dealing correctly with lattice ion polarization. This is a demanding task for which we present some initial calculations.

2. Method

These *ab initio* calculations are performed with two different approaches. In the first method, there is a self-consistent coupling of the quantum mechanical cluster ions with the surrounding lattice ions. This calculation employs the ICECAP computer code [14–16] that has been described in detail [17]. Briefly, the lattice ions are capable of simulating electronic polarization and displacement within the shell model [18] representation. These ions respond to the multipole moments of the cluster charge distribution. Thus, a typical calculation proceeds by first taking an approximate charge distribution on the cluster ions to which the lattice ions respond. Then the unrestricted Hartree–Fock calculation proceeds for the cluster ions in the field of the simulated lattice ions. New charge distributions are generated and used to reposition the lattice ions. At the conclusion of the calculation a self-consistency is reached between the multipole moments of the charge distributions. In these calculations we employ the interatomic shell model potential in two-body form taken from [19]. The nearest-neighbour distance of 2.7532 Å appropriate to 0 K is taken. These calculations employ pseudopotentials [20] for the Ag and Cl ions. The basis sets are double-zeta for the valence orbitals. We refer to this calculation procedure by the name ICECAP.

A second procedure employing larger basis sets for the quantum cluster was also applied to this problem. Here a quantum cluster is embedded in approximately 1200 point ions spherically arranged on AgCl lattice sites to achieve an overall charge neutral perfect lattice system. A restricted Hartree–Fock calculation for closed or appropriate open shell systems is applied to the embedded cluster. A Born–Mayer repulsive potential is applied to each of the 24 point ions nearest to ions of the quantum cluster. The parameters $A = 7000.0$ eV and $\rho = 0.278\,69$ Å were determined to give the correct AgCl lattice constant for a $AgCl_6^{5-}$ cluster. The quantum calculation is performed by optimizing the positions of the cluster ions in order to achieve an energy minimum. This gives the system energy apart from lattice polarization energy components. We employ a pseudopotential [21] for Ag with up to double-zeta plus polarization basis sets. The Cl ions are treated fully with up to double-zeta plus polarization basis sets. We employ the CADPAC computer code [22] for these calculations.

The lattice polarization effects are computed using the shell model representation of ions described above. We employ the HADES [23] and CASCADE [24] codes for these calculations. In this calculation the positions of ions corresponding to ions in the quantum cluster are held fixed and the change in energy due to polarization of the remaining lattice ions is computed and taken as the polarization energy. To avoid double counting of the short-range energies between the quantum cluster and lattice ions the energy due to the Born–Mayer terms described above is removed from the total energy. We have used a similar procedure previously [25] for metal halide systems and similar types of calculation have been employed for other ionic systems [26, 27]. It is also possible to carry out this procedure for a second cycle in which some of the point ions are repositioned based upon their positions found in the shell model calculation. In this case we reposition the 24 nearest point ions and repeat the quantum mechanical calculation and lattice polarization calculation just described. The entire calculation accounts for any effects due to changes of the Coulomb field from the positions of the point ions. We refer to calculations performed by this procedure as CADPAC.

The cluster models we employ are centred on a silver ion site in the AgCl lattice. We have considered $Ag_2Cl_6^{4-}$, $Ag_2Cl_8^{6-}$ and $Ag_2Cl_8Ag_6^0$ cluster models. Figure 2 is a sketch of the smaller models for the split interstitial geometry, where, in the left-hand representations, we have rotated the {111} axis to the vertical axis of the figure. The $Ag_2Cl_8Ag_6^0$ cluster model is found by adding the six next silver ions to the $Ag_2Cl_8^{6-}$ model. Note that the normal interstitial geometry has one silver ion centred between six chlorine ions and the second silver ion off centre and is achieved simply by moving the Ag pair along the vertical axis. The C_3 symmetry about the {111} axis, along which the two silver ions lie, is maintained throughout the calculation.

3. Results

3.1. Relative energies of interstitial structures

The energies of the normal and split interstitial model were calculated for several clusters with different basis sets. The relative energies of these geometry-optimized configurations are given in table 1. The relative energies are rather close for the normal charge state interstitials. Consider the $Ag_2Cl_8^{6-}$ cluster where the electronic energy favours the split interstitial, but the correction for lattice polarization considerably reduces this difference. Use of the double-zeta plus polarization basis set further increases the stability of the split interstitial by 0.07 eV relative to the comparison using the double-zeta basis set. Further correction of the positions of the nearest-neighbour point ions, as was described above, improves the relative stability of the split interstitial by 0.43 eV. These data can be compared to the results of the self-consistent ICECAP calculation for the $Ag_2Cl_6^{4-}$ cluster, which favours the split interstitial geometry by 0.63 eV relative to the normal geometry. These two calculations probably best account for the lattice polarization effects and both favour the split interstitial geometry.

Table 1. The relative energy of the split interstitial versus the normal interstitial model in AgCl. Negative values indicate a more stable split interstitial.

Cluster	Basis set [a]	Electronic energy (eV)	Energy plus polarization (eV)
CADPAC calculation with/without polarization energy			
$Ag_2Cl_8^{6-}$	DZ	−1.19	0.06
$Ag_2Cl_8^{6-}$	DZP	−1.22	−0.01
$Ag_2Cl_8^{6-}$ [b]	DZP	−1.33	−0.43
$Ag_2Cl_6^{4-}$ [c]	DZ	−1.90	−1.15
$Ag_2Cl_8Ag_6^0$	DZ	−0.35	0.11
$Ag_2Cl_8^{7-}$	DZP	0.66	1.02
$Ag_2Cl_8^{5-}$	DZP	−1.05	−0.34
$Ag_2Cl_8^{4-}$	DZP	−0.88	−0.66
ICECAP calculation			
$Ag_2Cl_6^{4-}$	DZ	—	−0.63

[a] DZ or DZP refers to double-zeta with or without polarization, respectively.
[b] Adjusted positions of nearest-neighbour point ions.
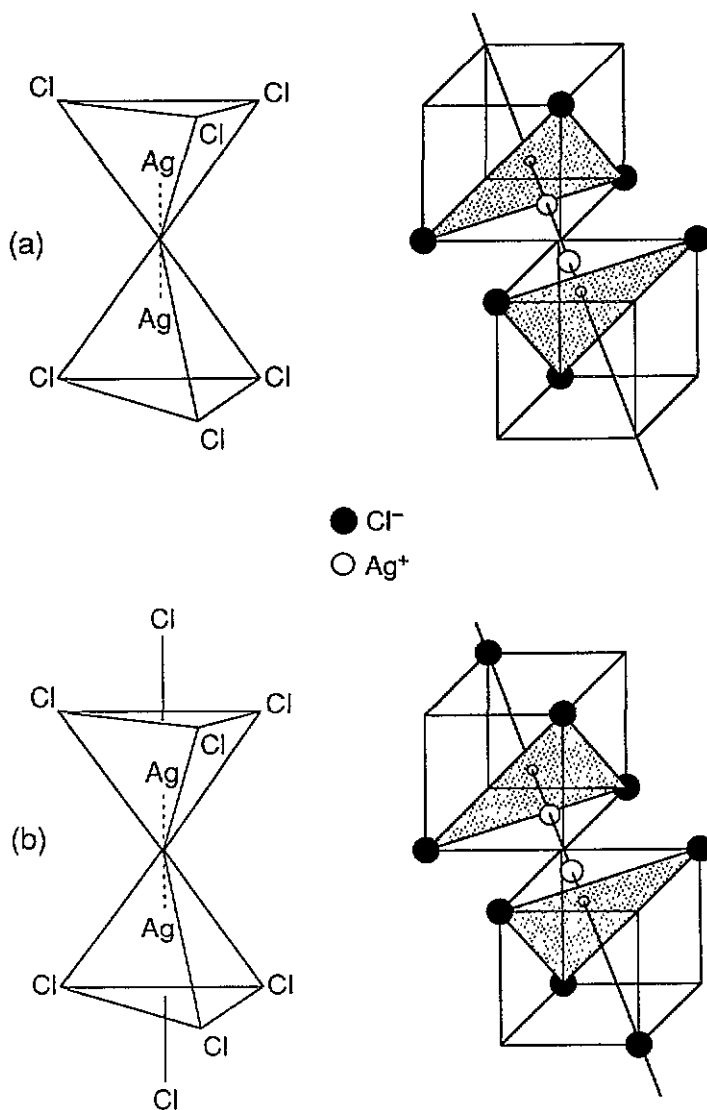[c] MP2 correlation energy calculation included.

Figure 2. Sketches of models used for the quantum cluster representations of the silver ion split interstitial in this work are shown. On the left-hand side of the figure, we have rotated the {111} crystal axis to lie along the vertical axis of this page. We consider $Ag_2Cl_6^{4-}$ in (a) and $Ag_2Cl_8^{6-}$ in (b). A sketch from the crystal lattice is shown alongside each cluster. The normal interstitial geometry is found by moving the Ag_2 core along the vertical axis of the figure.

The larger cluster model, $Ag_2Cl_8Ag_6^0$, was considered with the double-zeta basis sets. Upon full geometry optimization, the normal geometry is favoured by 0.11 eV. Use of double-zeta plus polarization basis sets for this cluster would exceed our computational resources, but would be expected to shift the relative energy in favour of the split interstitial based upon the above results.

We have examined two additional factors that could have a bearing upon our interpretations of the data in table 1. One concerns possible basis set superposition errors

(BSSE) arising from overlap of the polarization functions on Ag^+ with the cores of the Cl^- ions. We performed calculations of the Cl_8^{8-} segment of the $Ag_2Cl_8^{6-}$ cluster with the ions located at the calculated equilibrium positions, both with and without the presence of polarization functions at the silver ion positions. The estimates of the BSSE computed in this way are 2.01 eV for the normal interstitial geometry and 2.05 eV for the split interstitial geometry. This calculation employed double-zeta plus polarization functions on the Cl^- ions. When only double-zeta functions were used for Cl^- ions, the BSSE was calculated to be 2.14 eV for both geometries. We conclude that the small differences in BSSE calculated for the two geometries are not a major factor in favouring one geometry of the interstitial over the other. A second factor to be considered is the electron correlation energy. We performed Moller–Plesset second-order perturbation calculations (MP2) for the $Ag_2Cl_6^{4-}$ cluster at the double-zeta basis set level as shown in table 1. The correlation energy difference is roughly 0.5 eV in favour of the split interstitial geometry relative to the normal geometry. We observe a strongly favoured split interstitial geometry for this calculation. Thus, the calculations without correlation would be expected to be more favourably shifted to the split interstitial geometry if this effect could be included for all of them.

We have compared the calculated relative stability of the normal and split interstitial structure for other charge states. These data are shown in table 1. The cluster with net charge -7 might be considered to represent Ag_2^+ since an additional localized electron is present. We find greater stability for the normal versus the split interstitial geometry for this charge state. In this most stable geometry, the charge of the silver ions is polarized with the ion on the lattice site having the more positive charge. The clusters with net charge of -5 or -4 are more stable in the split interstitial geometry. In this case, the Mulliken populations suggest that the halide ions become less negative in charge, providing the source of the electrons being removed from the system.

3.2. Electron affinity

We have evaluated the electron affinity of the $Ag_2Cl_8^{6-}$ cluster in both normal and split interstitial geometries. This is achieved by computing the total energy of the $Ag_2Cl_8^{7-}$ cluster at its equilibrium distance. The differences between the energies of the normal charge state and the anion charge state are used to determine the electron affinity. Table 2 shows calculated values for the two methods of calculation. Much larger values of the electron affinity are calculated with the CADPAC type of calculation apparently because of the use of the double-zeta plus polarization basis sets, which should be more realistic. We observe that the normal interstitial geometry has the greatest electron affinity. The value calculated for the split interstitial geometry would be slightly increased if the anion state were allowed to relax to the more energetically favourable normal site geometry.

Table 2. The computed electron affinity of clusters in normal charge state.

Cluster	Method	Basis set	Geometry	EA(eV)
$Ag_2Cl_8^{6-}$	CADPAC	DZP	Normal	2.88
$Ag_2Cl_8^{6-}$	CADPAC	DZP	Split interstitial	1.85
$Ag_2Cl_6^{4-}$	ICECAP	DZ	Normal	−0.15
$Ag_2Cl_6^{4-}$	ICECAP	DZ	Split interstitial	−0.08

3.3. Bond length

The calculated equilibrium silver–silver bond length is shown for several calculations in table 3. It is interesting that a relatively short bond length is found for the normal and the split interstitial geometry. This indicates some degree of bond formation even though the two silver ions have formal charges of $+1$. A gas phase Ag_2 molecule has a bond length of 2.48 Å [28] to use as a relative comparison to the data in table 3. Apparently the bonding in the normal and split interstitial structures involving cations of d^{10} configuration takes place perhaps due to the high polarizability of the d shell.

Table 3. The calculated equilibrium Ag–Ag bond length (Å).

Cluster	Basis set	Normal	Split interstitial
CADPAC calculation			
$Ag_2Cl_8^{6-}$	DZP	2.12	2.36
$Ag_2Cl_8^{7-}$	DZP	2.15	2.23
$Ag_2Cl_8Ag_6^0$	DZ	2.37	2.48
ICECAP calculation			
$Ag_2Cl_6^{4-}$	DZ	2.73	2.86
$Ag_2Cl_6^{5-}$	DZ	2.61	2.89

3.4. Charge distribution

The charge distribution in the quantum clusters was calculated with the Mulliken analysis and by using the monopole term in a distributed multipole analysis [29]. Table 4 shows these results for both silver ions in various clusters and gives the average value for the chlorine ions. The monopole term indicates a more ionic charge distribution than the Mulliken values for each case. In the normal interstitial geometry, the silver ion at the interstitial site has a greater electron density than the other silver ion near the normal lattice site. Both the Mulliken analysis and distributed multipole analysis indicate some bonding between the two silver ions when the basis set having polarization functions is employed. This judgment is based upon the values of the partial charges on silver ions that suggest some occupation of the expected 5s molecular orbital. For the basis sets having no polarization functions, the silver ions appear more fully ionic and hence one would expect less silver–silver bonding.

Table 4. Calculated charges of ions in clusters using Mulliken analysis (MPA) and distributed multipole analysis (DMA) for silver ions and the average for chlorine ions.

Cluster	Basis set	Geometry	Procedure	Ag	Ag[a]	Cl
$Ag_2Cl_8^{6-}$	DZP	Normal	MPA	0.13	−0.88	−0.60
$Ag_2Cl_8^{6-}$	DZP	Normal	DMA	0.96	0.42	−0.92
$Ag_2Cl_8^{6-}$	DZP	Split interstitial	MPA	−0.57	−0.57	−0.61
$Ag_2Cl_8^{6-}$	DZP	Split interstitial	DMA	0.62	0.62	−0.91
$Ag_2Cl_8Ag_6^0$	DZ	Normal	MPA	0.76	0.45	−0.85
$Ag_2Cl_8Ag_6^0$	DZ	Normal	DMA	1.18	1.01	−1.06
$Ag_2Cl_8Ag_6^0$	DZ	Split interstitial	MPA	0.61	0.61	−0.88
$Ag_2Cl_8Ag_6^0$	DZ	Split interstitial	DMA	1.06	1.06	−1.06

[a] Silver ion at interstitial site in normal geometry.

4. Discussion

Our calculations indicate that the split interstitial is a plausible structure for the interstitial silver ion at low temperature in AgCl. The ground state relative energy differences of the normal and split interstitial geometry reflect a delicate energy balance involving electronic effects and lattice polarization effects. We find that the split interstitial structure is favoured when the calculation is performed with polarization functions in the basis set, or correlation effects are treated, or lattice polarization effects are treated more accurately. These factors tend to argue for the possibility that the split interstitial can exist at low temperature in the AgCl lattice as proposed by Bennebroek *et al* [10].

The Ag_2^+ species represented by the embedded $Ag_2Cl_8^{7-}$ cluster was not found to be stable in either the split interstitial or normal geometry. The calculated ionization potential was 2.88 eV or 1.85 eV for the normal or split interstitial geometry, respectively, from the data in table 2. We have compared this energy to the conduction band edge in AgCl determined from the experimental band gap and calculated $AgCl_6^{5-}$ ionization potential. The $AgCl_6^{5-}$ cluster is embedded in point charges and treated exactly in the manner that we used to treat the interstitial species in this report. The calculated band edge is 3.6 eV, which indicates that the localized electron on a potential bulk Ag_2^+ species would enter the conduction band. This result explains why the well known Ag_2^+ species, which exhibits a characteristic EPR signal in alkali halides, zeolites, and frozen glasses [30], is not observed in silver halides [31]. Of course, the Ag_2^+ species may be stable at surfaces where the adsorption site may be different than the bulk. We also point out that our calculation does not interfere with the possibility that the interstitial can act as a shallow electron trap since this mode of trapping proceeds by Coulombic means.

The possibility of a split interstitial species existing in AgCl is not found when using classical shell model calculations. We have found that the split interstitial is as much as 0.5 eV less stable than the normal interstitial geometry using calculations with various interatomic potentials and also treating the possibility that there may be some bond formation between the silver ions. Apparently, the quantum mechanical treatments are required to better represent the interactions that lead to bond formation between the silver ions. It may be suggested that the rather complex polarizability of the silver ion is more fully treated in quantum mechanical methods.

In conclusion, the relative energy calculations support the hypothesis of Bennebroek *et al* [10] that the stable configuration for the interstitial silver ion at 1.2 K is likely to be the split interstitial geometry and that this centre acts as a shallow trap for photoelectrons.

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