

Brief Reports

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Energetics and electronic structure of silver chloride

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The density-functional pseudopotential method has been used to study the equilibrium lattice parameter, elastic constants, TO frequency, band structure, and valence charge distribution of AgCl. The Ag 4d electrons are fully included using an optimized pseudopotential. Results for the lattice parameter and the elastic and vibrational quantities are in satisfactory agreement with experiment, as is the calculated valence-band width. The relation of the present results with recent Hartree-Fock calculations is discussed.

I. INTRODUCTION

Silver compounds are of great importance as photographic materials, as solid electrolytes,¹ as liquid semiconductors,² and for many other reasons. Silver chloride (AgCl) is one of the simplest of these compounds, and has been very widely studied by both experimentalists and theorists. The purpose of this short paper is to report a study of the energetics and electronic structure of AgCl using density-functional theory (DFT) and the pseudopotential approximation.³ We shall show that this approach gives a satisfactory description of the known elastic and vibrational properties of the perfect AgCl crystal, and of its electronic structure. We have undertaken this work as the first step in an extensive project on solid and liquid Ag-based semiconductors, but we believe that the results to be presented are also of general significance for the study of solid silver compounds. Our results suggest, for example, that the present methods could be used to study defects and surfaces in solid Ag compounds, as has already been done in other ionic and semi-ionic materials.⁴

Silver chloride crystallizes in the rock-salt structure, but the presence of Ag-4d electrons makes its properties very different from those of other rock-salt compounds such as the alkali halides. It is known from photoelectron spectroscopy (PES) (Ref. 5) and from earlier electronic structure calculations⁶⁻⁸ that AgCl is a wide-gap semiconductor, with the top of the valence band consisting mainly of hybridized Ag-4d and Cl-3p orbitals. A striking difference between AgCl and the alkali halides is the enormous Cauchy anomaly in its elastic constants.⁹ The ratio c_{44}/c_{12} is roughly equal to unity (the Cauchy condition) in all the rock-salt alkali halides, but in AgCl it is 0.18 (Ref. 9)—an effect that must be due to the electronic properties of the Ag ion. It is noteworthy also that the nature of thermally generated lattice disorder is very different in AgCl. Schottky disorder (cation and anion vacancies) is dominant in alkali halides, but the disorder in AgCl is of the cation Frenkel type (Ag vacancies and

interstitials). Not surprisingly, efforts to model the energetics of perfect and defective AgCl using empirical interaction potentials have been only partially successful.¹⁰ The structure and energetics of AgCl have also been studied recently by the Hartree-Fock approach,⁸ and we shall comment on that work later in the paper.

II. TECHNIQUES

We have used the DFT-pseudopotential method³ to calculate the equilibrium lattice parameter, the three elastic constants, and the zone-center transverse optic frequency of AgCl, as well as its electronic band structure and the spatial distribution of valence electrons. The Ag-4d electrons are, of course, explicitly included in the pseudopotential description. (The inclusion of d electrons in pseudopotential total-energy calculations has become fairly common in the past few years.¹¹) The calculation technique we use is standard, with the occupied orbitals expanded in plane waves, and the band-by-band conjugate gradients technique¹² used to relax the occupied orbitals to the self-consistent ground state. Exchange and correlation are included *via* the local density approximation,³ using the Ceperley-Alder form.¹³ The calculations were performed with the CASTEP (Cambridge Serial Total Energy Package) code.¹²

In order to economize on the number of plane waves needed to obtain basis-set convergence, it is crucially important to work with a carefully constructed Ag pseudopotential. We have constructed this pseudopotential using the optimization scheme due to Lin *et al.*,¹⁴ which is a refinement of the scheme due to Rappe *et al.*¹⁵ The s and p components of the Ag pseudopotential were generated using the atomic configuration $4d^{10} 5s^{0.25} 5p^{0.25}$, and the d component using the configuration $4d^{10} 5s^{0.5}$; the core radii for all three angular momenta were chosen to be 2.0 a.u. The chlorine core is represented by a standard Kerker pseudopotential,¹⁶ generated from the configuration $3s^2 3p^5$ for the s and p waves and $3s^2 3p^3 3d^1$ for the d wave. Our tests show that with these pseudopotentials a plane-wave cutoff of 59 Ry leaves an error

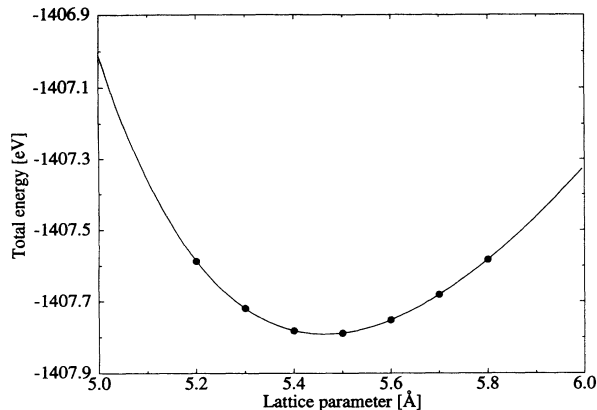


FIG. 1. The calculated total energy of the AgCl crystal as a function of lattice parameter a_0 . Symbols represent the calculated points and the solid curve shows the fit using the Murnaghan equation of state (Ref. 18).

of only 2 mRy in the total energy of the AgCl unit cell, which is more than adequate for present purposes. We have used this cutoff except where otherwise mentioned.

III. RESULTS

The equilibrium lattice parameter has been determined in the usual way by calculating the total energy at a series of lattice parameters. Sampling of k points was done by the Monkhorst-Pack scheme,¹⁷ with ten points in the irreducible Brillouin zone. We have demonstrated by tests using smaller numbers of k points that this sampling is more than adequate. Our results for the total energy are shown in Fig. 1. Fitting of the Murnaghan equation of state¹⁸ to these results yields the equilibrium lattice parameter $a_0 = 5.46$ Å and the bulk modulus $B = 62$ GPa; experimental values are $a_0 = 5.548$ Å (Ref. 19) and $B = 51.3$ GPa,⁹ so that we have errors of 1.5% and 20% in the two quantities. The agreement with experiment is somewhat less than that achieved by DFT on electronically simpler materials (agreement within 1% for a_0 and within 5% for B is typical for sp^3 semiconductors), but is not unsatisfactory.

The three elastic constants have been calculated by examining the energy variation caused by applying appropriate strains. Considerable care needs to be taken over k -point sampling and plane-wave cutoff for these calculations, since the energy differences are very small. We find it necessary to increase the plane-wave cutoff to 74 Ry to

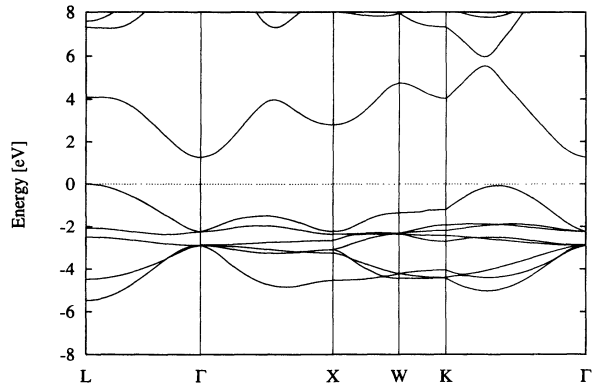


FIG. 2. Calculated electronic bands of AgCl crystal at the equilibrium lattice parameter. The conventional notation is used for the Brillouin-zone symmetry points associated with the fcc real-space lattice. The zero of energy is at the top of the valence band.

achieve convergence. For c_{11} and c_{12} , ten k points in the irreducible zone are more than enough, but c_{44} is very sensitive to sampling, and we have used 28 k points for this elastic constant. Our calculated values for the elastic constants (experimental values in parentheses) are $c_{11} = 98$ GPa (76 GPa), $c_{12} = 42$ GPa (39 GPa), $c_{44} = 1.3$ GPa (6.9 GPa). It should be noted that the value of c_{44} is anomalously small in AgCl, so that the percentage error is bound to be rather large in the present state of the art. In fact, we are not entirely confident that our calculated c_{44} is fully converged even with 28 k points: our results are not fully satisfactory with fewer k points, but we have not so far been able to go to more k points. The most important result is that the large Cauchy anomaly is fully reproduced; this is important, because it should make it possible to give a detailed electronic interpretation of this anomaly—a matter which will need separate investigation.

The transverse optic frequency has been calculated by the frozen-phonon method. The total energy is calculated for a series of distorted configurations in which all ions on the cation sublattice are displaced by the same amount relative to the ions on the anion sublattice. Because of the cubic symmetry, the *direction* of displacement does not make any difference to the calculated frequency. Our detailed calculations have been done for displacement in the (111) direction, but we have also made check calculations in the (100) and (110) directions. We find that the energy variation is accurately described by a

TABLE I. Comparison of characteristic electronic band energies of AgCl obtained in the present work compared with experimental values and results of earlier theoretical work. LDA denotes local-density approximation and HF denotes Hartree-Fock.

	DFT-LDA	DFT- X_α ^a	HF ^b	Expt. ^c
Direct gap at Γ [eV]	3.5	5.69	15.4	5.6
Indirect L- Γ gap [eV]	1.25	3.77	13.5	3.25
Bandwidth [eV]	5.48	4.12	6.18	5 - 6

^aReference 7.

^bReference 8.

^cReference 5.

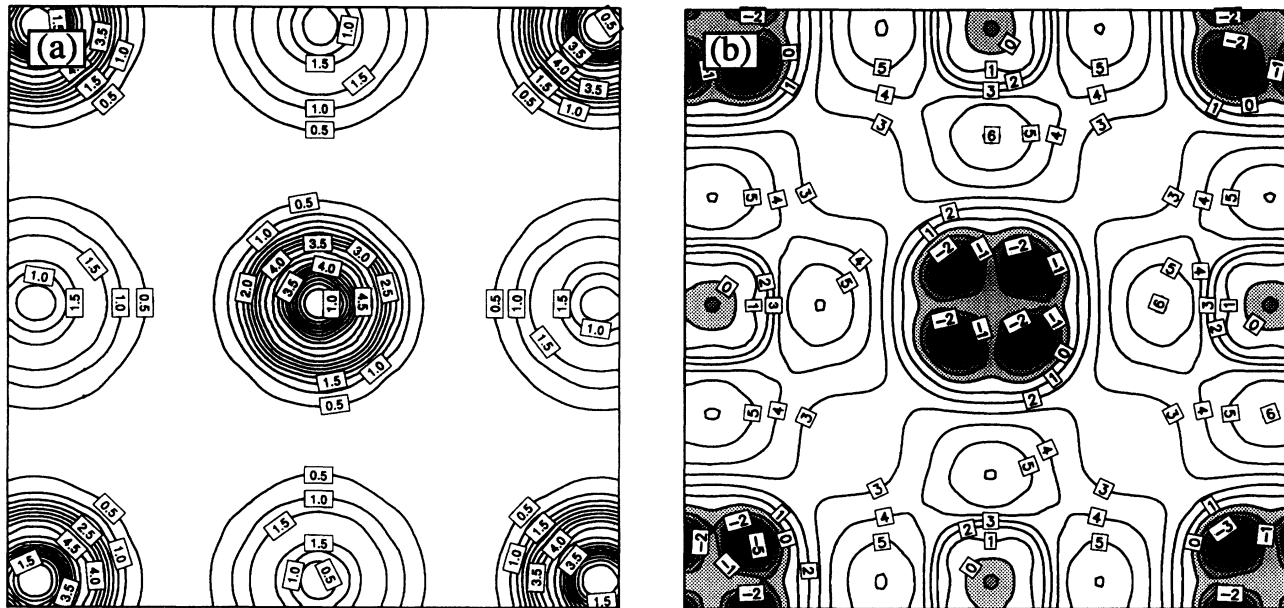


FIG. 3. (a) Contour plot of the valence electron pseudodensity $\rho(\mathbf{r})$ on a (100) plane passing through Ag and Cl sites. Contours are marked in units of electrons/ \AA^3 , with intervals of 0.5 electrons/ \AA^3 between contours. (b) Contour plot of the subtracted density $\Delta\rho(\mathbf{r})$ described in the text. Contours are drawn at intervals of 10^{-2} electrons/ \AA^3 , with regions of negative $\Delta\rho(\mathbf{r})$ shown shaded.

parabola for displacements up to $\sim 0.3 \text{ \AA}$, and it is a simple matter to extract the frequency from the curvature. Our calculated value is 3.92 THz, which compares reasonably well with the experimental value of 3.57 THz.²⁰

Our calculated electronic band structure is shown in Fig. 2, and we compare some of the key band energies with experiment and with earlier theoretical work in Table I. The valence band consists of Ag-4*d* and Cl-3*p* levels, the Cl-3*s* level lying considerably lower at an energy of ca. -14 eV . Our calculated valence bandwidth is in very satisfactory agreement with PES data. Our underestimate for the direct and indirect band gaps is a very common feature of DFT calculations, as is known from work on a wide variety of other materials.

Finally, we display our results for the spatial distribution of valence electron density (actually the pseudodensity) $\rho(\mathbf{r})$ in Fig. 3(a). The charge distribution consists of almost spherical concentrations centered on the lattice sites. It is clear also that the charge distribution centered on the Ag site must consist mainly of 4*d* electrons.

In order to analyze the density in more detail, we have calculated separately the pseudocharge distributions for the Ag^+ ion and the neutral Cl atom, and we have subtracted these from the valence distribution. The effect of this subtraction is to leave a single electron per primitive cell, which we can regard as being originally the Ag-4*s* electron. We are asking how this electron has become redistributed. The subtracted charge distribution $\Delta\rho(\mathbf{r})$ shown in Fig. 3(b) has regions of negative density on the Ag sites and positive density on the Cl sites. We have been able to show that the amount of charge contained in the negative features around the Ag site is extremely small. To demonstrate this, we have computed the fractional number of electrons in $\Delta\rho(\mathbf{r})$ within a sphere of

variable radius r centered on the Ag site, i.e., the integral:

$$n_{\text{Ag}}(R) = 4\pi \int_0^R \Delta\rho(\mathbf{r}) r^2 dr, \quad (1)$$

where the origin of the integration is at the Ag site. From the results for $n_{\text{Ag}}(r)$ displayed in Fig. 4, it is clear that the fractional number deviates only slightly from zero for radii less than $\sim 1.1 \text{ \AA}$. The small deviation that we see is negative, suggesting that the *d*-electron distribution in the crystal is slightly broader than in the free ion. The curve for $n_{\text{Ag}}(r)$ thus implies that the single electron per

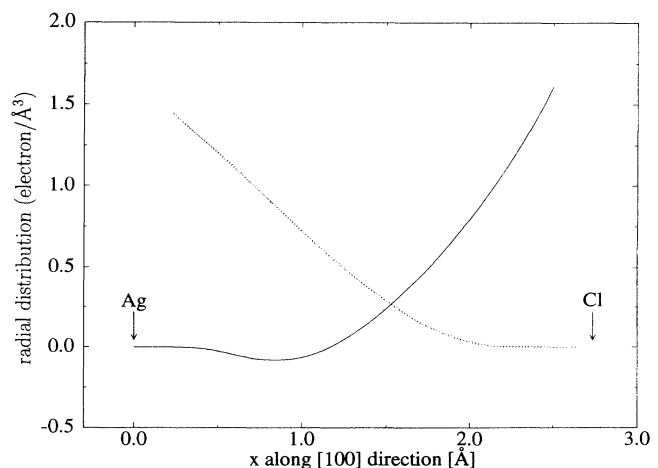


FIG. 4. The integrated radial distributions $n_{\text{Ag}}(r)$ and $n_{\text{Cl}}(r)$ associated with $\Delta\rho(\mathbf{r})$. Distributions centered on Ag and Cl sites are indicated by solid and broken lines, respectively.

cell contained in $\Delta\rho(\mathbf{r})$ is mainly in the peaks surrounding each chlorine atom [see Fig. 3(b)]. The distribution of the extra electron about the chlorine site is, however, broad. To show this, we display in Fig. 4 the integrated radial distribution $n_{\text{Cl}}(r)$ defined as in Eq. (1), but with the origin at the Cl site. We see that we have to go to a radius of ~ 2.0 Å to include one electron.

The picture that emerges from this analysis is thus that in AgCl crystal the Ag-4s electron is redistributed into well-defined regions surrounding the Cl sites, and lying on the lines connecting these sites to their neighboring Ag sites. This is compatible with the fully ionic model suggested by previous authors,⁸ but could be equally well interpreted as indicating partial covalent bonding. Our view is that a conclusive verdict cannot be arrived at by studying the density alone.

IV. CONCLUSIONS

Fairly satisfactory agreement with experiment has been obtained for the equilibrium lattice parameter, the elastic constants and the zone-center TO frequency, though the agreement is not as good as is usually obtained for electronically simpler materials by the DFT-pseudopotential method. It should be noted that nonlinear core corrections have not been included in the present work, and it is possible that the overlap between valence and 4s and 4p semicore electrons might lead to significant corrections. However, the quality of our results is similar to that obtained in recent correlation-corrected

Hartree-Fock work on AgCl.⁸

Our calculated valence band width is in close agreement with experiment and with the Hartree-Fock calculations. As always with DFT, our band gap is somewhat too small. Our analysis of the valence charge distribution is consistent with a strongly ionic model of AgCl, but does not exclude other interpretations.

We are now extending our first-principles calculations to more complicated Ag compounds including Ag₂S and Ag₂Se, which are of great interest both as solid electrolytes and as liquid semiconductors. We note also the possible relevance of the present results to work on the energetics of point defects in Ag compounds, particularly AgCl and AgBr. The treatment of these defect problems using empirical interaction models has proved difficult. Recent successes in treating defect energetics in ionic materials by DFT-pseudopotential methods⁴ suggest the possibility of a direct attack on the energetics of defects in Ag compounds by these methods.

ACKNOWLEDGMENTS

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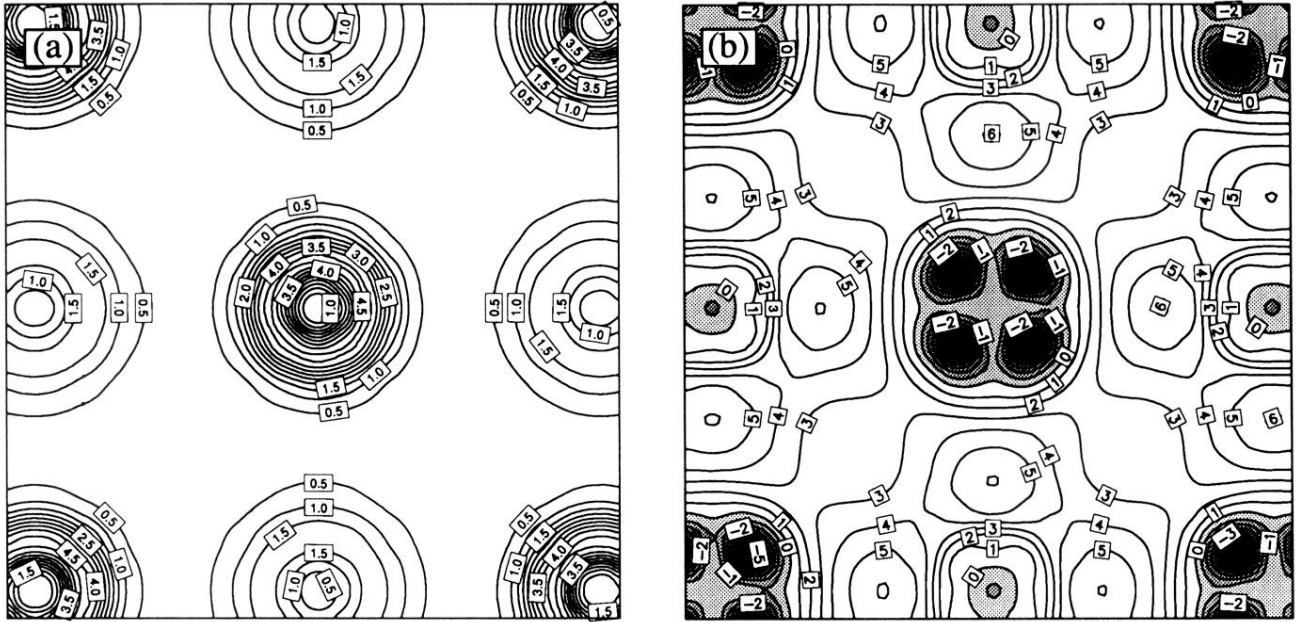


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