The electronic structure of liquid silver chalcogenides: a tight-binding approach

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Abstract. We present a computational study of the electronic structure of the stoichiometric liquid zero-gap semiconductors Ag_2S, Ag_2Se and Ag_2Te. The geometry of the fluids is described by the primitive model of charged hard spheres; the electronic structure is modelled using a tight-binding Hamiltonian. The density of states is computed considering the Madelung potential fluctuations and the topological disorder characteristic of an ionic fluid. Only the introduction of nonzero tight-binding hopping matrix elements—equivalent to the formation of chemical bonds—induces a pseudogap between the chalcogenide conduction band and the silver valence band. The Fermi level can be located in a region of a small density of states; eigenstates at E_F are likely to exhibit disorder-induced localization.

1. Introduction

Since Cutler's statement that 'Semiconducting liquids are a poorly understood class of materials, as compared to others' made in his landmark monograph on the subject [1], a considerable amount of experimental work and theoretical reasoning has been devoted to this unusual class of fluids [2]. For liquid semiconductors, conductivity values at stoichiometry lie below 5000 S cm^{-1} in a regime where the mean free path is of the order of the interatomic separation [3]. Neither the simple picture of a gas of free electrons scattered by atomic pseudopotentials with σ in excess of some thousand S cm^{-1}—as in the Faber–Ziman theory of liquid metals [4]—nor the ionic point of view of a well-separated anionic valence and a cationic conduction band (with σ of the order of or less than 10 S cm^{-1}) seems to hold.

The silver chalcogenides Ag_2X (with X = S, Se or Te) are typical examples of liquid semiconductors. Conductivity values of $\sigma(Ag_2S) = 280$ S cm^{-1}, $\sigma(Ag_2Se) = 400$ S cm^{-1} and $\sigma(Ag_2Te) = 230$ S cm^{-1} have been measured at $T = 1273$ K [5]. For all compounds, the activation energy of the conductivity is close to k_BT. The silver chalcogenides are often referred to as *zero-gap semiconductors*. Above the melting point, the sign of $d\sigma_e/dT$ shows an unexpected behaviour: the electronic conductivity decreases with increasing temperature for X = S and X = Se—a behaviour usually associated with a metallic character—whereas $d\sigma_e/dT$ is positive for Ag_2Te, which should exhibit the least ionic character.

Located in the boundary region between metallic and nonmetallic fluids, two-component liquid semiconductors exhibit an additional degree of freedom that determines the behaviour of their conductivity. Above the demixing point, their composition can be varied continuously from stoichiometry ($Ag_{1-x}X_x$ with $x = 1/3$) to the pure metallic phase ($x = 0$). Similar to the case for alkali–alkali halides [6] and the $Cs_x[CsAu]_{1-x}$ system,

a nonmetal→metal transition is inevitable at a sufficiently high x. Recent work on liquid silver chalcogenides covers neutron diffraction measurements [7] and a detailed study of the conductivity, the thermopower and the magnetic susceptibility [8]; see also [2].

In this work, we focus on the computation of the electronic structure of liquid silver chalcogenides at stoichiometry in the framework of a simple and transparent model. We will not try to address the question of the anomalous slope of $d\sigma_e/dT$ close to the melting point, but study the computation of the number of charge carriers available close to E_F, their localization character and the partial density of states, all of which are of relevance when discussing transport properties. In the next section, details of the models and methods applied will be given. Results are presented and discussed in the third section; conclusions are derived in the last section.

Table 1. Parameters used in the Monte Carlo simulation and the electronic structure computation, average electronic Madelung potentials $\langle V_M \rangle$ and corresponding RMS fluctuations ΔV_M.

		Ag_2S	Ag_2Se	Ag_2Te
ρ	Å^{-3}	0.046	0.044	0.039
σ_+	Å	1.92	1.92	1.92
σ_-	Å	3.08	3.36	3.64
ϵ^0_{s+}	eV	−6.41	−6.41	−6.41
ϵ^0_{p+}	eV	−2.05	−2.05	−2.05
ϵ^0_{s-}	eV	−20.80	−20.32	−17.11
ϵ^0_{p-}	eV	−10.27	−9.53	−8.59
$\langle V_M^+ \rangle$	eV	9.75	7.18	8.64
$\langle V_M^- \rangle$	eV	−17.76	−16.88	−16.04
ΔV_M^+	eV	1.27	1.22	1.30
ΔV_M^-	eV	1.09	0.96	1.05
T_m	°C	830–836	897 ± 3	860–877

2. Models and methods

To describe the geometry of liquid chalcogenides, we use the so-called primitive model of charged hard spheres. Systems containing 432 ions have been simulated close to the melting point using the standard Metropolis Monte Carlo method. The experimental densities have been used; full formal charges of $z_{Ag} = 1$ and $z_X = -2$ have been assigned to the ions. The simulation parameters are detailed in table 1. To avoid the costly Ewald summation in the computation of the Madelung potentials, we have utilized the cut-off strategy of Adams [9], ensuring both charge neutrality and a spherically symmetric potential. For each system, we have performed 2500 Monte Carlo steps for equilibration and 2500 steps to provide 50 snapshots to be used within the electronic structure calculation.

The electronic structure is described by a tight-binding Hamiltonian

$$H = \sum_{ia} \epsilon^0_{ia} c^\dagger_{ia} c_{ia} + \sum_{i \neq j, ab} t_{ijab} c^\dagger_{ia} c_{jb} \tag{2.1}$$

with creation/annihilation operators $c_{ia}^\dagger/c_{ia}$ acting upon atomic orbitals indexed a, b centred at atom i, j. A set of one s and three p orbitals has been used for both the Ag and the chalcogenide atom. The ϵ_{ia}^0-parameters specifying the diagonal of the tight-binding Hamiltonian are given by the corresponding ionization potentials. Numerical values are listed in table 1. Harrison [10] has noted that the relative position of the diagonal energies is remarkably close to a parametrization scheme using a combination of the Madelung potentials, polarization energies and the ionization potential (cation) or the electron affinity (anion). The present author has recently discussed the related parametrization problem for liquid alkali halides [11]. In an ionic fluid, the Madelung potential—and consequently the diagonal of the Hamiltonian matrix—becomes a function of the centre-of-mass coordinates due to the underlying topological disorder [12, 13]. Potential energy fluctuations are of the order of ~ 1 eV and have to be properly incorporated into the tight-binding scheme. As the average site energies are well represented by the parametrization scheme described above, we just consider fluctuations around these averages via

$$\epsilon_{ia} = \epsilon_{ia}^0 - \frac{e^2}{4\pi\epsilon_0} \sum_{j\neq i} \frac{z_j}{r_{ij}} + \langle V_M \rangle_i. \tag{2.2}$$

In practice, the sum in equation (2.2) is again evaluated using the Adams cut-off strategy [9]. It has to be noted that the Madelung potential entering the Hamiltonian is defined as the potential energy seen by an electronic test charge placed at site i.
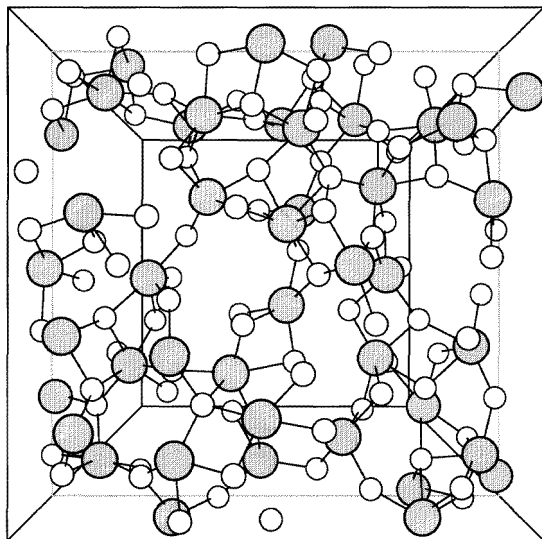
Figure 1. A snapshot of the Monte Carlo simulation of Ag_2S. The sulphur ions are shaded; the plotted sizes of the ions reflect half the hard-sphere diameter. For clarity, only ions in the range $0 \leqslant z \leqslant r_{max}$ are shown.

For the off-diagonal hopping matrix elements t_{ijab} we have used the standard r^{-2}-parametrization of Harrison [10] at contact, falling off exponentially to meet the Pantelides values for second-nearest neighbours [14]. For ionic solids, the latter determine the band widths [14]. Neighbours are defined via the corresponding partial pair distribution functions; a hopping matrix element cut-off between the second and the third shell of neighbours has

been introduced. To diagonalize the resulting large sparse Hamiltonian matrices, a Lanczos algorithm has been used [15, 16, 17].

3. Results and discussion

For Ag_2X, a typical snapshot of the Monte Carlo simulation of the primitive model is presented in figure 1. Short-range chemical order and charge cancellation is evident; similar characteristics can be deduced from the partial pair distribution functions—not plotted here—which unspectacularly resemble those of any 2:1 electrolyte in the regime of a large MSA (mean-spherical approximation) coupling constant once polarization effects are neglected [18]. A refined potential taking into account polarization effects is available for Ag_2Se [19]. We have nevertheless used the primitive model to study general trends across the chalcogenide group of the periodic system with the simplest and most transparent concepts possible.

The density of states in the absence of hopping—tantamount to breaking all chemical bonds—is plotted in figure 2 for the three chalcogenides studied in this work. For X = S and Se, the distinct peaks of the DOS are centred at the corresponding values of valence orbital ionization potentials, with $\epsilon^0_{X,s} < \epsilon^0_{X,p} < \epsilon^0_{Ag,s} < \epsilon^0_{Ag,p}$ (cf. table 1). The centre of the low-lying chalcogenide s band lies outside the range of figure 2; this band is of no practical relevance to the following discussion. The diagonal density of states finds an excellent representation as the sum of four Gaussians (see figure 2), with RMS fluctuations computed from the raw data of the Monte Carlo simulation. It is interesting to note that the Gaussian shape of the probability distribution function of the Madelung potential—as predicted by all linear theories of fluids [12] and confirmed by computer simulations [13]—is obeyed even in the case of strongly different ionic diameters and charges. The numerical values of the Madelung potentials and their fluctuations are listed in table 1. Due to stronger local ordering induced by a larger ionic charge, the (electronic) Madelung potential fluctuations are about 0.2 eV smaller for anions than for cations.

Whereas band broadening induced by Madelung potential fluctuations does not change the ionic character of molten alkali halides [11]—for all practical purposes, anion and cation bands can be considered to be separated by an optical gap of the order of $\sim$6 eV—their impact upon the electronic structure is tremendous for the silver chalcogenides: the band gap has ceased to exist. The Fermi level is pinned in a shallow minimum between the chalcogenide p and the silver s band. The density of states at E_F is of the order of that of the maximum of the silver s band; inspecting the DOS one would presume nothing but a metallic character for stoichiometric Ag_2S and Ag_2Se once a small amount of hopping is introduced. Evidently, this finding not only contradicts the assumption that these materials can be described by an ionic model, but also is in discord with all of the experimental work referenced above. The situation can be considered as even worse for Ag_2Te: the silver s and the tellurium p band have merged almost completely; the Fermi level is located deep within the resulting band.

To resolve this problem, one may check whether the simple diagonal approximation—neglecting the hopping term in equation (2.1)—is as valid for the silver chalcogenides as it is for simple ionic fluids. Introducing chemical bonds according to the rules specified in section 2 and diagonalizing the resulting Hamiltonians, we find the DOS displayed in figure 3. For all chalcogenides, the Fermi level now lies in a deep minimum of the density of states; valence and conduction bands can be identified clearly. In a simplified picture, hopping leads to the formation of a bonding band—lowering the energies of the chalcogenide p band—and an antibonding band—shifting the energies of the silver s band to higher energies [1]. The
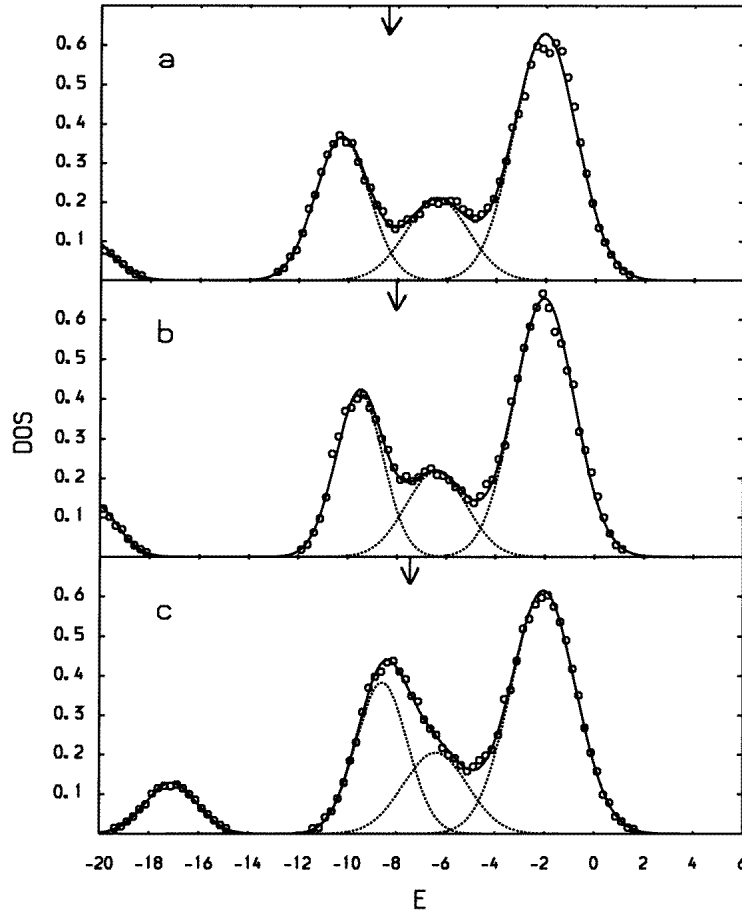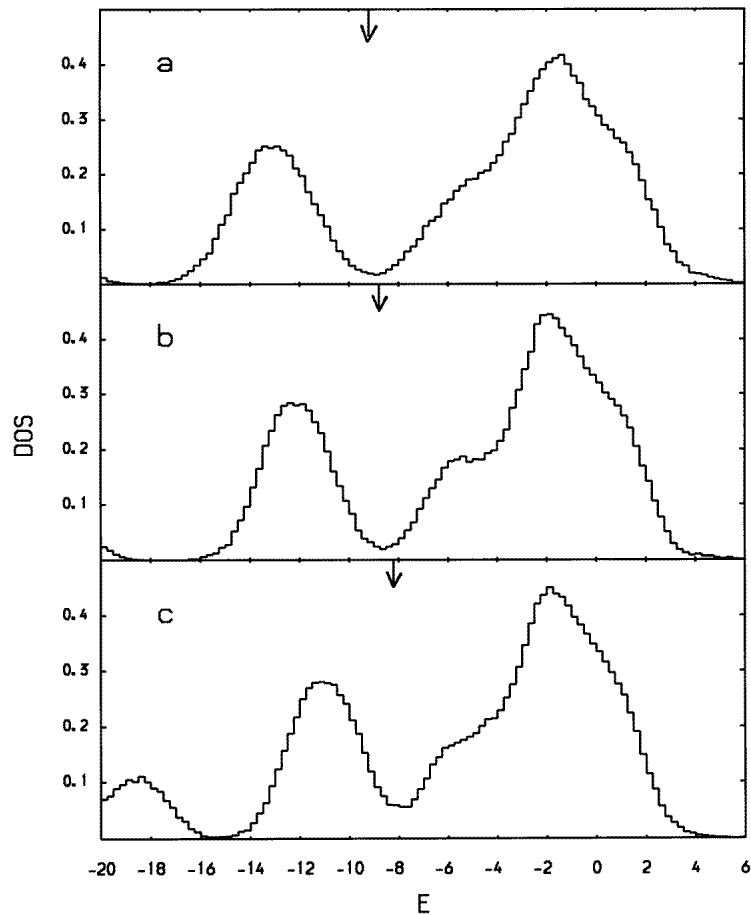
Figure 2. The densities of states of the silver chalcogenides in the diagonal approximation ($\bigcirc$). (a) Ag$_2$S, (b) Ag$_2$Se and (c) Ag$_2$Te. Dotted line: the Gaussian approximation to the DOS contribution; solid line: the corresponding sum. The Fermi levels are indicated by arrows. Energy is in electron volts; DOS is in number of eigenstates per electron volt and atom.

combination of the two effects opens a pseudogap, in which E_F now lies. We note that $\text{DOS}(E_F)(\text{S}) \simeq \text{DOS}(E_F)(\text{Se}) \simeq \text{DOS}(E_F)(\text{Te})/2$, indicating a trend towards a stronger metallic character (not necessarily implying metallic conduction) moving down the periodic system of elements.

Once the eigenvectors of the model system are known, a population analysis can be performed [20]. Here, we are interested in the contribution of chalcogenide or silver atomic orbitals to the valence and the conduction band once chemical bonds are formed. This implies the question of whether the resulting bands can still be considered as ionic. The charge order at a given energy E_α is defined by

$$q^\alpha = \sum_{ia}{}' a_{ia\alpha}^2 \tag{3.1}$$

where the sum is restricted to the orbital type of interest and $a_{ia\alpha}$ denotes the expansion coefficient of the eigenfunction $|\alpha\rangle$ in terms of atomic orbitals. The definition of the charge

Figure 3. The density of states of the silver chalcogenides in the presence of chemical bonding. (a) Ag$_2$S, (b) Ag$_2$Se and (c) Ag$_2$Te. The Fermi levels are indicated by arrows. Energy is in electron volts; DOS is in number of eigenstates per electron volt and atom.

order—and the charge resulting from the summation of all q^α up to the Fermi level—is not unique. In the terminology of solid-state physics, the product of q^α and the DOS(E) is the partial density of states, PDOS(E).

For Ag$_2$S, the charge orders as a function of the energy around E_F are displayed in figure 4. The sulphur p charge order has a value of $q_{S,p} \simeq 0.8$ close to the maximum of the valence band DOS, increases slightly with increasing energy and drops off steeply while crossing the Fermi level. The silver s charge shows a similar behaviour in the conduction band. A maximum of $q_{Ag,s} \simeq 0.8$ is found close to the s-band shoulder in the conduction band; the charge order decreases with decreasing energy and is reduced to a residual of $q_{Ag,s} \simeq 0.1$ on crossing the Fermi level. The silver p contribution is small, but not negligible close to the Fermi level. As expected, its value ascends once $q_{Ag,s}$ drops off in the conduction band. There is little to no contribution of sulphur s orbitals to eigenfunctions close to the Fermi level. The values of charge orders observed within the bulk of the bands are typical for ionic systems; using the same form of analysis, it is hardly possible to observe a charge
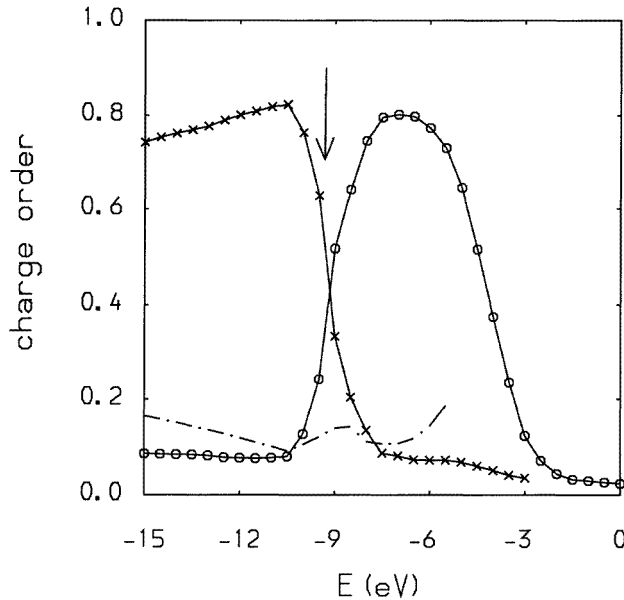
Figure 4. Dimensionless sulphur p ($\times$), silver s ($\circ$) and silver p (chain line) charge order for Ag$_2$S as functions of energy. The Fermi level is indicated by an arrow. Energy is in electron volts.

order in excess of 0.8 for the alkali halides [21].

From a fundamental theorem of Anderson [22], all eigenstates of a disordered system become localized if the strength of disorder exceeds a specific value. Systems with a moderate disorder exhibit mobility edges, separating regions in the density of states that are governed by localized states from regions containing extended states [23]. Whenever the Fermi level lies in a region of localized states, the system shows a nonmetallic (insulating or semiconducting) character; electronic transport is enabled only by thermally activated processes. Localization is usually favoured by a small density of states, a strong p charge order and an antibonding character of the eigenfunction [24]. It is not unlikely that liquid silver chalcogenide eigenstates at the Fermi level are localized due to the topological disorder and Madelung potential fluctuations characteristic of liquid ionic alloys. As a measure of localization, we consider the inverse participation ratio (IPR), defined as

$$\text{IPR}^\alpha = \sum_{ia} a_{ia\alpha}^4. \tag{3.2}$$

Its inverse—the participation ratio—is a rough approximation of the number of orbitals over which a wavefunction is spread. For eigenstates confined to a single atomic orbital, the IPR equals one. Fermi level IPRs computed for the materials studied in this work range from 0.22 (Ag$_2$Te) to 0.33 (Ag$_2$S and Ag$_2$Te), typical of localization over a small fraction of the size of the system.

4. Conclusions

We have presented a numerical study of the liquid zero-gap semiconductors Ag$_2$X, with X = S, Se and Te. The interionic interactions have been—simplistically—described by

the primitive model of charged hard spheres. Geometries have been generated by a Monte Carlo simulation; the electronic structure of the resulting centre-of-mass configurations has been computed using a tight-binding *ansatz.*

The presence of Madelung potential disorder—characteristic of molten ionic fluids— broadens the valence and the conduction band to such a degree that a considerable band overlap occurs if the formation of chemical bonds is neglected. On switching on electron hopping in a computer experiment, chalcogenide and silver bands are shifted by the formation of bonding and antibonding orbitals, leading to the opening of a pseudogap, in which the Fermi level now lies. A population analysis has confirmed the ionic character of the liquid. States at the Fermi level are likely to be localized by Anderson disorder. Any quantitative comparison to experimentally determined transport properties beyond the statement that the silver chalcogenides nontrivially exhibit a nonmetallic character would require the computation both of the DOS and of the electron mobility around E_F.

In the case of liquid silver chalcogenides, partial covalency [25] is not only compatible with an ionic picture of the chemical bond in these materials, but is absolutely essential for the formation of a pseudogap and thus plays a major role in enforcing the ionic character of these materials.

Acknowledgments

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  that 'Most scientists hold clear views on *ionicity* and *covalency*. If they all held the same view as their colleagues, this paper would be unnecessary.'