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Disordered Madelung potentials and the electronic structure of ionic liquid alloys, with application to $\text{Cs}_x[\text{CsAu}]_{1-x}$

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Abstract. We consider the distribution of Madelung potentials (MP) in liquid monovalent binary alloys C_xA_{1-x} exhibiting a significant degree of charge transfer, with particular attention to the $\text{Cs}_x\text{Au}_{1-x}$ system. For canonical models of ionic liquids, and within the framework of linear theories such as the mean spherical approximation, the MP probability distributions are shown to be Gaussian and are studied in some detail. Fluctuations in the effective electronic site energies, arising from disorder in the distribution of site MPs, are shown to occur on the eV scale. We consider the consequences for electronic properties of this coulombic disorder, and its interplay with the effects of on-site electron correlations, with particular emphasis on the C-rich composition domain close to stoichiometry.

1. Introduction

In a simple ionic crystal, the electrostatic potential experienced by a test charge at an ion is the same for all equivalent ions of a given species, as follows by translational invariance. With the loss of long-range order consequent upon melting, this relatively simple situation changes. Ions in different local ionic environments in a liquid will typically experience different electrostatic potentials, and the Madelung potentials (MP) for ions of a given species are characterized by a probability distribution. What can be learned about the MP probability distributions for simple models of ionic liquids? In particular, what are the energy scales which characterize fluctuations in the distributions? And, importantly, what are the likely implications of this coulombic disorder for the excess electrons which result with the cation species element somewhat in excess of stoichiometry?

This paper is an attempt to address some aspects of these questions. The work is in part motivated by the properties of the liquid alloy $\text{Cs}_x\text{Au}_{1-x}$ in the stoichiometric and Cs-rich regime ($x \geq \frac{1}{2}$). A wide range of experiments has been performed on this system [1], probing the composition and temperature dependence of electrical conductivity [2–5], thermopower [3, 4] and magnetic susceptibility [6]; studies of electromigration [7], thermodynamic and structural properties [8–11]; and spectroscopic experiments—optical [12] and NMR [13, 14]. Similarly, important theoretical work [15–23] has been devoted to the structural and electronic properties of the liquid alloy. At stoichiometry, it is known that $\text{Cs}_{1/2}\text{Au}_{1/2}$ is a molten salt-like ionic insulator consisting essentially of Cs^+ and Au^- ions. And with Cs up to $\sim 7\%$ in excess, NMR experiments [13, 14], in particular, indicate the excess electrons which nominally

populate the conduction band to be present in the form of localized paramagnetic centres, behaviour which is not observed in the corresponding near stoichiometric solid [14].

In section 2 we directly motivate the present work with reference to a simple model Hamiltonian for a monovalent binary alloy C_xA_{1-x} . In addition to one-electron contributions of tight-binding form, and on-site electron-electron repulsions, the Hamiltonian contains the inter-site Coulomb interactions on which we focus. With a Hartree field decoupling of the inter-site electron-electron repulsions, an effective electronic Hamiltonian arises in which the bare site energy for an electron on an ion is replaced by an effective or coulombic site energy, to which the net MP at that site directly contributes. Disorder in the distribution of site MP thus generates disorder in the effective electronic site energies, and may in consequence play an important role in determining electrical and magnetic properties of the system (as discussed in sections 6 and 7).

In sections 3-5 we consider the distribution of MP† characteristic of simple ionic liquids, in which the long-ranged part of the interaction potential is essentially the total Madelung energy arising from the model Hamiltonian considered in section 2. This problem is a further addition to a range of different physical problems which have recently attracted attention, and which require a knowledge of local field distributions of one kind or another [24]. In particular, much attention has been given to the distribution of electric microfields [25-32] in plasmas and ionic solutions, relevant for example to spectral line broadening in very hot plasmas. A knowledge of local field distributions also plays a key role in theories of inhomogeneous spectral line broadening of impurities in solids [33], liquids [34] and glasses [35]; and in determining average rates for incoherent electron transfer [36].

In section 3 we briefly formulate the current problem via a familiar charging strategy [37]. In section 4 the distribution of MP is considered within the framework of so-called linear theories, which include as examples the mean spherical approximation (MSA) and the linear hypernetted chain approximation. Simple graph theoretical arguments show the resultant MP distribution for ions of a given species to be exactly Gaussian; and when the short-ranged contributions to the interaction potential are the same for both ionic species the second moment is trivially related to the first, enabling a simple characterization of the full distribution via the mean. This is the case for the much studied primitive model of electrolytes [38], used for example by Evans and Telo da Gama [20] to model the experimental structure factor of stoichiometric $Cs_{1/2}Au_{1/2}$.

Explicit MSA results for the primitive model relevant to the distribution of MP are given briefly in section 5, and in section 6 they are applied to liquid caesium-gold, in particular the stoichiometric alloy. The behaviour of the mean liquid-state cation MP is considered and, at the melting point, is compared with that of the crystalline stoichiometric alloy. Fluctuations in the MP distribution are likewise examined, and are found to occur on significant electronic energy scales on the order of eV. And a series of crude calculations on the optical density of states suggest that the experimentally observed [12] melting-induced red shift of ~ 0.8 eV in the optical absorption edge of $Cs_{1/2}Au_{1/2}$, may arise at least in part from fluctuations in the distribution of MP

† The quantity calculated in practice is the distribution of Madelung potential energies for an electron on an ion of species α , $V_{M;i_\alpha} = e\phi_{M;i_\alpha}$ where $\phi_{M;i_\alpha}$ is the MP. To avoid extraneous factors of e , we do not belabour the distinction.

which typify the liquid, and which come into play upon melting.

In the final section we consider possible implications of the coulombically generated site disorder for the behaviour of Cs_xAu_{1-x} with Cs somewhat in excess. A short discussion is first given of experimental properties relevant in particular to the domain of strongly localized spins for up to $\sim 7\%$ excess Cs, and to the composition-controlled insulator-metal transition in the alloy. A qualitative account of the observations from the present perspective is then given. This involves an interplay between the effects of the coulombically generated site disorder leading to localization of pseudoparticle states in the edge of the conduction band, and the consequent enhancement of electron correlation effects, resulting in strong local moments and hence strong paramagnetism for the excess electrons at low excess metal concentration [39]. The origin of this so-called quasi-atomic regime is then discussed more formally via a specific model Hamiltonian closely related to that considered in section 2. Finally, we mention the possible role of polaronic processes consequent upon disorder-induced charge localization, and contrast briefly the behaviour of Cs_xAu_{1-x} with alkali metal/metal-halide melts.

2. Motivation: a model alloy Hamiltonian

We consider a monovalent binary alloy of form $C_xA_{1-x} \equiv C_y[CA]_{1-y}$, where $x = N_C/(N_C + N_A)$ denotes the mole fraction of the cation species element; equivalently, $y = (2x - 1)/x = (N_C - N_A)/N_C$ prescribes the excess cation fraction above the stoichiometric limit of $x = \frac{1}{2}$, $y = 0$. Each atom/site is assumed to contain a single valence s electron, and for a given centre-of-mass configuration we consider the model Hamiltonian

$$H' = H_{TB} + H_{intra} + H'_{Coul} \quad (2.1a)$$

with

$$H_{TB} = \sum_{\sigma, \alpha} \sum_{i_\alpha} \epsilon_\alpha n_{i_\alpha \sigma} + \sum_{\sigma, \alpha} \sum'_{i_\alpha, j_\gamma} T_{ij}^{\alpha\gamma} C_{i_\alpha \sigma}^+ C_{j_\gamma \sigma} \quad (2.1b)$$

$$H_{intra} = \frac{1}{2} \sum_{\sigma, \alpha} \sum_{i_\alpha} U_\alpha n_{i_\alpha \sigma} n_{i_\alpha -\sigma}. \quad (2.1c)$$

Here, α, γ denote the species (C or A), and i_α, j_γ denote sites of the appropriate species, with centre-of-mass positions $\mathbf{R}_{i_\alpha}, \mathbf{R}_{j_\gamma}$; $C_{i_\alpha \sigma}^+/C_{j_\gamma \sigma}$ are creation/annihilation operators for σ -spin electrons on appropriate sites, and $n_{i_\alpha \sigma} = C_{i_\alpha \sigma}^+ C_{i_\alpha \sigma}$ is the corresponding σ -spin number operator. H_{TB} is a one-electron contribution of tight-binding form with site energies $\epsilon_\alpha = \epsilon_C$ or ϵ_A ; and $T_{ij}^{\alpha\gamma} \equiv T^{\alpha\gamma}(|\mathbf{R}_{i_\alpha} - \mathbf{R}_{j_\gamma}|)$ is an inter-site electron hopping matrix element. H_{intra} describes on-site inter-electron repulsions of familiar Hubbard form.

H'_{Coul} , on which we focus here, describes *inter-site* Coulomb interactions and is taken to have the simple form

$$H'_{Coul} = \frac{1}{2} \sum_{\alpha, \gamma} \sum'_{i_\alpha, j_\gamma} (1 - n_{i_\alpha}) U_{ij}^{\alpha\gamma} (1 - n_{j_\gamma}) \quad (2.2)$$

where $n_{i_\alpha} = \sum_\sigma n_{i_\alpha\sigma}$ is the number operator for the total electronic charge on site i_α , and

$$U_{ij}^{\alpha\gamma} = \frac{e^2}{4\pi\epsilon_0|\mathbf{R}_{i_\alpha} - \mathbf{R}_{j_\gamma}|}. \quad (2.3)$$

H'_{Coul} thus describes coulombic repulsions between the positively charged ion cores, inter-site electron/ion-core interactions (terms linear in n_{i_α}), and inter-site electron-electron Coulomb repulsions. In arriving at (2.2) we have, for simplicity, neglected inter-site electron-electron exchange matrix elements, and have taken the inter-site electron-ion and electron-electron interactions to have pure Coulomb form.

To render H'_{Coul} more transparent, we define $\delta n_{i_\alpha} = n_{i_\alpha} - \bar{n}_{i_\alpha}$ (where the overbar denotes a quantum expectation value for the given centre-of-mass configuration) and use the identity

$$n_{i_\alpha} n_{j_\gamma} = \bar{n}_{i_\alpha} n_{j_\gamma} + \bar{n}_{j_\gamma} n_{i_\alpha} - \bar{n}_{i_\alpha} \bar{n}_{j_\gamma} + \delta n_{i_\alpha} \delta n_{j_\gamma} \quad (2.4)$$

on the inter-site electron-electron terms in H'_{Coul} . The final term in (2.4) gives a contribution to H'_{Coul} of

$$H_{\text{irr}} = \frac{1}{2} \sum_{\alpha,\gamma} \sum'_{i_\alpha, j_\gamma} \delta n_{i_\alpha} U_{ij}^{\alpha\gamma} \delta n_{j_\gamma}.$$

The three remaining terms in (2.4) yield a Hartree approximation to the inter-site electron repulsions, the c -number term $-\bar{n}_{i_\alpha} \bar{n}_{j_\gamma}$ properly eliminating double counting of the Coulomb repulsions. We now neglect H_{irr} (and thus any consideration of the Coulomb gap problem [40, 41]) and work within a Hartree approximation to the inter-site electron-electron interactions: for a given centre-of-mass configuration this is clearly a mean-field approximation in the quantum sense. The net ionic charge on site j_γ , arising from both the core charge and mean electronic occupancy, is thus $Z_{j_\gamma} = 1 - \bar{n}_{j_\gamma}$; for example, $Z_{j_\gamma} = +1$ or -1 ($\bar{n}_{j_\gamma} = 0$ or 2) corresponds to a 'classical' cation or anion.

Using (2.4), and neglecting H_{irr} , (2.2) reduces after some rearrangement to

$$H'_{\text{Coul}} = H_{\text{Coul}} + C \quad (2.5a)$$

where

$$H_{\text{Coul}} = \sum_\alpha \sum_{i_\alpha} V_{M;i_\alpha} n_{i_\alpha} \quad (2.5b)$$

$$C = - \sum_\alpha \sum_{i_\alpha} V_{M;i_\alpha} \bar{n}_{i_\alpha} + E_{\text{MAD}}(\{Z_{j_\gamma}\}). \quad (2.5c)$$

Here, $V_{M;i_\alpha}$ is the MP energy (see footnote p 2) experienced by an electron on site i_α , arising from the mean coulombic fields due to all other ions in the system

$$V_{M;i_\alpha} = - \sum_\gamma \sum'_{j_\gamma} U_{ij}^{\alpha\gamma} Z_{j_\gamma}. \quad (2.6a)$$

Similarly, E_{MAD} appearing in the c -number term C is given by

$$E_{\text{MAD}}(\{Z_{j\gamma}\}) = \frac{1}{2} \sum_{\alpha,\gamma} \sum'_{i_\alpha j_\gamma} Z_{i_\alpha} U_{ij}^{\alpha\gamma} Z_{j_\gamma} = -\frac{1}{2} \sum_{\alpha} \sum_{i_\alpha} V_{M;i_\alpha} Z_{i_\alpha} \quad (2.6b)$$

and is the total electrostatic Madelung energy for the given centre-of-mass configuration: from (2.5)

$$E_{\text{MAD}}(\{Z_{j\gamma}\}) = \bar{H}'_{\text{Coul}}. \quad (2.7)$$

H_{Coul} gives the purely quantum mechanical contribution to H'_{Coul} . Thus $H = H_{\text{TB}} + H_{\text{Coul}} + H_{\text{intra}}$ gives the purely quantum contribution to H' , and from (2.5b) and (2.1) reduces to

$$H = H_{\text{TB}}(\{\epsilon_{i_\alpha}\}) + H_{\text{intra}}. \quad (2.8a)$$

$H_{\text{TB}}(\{\epsilon_{i_\alpha}\})$ is precisely of tight-binding form (2.1b), but with the bare site energies ϵ_α ($\alpha \equiv C$ or A) replaced by

$$\epsilon_{i_\alpha} = \epsilon_\alpha + V_{M;i_\alpha} \quad (2.8b)$$

which is the effective site energy for an electron on site i_α , including the coulombic fields due to all other ions in the system. The observation which motivates the present work is simple: in a disordered system such as a liquid, the MP felt by an electron on sites of a given species will clearly not be the same for all such sites, but will be characterized by a probability distribution which is not δ -function distributed. From (2.8b), disorder in the $\{V_{M;i_\alpha}\}$ leads to site-diagonal disorder in the effective site energies $\{\epsilon_{i_\alpha}\}$ appearing in the electronic Hamiltonian (2.8a), and as discussed in sections 6 and 7 this may play a central role in determining the electrical and magnetic properties of the system. What can be said about the distribution of $\{V_{M;i_\alpha}\}$ and hence the $\{\epsilon_{i_\alpha}\}$, and in particular what are the energy scales which characterize fluctuations in these quantities? Assuming self-averaging, we would thus like to know the probability density for $V_{M;i_\alpha}$ over the ensemble of ionic configurations, which we denote by $F_\alpha(V_{M;i_\alpha})$.

Disorder in the MPs obviously stems from the disorder inherent in the centre-of-mass positions, $\{R_{i_\alpha}\}$, of the ions. This is explicit in (2.6a) via the dependence of $U_{ij}^{\alpha\gamma} \equiv U(|R_{i_\alpha} - R_{j_\gamma}|)$ on the ionic positions, and is the major feature responsible for the disorder in the $\{V_{M;i_\alpha}\}$ considered in sections 3 and afterwards. It is also implicit in the $\{Z_{j_\gamma}\}$ dependence of $V_{M;i_\alpha}$, as $Z_{j_\gamma} = 1 - \bar{n}_{j_\gamma}$, and for each configuration the mean electronic occupation numbers $\{\bar{n}_{j_\gamma}\}$ ought, in principle, to be determined self-consistently from the Hartree equations corresponding to H . The usual approach [15–19] to the latter intricate self-consistency procedure is to simplify it by ‘coarse graining’ the charges: for all sites i_γ of each species γ , Z_{i_γ} is replaced by its ensemble averaged mean value Z_γ ; and Z_C, Z_A are then determined by the bulk charge neutrality condition

$$\sum_{\gamma} x_{\gamma} Z_{\gamma} = 0 \quad (2.9)$$

(where $\{x_\gamma\}$ are the species mole fractions), together with a Hartree self-consistency equation for Z_C/Z_A at the ensemble averaged level. At stoichiometry, for example, (2.9) gives $Z_C = |Z| = -Z_A$, where the self-consistently determined $|Z|$ reflects the degree of ionicity or charge transfer.

As far as estimating the probability distribution of $V_{M;i_\alpha}$ is concerned, coarse graining of the $\{Z_{j_\gamma}\}$, while likely to underestimate fluctuations in the MPs, is probably a reasonable first approximation for systems in which electronic charge transfer is significant and dominated by a sufficiently large electronegativity difference between the cation and anion species elements. This is the case in Cs–Au for example. Stoichiometric liquid $\text{Cs}_{1/2}\text{Au}_{1/2}$ is an ionic insulator, with a filled valence (anion) band and an empty conduction (cation) band. In this split band case one clearly expects $\bar{n}_{j_{\text{Cs}}} \simeq 0$ and $\bar{n}_{j_{\text{Au}}} \simeq 2$ corresponding essentially to classical ions with $Z_{j_{\text{Cs}}} = +1$ and $Z_{j_{\text{Au}}} = -1$. The experimental properties of stoichiometric liquid Cs–Au indeed appear to conform to those of a 1:1 molten electrolyte [1]; and with Cs somewhat in excess, the contribution of $\{Z_{j_\gamma}\}$ to the distribution of MPs potentially experienced by the $N_e = N_{\text{Cs}} - N_{\text{Au}}$ ‘excess’ electrons which nominally populate the conduction band is likely to be dominated by the significant degree of stoichiometric charge transfer.

To illustrate the above at its simplest, suppose that at stoichiometry charge transfer is complete so that $Z_{j_{\text{Au}}} = -1$ and $Z_{j_{\text{Cs}}} = +1$; and that with Cs in slight excess $Z_{j_{\text{Au}}} = -1$ remains. From (2.6a), the stoichiometric MP distribution is then determined solely by the disorder inherent in the centre-of-mass positions of the Cs^+ and Au^- ions, a determination of $F_\alpha(V_{M;i_\alpha})$ thus being essentially a problem of classical liquid-state theory for a 1:1 electrolyte, as considered in the following sections. In calculating F_α with Cs in slight excess, the coarse graining prescription in effect distributes the small number $N_e = N_{\text{Cs}} - N_{\text{Au}}$ of ‘excess’ electrons uniformly over the cation sites, i.e. $\bar{n}_{j_{\text{Cs}}} = N_e/N_{\text{Cs}} = y$ is taken, with the net cation charge $Z_{i_{\text{Cs}}} = 1 - y \lesssim 1$ mainly due to the core charge appropriate to $y = 0$. Again, a calculation of $F_\alpha(V_{M;i_\alpha})$ essentially reduces to a classical liquid-state problem and is determined by the disorder in the centre-of-mass positions of the $\text{Cs}^{Z_{i_{\text{Cs}}}}$ and Au^- ions.

We too will adopt the usual [15–19] coarse graining of $\{Z_{j_\gamma}\}$ in calculating $F_\alpha(V_{M;i_\alpha})$. In particular we further note the following.

(i) That one-electron hybridization effects embodied in the interspecies matrix elements $\{T_{ij}^{AC}\}$, which even in the stoichiometric split-band limit may act to reduce Z_C/Z_A slightly below the ‘classical’ values [17–19], are for generality assumed to be included in the appropriate bulk Hartree self-consistency equation which (together with charge neutrality (2.9)) determines the Z_γ s.

(ii) Given the coarse graining prescription, electron–electron screening at the Hartree level are partially included in counterion screening effects of the classical ionic liquid $(\text{C}^{Z_C})_x(\text{A}^{|Z_A|})_{1-x}$, since the net ionic charges therein are a composite of core charge and Hartree field electron occupancy.

We now consider a potentially important omission in previous work. As mentioned, a Hartree approximation to the inter-site electron–electron interactions is mean field in the quantum sense for a given centre-of-mass configuration. However, much previous work concerned with the electronic structure of liquid alloys employs in effect a *double* mean-field theory. That is, mean field not solely in the Hartree quantum sense for a given disorder realization, but mean field also in a *statistical*

sense: $V_{M;i_\alpha}$ occurring in the effective electronic site energy ϵ_{i_α} (equation (2.8b)) is, for each site of any species, replaced by its constant mean value $\langle V_{M;i_\alpha} \rangle$ averaged over the ensemble of centre-of-mass positions. The site MP is thus, in effect, taken as being δ -function distributed on its mean. Any disorder in the electronic site energies arising from fluctuations in the MPs is thus entirely ignored, the mean MP simply giving a constant shift to each site energy of a given species; and any effects coulombically generated site disorder may have on electrical and magnetic properties of the system are hence *a priori* neglected. We clearly wish to avoid a double mean-field approach.

3. Formulation of the problem

With

$$V_{M;i_\alpha} = - \sum_{\gamma} \sum'_{j_\gamma} U_{ij}^{\alpha\gamma} Z_\gamma \quad (3.1)$$

we thus consider the probability distribution $F_\alpha(V_{M;i_\alpha})$ over the ensemble of centre-of-mass configurations of the liquid. $F_\alpha(x)$ and its Fourier transform $\hat{F}_\alpha(k_1)$ are given by

$$F_\alpha(x) = \langle \delta(V_{M;i_\alpha} - x) \rangle \quad \hat{F}_\alpha(k_1) = \langle \exp(ik_1 V_{M;i_\alpha}) \rangle \quad (3.2)$$

where $\langle \bullet \rangle$ denotes a configurational average, the nature of which must be specified. We take

$$\langle \bullet \rangle = \int d\Gamma e^{-\beta\Phi}(\bullet) / \int d\Gamma e^{-\beta\Phi}$$

where $\beta = 1/kT$, $d\Gamma \equiv \prod_\alpha \prod_{i_\alpha} dR_{i_\alpha}$, and Φ denotes a classical interaction potential which determines the probability with which any configuration is generated. We decompose Φ into pairwise additive terms

$$\Phi = \frac{1}{2} \sum_{\alpha,\gamma} \sum'_{i_\alpha, j_\gamma} \phi_{ij}^{\alpha\gamma} \quad (3.3a)$$

and the pair potential $\phi_{ij}^{\alpha\gamma} \equiv \phi^{\alpha\gamma}(|R_{i_\alpha} - R_{j_\gamma}|)$ is further separated into short- and long-ranged contributions:

$$\phi_{ij}^{\alpha\gamma} = \phi_{ij;SR}^{\alpha\gamma} + \phi_{ij;Coul}^{\alpha\gamma} \quad (3.3b)$$

Since we are concerned with the distribution of MPs in ionic liquids exhibiting a significant degree of charge transfer, the long-ranged part of $\phi_{ij}^{\alpha\gamma}$ is taken to be the coulombic interaction between ions of species α and γ , i.e.

$$\phi_{ij;Coul}^{\alpha\gamma} = Z_\alpha U_{ij}^{\alpha\gamma} Z_\gamma \quad (3.4a)$$

with $U_{ij}^{\alpha\gamma}$ as in (2.3). Notice from (2.6b) and (2.7) (with $Z_{j_\gamma} \rightarrow Z_\gamma$) that Φ is thus decomposed as

$$\Phi = \Phi_{SR} + E_{MAD} \quad (3.4b)$$

where $E_{\text{MAD}} = \bar{H}'_{\text{Coul}}$ arises from the inter-site Coulomb Hamiltonian considered previously. The short-ranged interactions, necessary to ensure thermodynamic stability, do not at this stage need to be specified. Later we consider explicitly the case where the $\phi_{\text{SR}}^{\alpha\gamma}(R)$ are hard sphere interactions, the equisized limit of which corresponds to the much studied primitive model [38].

Equation (3.2) for $\hat{F}_\alpha(k_1)$ may be written using (3.1) as

$$\hat{F}_\alpha(k_1) = \left\langle \exp \left\{ -\beta \sum_\gamma \sum_{i_\gamma} U_{ij}^{\alpha\gamma} \right\} \right\rangle \quad (3.5a)$$

with

$$U_{ij}^{\alpha\gamma} = ik_1 \left(\frac{kT}{Z_\alpha} \right) \left[Z_\alpha U_{ij}^{\alpha\gamma} Z_\gamma \right] \quad (3.5b)$$

and is formally equivalent to

$$\hat{F}_\alpha(k_1) = \exp(-\beta \Delta \mu_\alpha)$$

where $\Delta \mu_\alpha$ is the excess interaction chemical potential for the 'tagged' ion i of species α when it additionally interacts with the other ions in the liquid via the complex 'potential' $U_{ij}^{\alpha\gamma}$. $\Delta \mu_\alpha$ may be calculated via the standard Onsager-Kirkwood-Widom charging strategy [37, 42] whereby one 'charges up' the additional interaction of the tagged particle with the other ions. This leads to

$$\hat{F}_\alpha(k_1) = \exp \left\{ -ik_1 \sum_\gamma \rho_\gamma Z_\gamma \int_0^1 d\lambda \int dR U(R) h_{\alpha\gamma}(R; \lambda) \right\}. \quad (3.6)$$

Here, $U(R) = e^2/(4\pi\epsilon_0 R)$, $\rho_\gamma = \rho x_\gamma$ is the partial number density of species γ ions; and $h_{\alpha\gamma}(R; \lambda) = g_{\alpha\gamma}(R; \lambda) - 1$ is the partial pair distribution function (PDF) for an effective liquid in which the tagged ion of species α at the origin interacts with ions of species γ via the effective pair potential $\phi_{ij}^{\alpha\gamma} + \lambda U_{ij}^{\alpha\gamma}$.

4. Madelung potential distributions: linear theories

To calculate the distribution we thus need $h_{\alpha\gamma}(R; \lambda)$. This we consider within the class of linear graphical theories which include as examples the mean spherical approximation (MSA), the linear hypernetted chain approximation (LHNC) and the linear exponential (LEXP or LIN) approximation [37]. The essential result here is that, for a linear theory, the MP distribution for ions of species $\alpha \equiv \text{C}$ or A is exactly Gaussian; and that in a particular simple but relevant case the second moment of the distribution is trivially related to the first, enabling a complete characterization of the distribution solely from a knowledge of the first moment $M_{1\alpha} = \langle V_{\text{M};i\alpha} \rangle$. The brief proof we now give is based on graphical arguments; the same result follows from a detailed analysis of the relevant integral equations appropriate to a particular linear theory.

Consider first $h_{\alpha\gamma}(R) = h_{\alpha\gamma}(R; \lambda = 0)$, the partial PDF of the actual ionic liquid. This may be analysed formally [37, 43] by regarding the short-ranged part

of the total interaction potential as a reference system, and developing a graphical expansion for $h_{\alpha\gamma}(R)$ in terms of reference system bonds (Mayer f-bonds or PDFs for the reference system), ρ_γ -circles and $\Phi^{\gamma\delta}(ij) \equiv -\beta\phi_{ij}^{\gamma\delta, \text{Coul}}$ bonds pertaining to the interionic Coulomb interactions. We employ the notation $h_{\alpha\gamma}(R) \equiv h_{\alpha\gamma}(1,2)$ where 1,2 label the root points (RP) and are shorthand for R_1, R_2 , the centre-of-mass positions of the ions of species α and γ respectively, such that $R = |R_1 - R_2|$.

Two essential approximations which characterize any linear theory are:

- (i) the maximum number of $\Phi^{\alpha\delta}$ bonds which intersect any field point (FP) is two; and, central to the present discussion,
- (ii) at most one $\Phi^{\gamma\delta}$ bond is connected to a RP.

From (ii) we may formally decompose $h_{\alpha\gamma}(1,2)$ as

$$h_{\alpha\gamma}(1,2) = h_{\alpha\gamma}^{(0)}(1,2) + h_{\alpha\gamma}^{(1)}(1,2) \quad (4.1)$$

where $h_{\alpha\gamma}^{(0)}(1,2)$ is the contribution to $h_{\alpha\gamma}(1,2)$ in which no $\Phi^{\alpha\delta}(1,j)$ bond is connected to RP1 associated with the ion of species α ; and $h_{\alpha\gamma}^{(1)}(1,2)$ is the sum of all contributions in which a single $\Phi^{\alpha\delta}(1,j)$ bond is so connected.

The function $h_{\alpha\gamma}(1,2;\lambda) \equiv h_{\alpha\gamma}(R;\lambda)$ appearing in (3.6) has precisely the same topological structure as $h_{\alpha\gamma}(1,2)$, but with $\Phi_\lambda^{\alpha\delta}(1,j)$ bonds connecting to the RP1 associated with the tagged species α particle, where

$$\begin{aligned} \Phi_\lambda^{\alpha\delta}(1,j) &= \Phi^{\alpha\delta}(1,j) + [-\beta\lambda U^{\alpha\delta}(1,j)] \\ &= \left[1 + ik_1\lambda \left(\frac{kT}{Z_\alpha} \right) \right] \Phi^{\alpha\delta}(1,j). \end{aligned} \quad (4.2)$$

From (ii) above it follows that $h_{\alpha\gamma}^{(0)}(1,2;\lambda) = h_{\alpha\gamma}^{(0)}(1,2)$; and, using (4.2), that

$$h_{\alpha\gamma}(1,2;\lambda) = h_{\alpha\gamma}^{(0)}(1,2) + h_{\alpha\gamma}^{(1)}(1,2;\lambda) \quad (4.3a)$$

where

$$h_{\alpha\gamma}^{(1)}(1,2;\lambda) = \left[1 + ik_1\lambda \left(\frac{kT}{Z_\alpha} \right) \right] h_{\alpha\gamma}^{(1)}(1,2). \quad (4.3b)$$

Hence using (4.1) we have the desired result that

$$h_{\alpha\gamma}(1,2;\lambda) = h_{\alpha\gamma}(1,2) + ik_1\lambda \left(\frac{kT}{Z_\alpha} \right) h_{\alpha\gamma}^{(1)}(1,2) \quad (4.4)$$

where the entire $k_1\lambda$ dependence of $h_{\alpha\gamma}(1,2;\lambda)$ is explicit.

Since $h_{\alpha\gamma}(R;\lambda)$ is linear in λk_1 , it follows from (3.6) that within the framework of any linear theory, the MP probability distribution is exactly Gaussian:

$$F_\alpha(x) = \frac{1}{\sqrt{2\pi}M_{2\alpha}} \exp \left\{ -[x - M_{1\alpha}]^2 / 2M_{2\alpha}^2 \right\}. \quad (4.5)$$

The mean MP for ions of species α , $M_{1\alpha} = \langle V_{M;i_\alpha} \rangle$, is given simply by

$$M_{1\alpha} = - \sum_\gamma \rho_\gamma Z_\gamma \int dR U(R) h_{\alpha\gamma}(R) \quad (4.6a)$$

and the second moment $M_{2\alpha} = \langle [V_{M;i_\alpha} - \langle V_{M;i_\alpha} \rangle]^2 \rangle^{1/2}$ characterizing the fluctuations is given by

$$M_{2\alpha}^2 = -\frac{kT}{Z_\alpha} \sum_\gamma \rho_\gamma Z_\gamma \int dR U(R) [h_{\alpha\gamma}(R) - h_{\alpha\gamma}^{(0)}(R)]. \quad (4.6b)$$

The distribution is thus naturally controlled by the structural characteristics (or chemical short-ranged order) of the ionic liquid, embodied in the partial PDFs.

That the MP distribution is Gaussian stems from the linearity of (4.4) in $k_1 \lambda$, which is the essential feature of a linear graphical theory. In a wider context, one expects generic local field distributions [24] to be Gaussian within the framework of linear theories. For example, Lado [29] has shown the distribution of electric microfields to be Gaussian within the MSA for a one-component plasma; and Vericat *et al* [31] (see also Blum and Hubbard [32]) find the same for the MSA microfield distribution appropriate to ionic and polar solutions.

The result (4.6b) for the second moment of the MP distribution simplifies usefully when the short-ranged interactions which characterize the reference system are the same for all species, so the reference liquid is in effect a one-component system. This is the case, for example, with the much studied primitive model of electrolytes [38], where the charged hard spheres of the various species have equal hard-sphere diameters. The basic structure of graphs contributing to $h_{\alpha\gamma}(1,2)$ in any linear theory is a connected polygonal chain of $\Phi^{\beta\delta}(j,k)$ and/or reference system bonds extending from RP1 to RP2, with the possibility of subsequent decoration by reference system bonds alone. For a one-component reference system, an FP k in any such graph which is intersected by $n = 1$ or 2 $\Phi^{\beta\delta}(j,k)$ bonds is associated with a factor of ρ_δ and hence in total with a factor of $\sum_\delta \rho_\delta Z_\delta^n$. The bulk charge neutrality condition $\sum_\delta \rho_\delta Z_\delta = 0$ thus implies that an FP can be intersected by two or zero $\Phi^{\beta\delta}$ bonds only. As $h_{\alpha\gamma}^{(0)}(1,2)$ is defined to be such that no $\Phi^{\alpha\delta}(1,k)$ bonds connect to RP1, it follows that $h_{\alpha\gamma}^{(0)}(1,2)$ contains reference system bonds alone, and is simply the PDF for the reference system appropriate to the specific linear theory. For example, with an equisized hard-sphere reference system appropriate to the primitive model, $h^{(0)}(R) \equiv h_{\alpha\gamma}^{(0)}(R)$ is the Percus–Yevick approximation to the hard-sphere PDF within the MSA [37, 43], and is the full hard-sphere PDF for LHNC.

Since $h_{\alpha\gamma}^{(0)}(R)$ is independent of the species for a one-component reference system, it follows from (4.6) using bulk electroneutrality that

$$M_{2\alpha}^2 = \frac{kT}{Z_\alpha} M_{1\alpha}. \quad (4.7)$$

This result enables a particularly simple characterization of the full MP probability distribution (4.5) solely from a knowledge of $M_{1\alpha}$, equation (4.6a). Different linear theories will naturally correspond to different specific approximations to the partial PDFs, $h_{\alpha\gamma}(R)$, of the ionic liquid; a specific case is now discussed.

5. Primitive model: MSA

Here we consider the MP distribution within the MSA for the primitive model of a binary electrolyte. The MSA primitive model is of relevance to liquid Cs–Au, as it

has been employed with some success by Evans and Telo da Gama [20] to model the experimental structure factor of stoichiometric liquid Cs–Au, and by Holzhey *et al* [19] in their double mean-field study of alkali–gold alloys.

From (3.4b), the excess internal energy per ion (over the reference system) is $U^{ex}/N = \langle E_{MAD} \rangle / N$ with $N = N_C + N_A$ the total number of ions; and thus from (2.6b) (with $Z_{j_\gamma} \rightarrow Z_\gamma$)

$$\frac{U^{ex}}{N} = -\frac{1}{2} \sum_{\alpha} x_{\alpha} Z_{\alpha} \langle V_{M;i_{\alpha}} \rangle. \quad (5.1a)$$

For the primitive model, $h_{\alpha\gamma}^{(0)}(R) \equiv h^{(0)}(R)$ within a linear theory as discussed above, and $h_{\alpha\gamma}^{(1)}(R)$ is of the form $Z_{\alpha} C(R) Z_{\gamma}$. From (4.1) and (4.6a) together with the bulk electroneutrality condition, it follows that $Z_C \langle V_{M;i_A} \rangle = Z_A \langle V_{M;i_C} \rangle$, and (5.1a) reduces to

$$\frac{U^{ex}}{N} = \frac{1}{2} Z_A \langle V_{M;i_C} \rangle = \frac{1}{2} Z_C \langle V_{M;i_A} \rangle. \quad (5.1b)$$

Knowledge of U^{ex}/N is thus sufficient to give $M_{1\alpha} = \langle V_{M;i_{\alpha}} \rangle$. For the MSA, Waisman and Lebowitz [44] have given the excess internal energy in closed form. It is a function of the MSA coupling constant ξ given via $\xi^2 = \xi_1^2 |Z_A Z_C|$ where

$$\xi_1^2 = 4\pi\rho^* \beta^*. \quad (5.2a)$$

$\rho^* = \rho\sigma^3$ is the reduced density, with σ the hard-sphere diameter of the constituent ions; and we have defined the reduced inverse temperature by $\beta^* = \beta[e^2/4\pi\epsilon_0\sigma]$. From the charge neutrality condition (2.9), $Z_C = -(1-y)Z_A$, whence

$$\xi^2 = (1-y)Z_A^2 \xi_1^2 \quad (5.2b)$$

with $y = 0$ corresponding to the stoichiometric alloy. From Waisman and Lebowitz's results [44], and using (5.1b), $M_{1\alpha}$ ($\alpha = C$ or A) is thus given in closed form by

$$(M_{1\alpha} \equiv) \langle V_{M;i_{\alpha}} \rangle = Z_{\alpha} \frac{e^2}{4\pi\epsilon_0\sigma} A(\xi) \quad (5.3a)$$

with

$$A(\xi) = \frac{2}{\xi} \left[1 + \xi - (1 + 2\xi)^{1/2} \right]. \quad (5.3b)$$

Note that $A(\xi) \rightarrow \xi$ as $\xi \rightarrow 0$ corresponds to the Debye–Hückel limit; and $A(\xi) \rightarrow 2$ as $\xi \rightarrow \infty$ corresponds to the Onsager bound [45] on the excess internal energy, reflected in a saturation of $M_{1\alpha}$ as $\xi \rightarrow \infty$. In the molten salt regime, relevant to our subsequent discussion of Cs–Au, $\xi \approx 20$ is typical. We also add that the accuracy of the MSA for $M_{1\alpha}$ can be assessed by comparison of the MSA for U^{ex}/N with Larsen's [46] Monte Carlo simulations of the restricted primitive model (i.e. at stoichiometry, $x_{\alpha} = \frac{1}{2}$): in the molten salt domain the MSA reproduces U^{ex}/N to $\lesssim 5\%$ accuracy, which is wholly adequate for present purposes.

With $M_{1\alpha}$ given from (5.3), $M_{2\alpha}$ follows from (4.7), and the MSA MP probability distribution $F_{\alpha}(x)$ (equation (4.5)) is thus specified.

6. Application: $\text{Cs}_{1/2}\text{Au}_{1/2}$, liquid and solid

In figure 1 we illustrate the MSA results for the case of stoichiometric Cs-Au ($y = 0$), which is known experimentally [1] to be a molten salt ionic insulator. The mean liquid-state cation MP, M_{1C} (in eV), and the root mean square (RMS) fluctuation in the distribution, M_{2C} , are shown as the temperature is increased from the melting point $T_M = 590^\circ\text{C}$. From the results of Martin *et al* [10], the ionic number density at T_M is $\rho \approx 2.24 \times 10^{22} \text{ cm}^{-3}$, and since ρ varies very little over the temperature range of figure 1 we have taken this value throughout. From the work of Evans and Telo da Gama [20], we take the effective hard ion diameter $\sigma = 3.15 \text{ \AA}$; thus $\rho^* = 0.70$, typical of a molten salt. At stoichiometry, $Z_C = |Z| = -Z_A$, and we have illustrated the MSA results for M_{1C} and M_{2C} for two choices of $|Z| = 1$ and 0.8 . The former corresponds to total charge transfer with 'classical' ions, and although this is largely the consensus choice in describing experimental properties of the stoichiometric alloy, we consider also the case $|Z| = 0.8$ to illustrate the possible role of partial charge transfer due to one-electron hybridization effects studied by Holzhey *et al* [17-19].

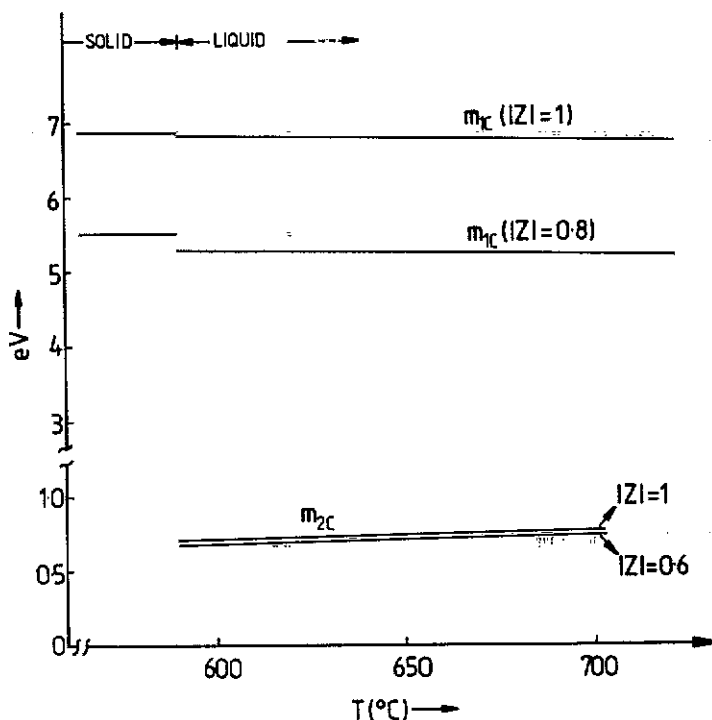


Figure 1. Mean liquid-state cation MP energy (M_{1C}), and RMS fluctuations (M_{2C}), obtained from the primitive model MSA with parameters appropriate to stoichiometric Cs-Au; as a function of T (in $^\circ\text{C}$) from the melting point ($T_M = 590^\circ\text{C}$). Results for different values of $|Z|$ ($= Z_C = -Z_A$) are shown. For $T < T_M$, corresponding solid state values for the mean are shown (see text).

Consider first the mean cation MP (note that $M_{1A} = -M_{1C}$ and $M_{2A} = M_{2C}$ at stoichiometry). As seen from figure 1, M_{1C} is only very weakly T -dependent but is naturally sensitive to the degree of charge transfer, embodied principally in the

explicit Z_α factor in equation (5.3a). In particular, for the liquid at its melting point, we find $M_{1C} = 6.83$ eV (for $|Z| = 1$) and 5.28 eV (for $|Z| = 0.8$).

It is now instructive to calculate the MP energy for the crystalline stoichiometric Cs–Au alloy, which has the CsCl structure. This is given by ($\alpha \equiv C$ or A)

$$V_{M;\alpha}(\text{solid}) = Z_\alpha \frac{e^2}{4\pi\epsilon_0 r_0} \gamma \quad (6.1)$$

where $\gamma = 1.762670$ is the Madelung constant for the CsCl structure and $r_0 = \sqrt{3}a/2$ is the nearest-neighbour distance with a the lattice constant. We note the similarity in form between the solid state result (6.1) and the MSA result (5.3a) for the mean liquid state MP, $A(\xi)/\sigma$ in the latter playing essentially the same role as γ/r_0 in the former. From the work of Spicer *et al* [47], $a = 4.263$ Å for crystalline $Cs_{1/2}Au_{1/2}$, so (6.1) yields $V_{M;C}(\text{solid}) = 6.87$ eV (for $|Z| = 1$) and 5.50 eV (for $|Z| = 0.8$). Notice that the two parametrically unrelated calculations—for the solid and the liquid at its melting point—are extremely close as illustrated in figure 1, being within $< 1\%$ of each other for $|Z| = 1$.

We now consider fluctuations in the MP, which clearly have no natural analogue in the crystalline solid but which typify the liquid, and which as discussed in section 2 lead to disorder in the effective site energies $\{\epsilon_{i\alpha}\}$ appearing in the model electronic Hamiltonian (2.8). As is evident from figure 1, the MSA RMS fluctuations M_{2C} are quite insensitive to either temperature or the degree of charge transfer (M_{2C} for $|Z| = 0.8$ lying between those shown for $|Z| = 1$ and 0.6). More importantly we note that fluctuations in the MPs, and hence the electronic site energies, occur on an appreciable energy scale of $\sim 3/4$ eV, possible implications for which are discussed later and in the following section.

These comments refer to stoichiometric Cs–Au, $y = 0$. To estimate the effect upon MP fluctuations of increasing the cation species somewhat above stoichiometry, note from (4.7) and (5.3) that

$$M_{2\alpha} = \left[\frac{e^2}{4\pi\epsilon_0\sigma} kT A(\xi) \right]^{1/2}. \quad (6.2)$$

For given T , the dependence of fluctuations on the (interdependent) variables $y, |Z_A|$ and ρ^* is contained solely in $A(\xi)$, (5.3b), with $\xi = |Z_A|[(1-y)4\pi\rho^*\beta^*]^{1/2}$; and $[A(\xi)]^{1/2}$ is a monotonically increasing but slowly varying function of ξ , increasing by only $\sim 10\%$ over the wide range $10 \leq \xi \leq 35$ which encompasses any reasonable ξ domain of interest. For example, at $T = 640$ °C, and for y in the range $0 - \frac{1}{3}$ (where the experimental DC conductivity [5] is $\lesssim 600 \Omega^{-1} \text{cm}^{-1}$), ξ lies in the range $\sim 22|Z_A|$ to $\sim 16|Z_A|$ using experimental densities from Martin *et al* [10] and Kempf and Schmutzler [1]; and M_{2C} varies only very slightly about ~ 0.7 eV for any reasonable estimate [19] of $|Z_A|$ in this y interval. In contrast, as expected, the mean liquid-state cation MP M_{1C} diminishes on the eV scale over this y range, due mainly to the explicit factor of $Z_C = (1-y)|Z_A|$ appearing in (5.3a) for M_{1C} .

Although the preceding theory is designed to estimate the MP distribution in ionic liquids exhibiting a non-negligible degree of charge transfer, and should not be pushed too far, we note that as $y \rightarrow 1$ the MSA $F_\alpha(V_{M;i_\alpha}) \rightarrow \delta(V_{M;i_\alpha})$ as expected for the non-ionic pure C species element where, given the usual coarse graining prescription described in section 2, the electrons completely screen out the C+ core

charge for $y = 1$. Experimentally [10], the pure Cs element reached as $y \rightarrow 1$ in the $\text{Cs}_y[\text{CsAu}]_{1-y}$ alloy has $r_s/a_0 \sim 6$ (where $\frac{4}{3}\pi\rho r_s^3 = 1$), typical of a fairly high density liquid metal; and one might reasonably model the system as an interacting electron gas in this limit. That $F_\alpha(V_{M;i_\alpha}) = \delta(V_{M;i_\alpha})$ for $y = 1$ as above may however be regarded as an analogue of the fact that, for an electron gas, the potential felt by an electron due to the ion cores is precisely cancelled by the direct ('bubble diagram') interaction describing the Hartree potential arising from the other electrons. In the electron gas the electrons do not totally screen the core charge, but are certainly highly effective in this regard: for example, with $r_s/a_0 \sim 6$, $\lambda/r_s \sim \frac{1}{4}$ where λ is the Thomas-Fermi screening length.

To see a possible implication of disorder in the distribution of effective electronic site energies $\{\epsilon_{i_\alpha}\}$ (equation (2.8b)) arising from the distribution of MPs, we consider again the stoichiometric alloy $\text{Cs}_{1/2}\text{Au}_{1/2}$. In figure 2 we show schematically the zero order electronic density of states ($D^0(E)$) arising if we neglect coulombically generated site disorder, and consisting at stoichiometry of a filled valence (anion) band and an empty conduction (cation) band separated by a gap. Also shown are the distribution of effective site energies for cation and anion species sites, which are essentially (see (2.8b)) just the Gaussian MP distributions for ions of the appropriate species. Clearly, a fraction of the ions will have effective site energies lying outside the unperturbed bands. What this implies when the DOS is calculated including the coulombically generated site disorder is that the DOS will 'smear out' somewhat into the gap, which is thus reduced from its zero-order value.

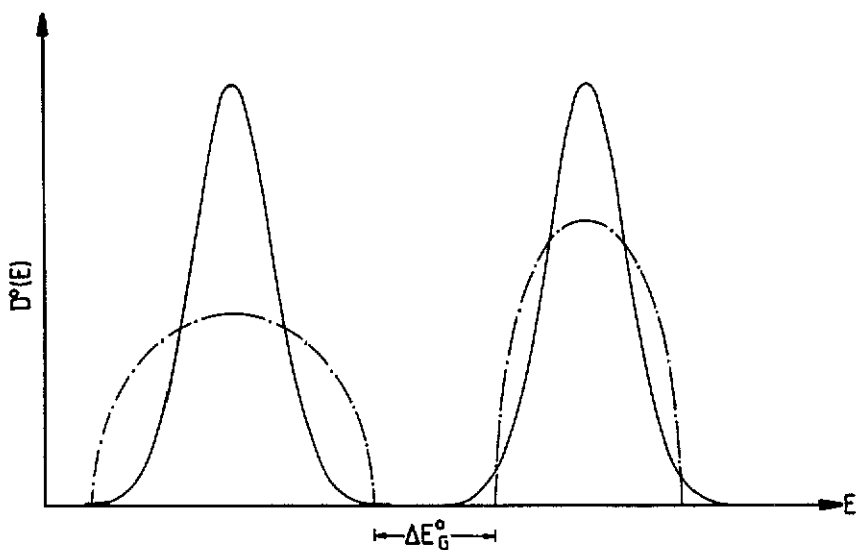


Figure 2. Schematic illustration of stoichiometric zero-order electronic DOS, $D^0(E)$ (chain curve), arising if coulombic site disorder is neglected; and consisting of filled valence and empty conduction bands separated by a gap ΔE_G^0 . The Gaussian distributions of coulombic site energies for cation and anion species sites are also shown (full curves).

An *ab initio* calculation of the band gap in the stoichiometric liquid alloy is exceedingly difficult; and previous theories, which neglect MP fluctuations, in effect choose model parameters to fit the gap. As hinted above, however, we can assess the relative shift in the band gap—reflected for example in the optical DOS—when

we bring into play fluctuations in the MPs, and hence site energies, which are typical of the liquid. This should provide a rough estimate of the sort of shift one might expect in the optical absorption edge when the crystalline solid is melted, assuming the principal change in the band gap on melting arises from the introduction of fluctuations in the distribution of MPs; and, in particular, that the mean ionic MPs in the liquid ($M_{1C} = -M_{1A}$) at its melting point do not differ appreciably from those for the crystalline solid—which, as above, appears to be the case for $Cs_{1/2}Au_{1/2}$.

To estimate a typical magnitude of the shift, we consider the optical DOS (to which the optical absorption is essentially proportional [48])

$$D_{\text{opt}}(\omega) = \int_{E_F - \hbar\omega}^{E_F} D(E)D(E + \hbar\omega) dE$$

as a function of photon energy $\hbar\omega$. The ODOS is first calculated without MP fluctuations (as would be the case for the solid), with a known band gap ΔE_G^0 which we take to be 2.1 eV—the gap for stoichiometric crystalline $Cs_{1/2}Au_{1/2}$ at its melting point found experimentally by Münster and Freyland [12]. We denote this by $D_{\text{opt}}^0(\omega)$ and estimate it very simply by assuming a simple semi-elliptic DOS for the zero-order valence and conduction bands. These have widths W_A^0 and W_C^0 respectively, and are centred on ϵ_A^0 and ϵ_C^0 (with $\epsilon_C^0 - \epsilon_A^0$ chosen so the given ΔE_G^0 is reproduced), where the effective ϵ_α^0 implicitly include effects due to the mean MP and on-site correlations at the Hartree level. We then calculate $D(E) = D_V(E) + D_C(E)$ in the presence of the coulombically generated site disorder. In practice, the ionic site energies $\epsilon_{i_\alpha} = \epsilon_\alpha^0 + (V_{M;i_\alpha} - \langle V_{M;i_\alpha} \rangle)$ are treated as independent random variables with a Gaussian distribution for $V_{M;i_\alpha}$ of halfwidth $(2 \ln 2)^{1/2} M_{2\alpha} = 0.84$ eV, obtained via the MSA from the known density and temperature of stoichiometric liquid $Cs_{1/2}Au_{1/2}$ at its melting point (as in figure 1); and $D_V(E)$, $D_C(E)$ are estimated very simply by a simple single-site approximation [49] requiring solely a knowledge of W_A^0 , W_C^0 and the site energy distribution. The resultant $D_{\text{opt}}(\omega)$ is then compared with $D_{\text{opt}}^0(\omega)$, and the shift to lower ω in the edge of D_{opt} can then be assessed.

These calculations should not be taken too seriously but, as one might expect physically, we find the shift to be of the order of the halfwidth of the coulombic site energy distribution, $(2 \ln 2)^{1/2} M_{2\alpha} \sim 0.85$ eV as above. In fact, with W_A^0/W_C^0 in the range $W_A^0 \sim 4-7$ eV, $W_C^0 \sim 2\frac{1}{2}-5$ eV (encompassing previous estimates [17-19]), and with ΔE_G^0 also scanned over a wide range of $\sim 2-6$ eV, we find the shift to lie in the range $\sim 0.8-1.2$ eV.

Albeit that this shift estimate is crude it is interesting, and perhaps not coincidental, that Münster and Freyland [12] observed a discontinuous redshift of about 0.8 eV in the optical absorption edge of stoichiometric $Cs_{1/2}Au_{1/2}$ when the solid was melted: the observed volt-scale, melting-induced shift may stem largely, or at least in part, from fluctuations in the distribution of MPs which typify the liquid, and which come into play when the solid is melted.

7. Discussion: $Cs_y[CsAu]_{1-y}$, $y > 0$

The stoichiometric split-band alloy CA, on which we have mainly focused, is effectively a zero-particle problem in the sense that there are no holes in the valence (anion) band and no electrons in the conduction (cation) band. We now consider the likely

effect of the coulombically generated site disorder on the $N_e = N_C - N_A$ 'excess' electrons as the excess cation fraction $y (= N_e/N_C)$ is increased above stoichiometry, $y = 0$.

The experimental properties of liquid $\text{Cs}_y[\text{CsAu}]_{1-y}$ with Cs in excess are rich. In particular, a ^{133}Cs NMR study by Dupree *et al* [13] of the Knight shift, K , and the spin-lattice relaxation rate, T_1^{-1} , points clearly to the existence of strongly localized spins for y up to ~ 0.07 (7% excess Cs). K is proportional to the electronic paramagnetic spin susceptibility χ_{ep} . For $0 < y \lesssim 0.07$, K is observed [13] to be linear in y , commensurate with a free-spin- $\frac{1}{2}$ Curie law paramagnetism for the excess electrons, which is also supported by the direct magnetic susceptibility measurements of Freyland and Steinleitner [6]; and above $y_C = 0.07$ this behaviour is rapidly lost. In the same y range, an enhanced T_1^{-1} characteristic of strongly localized spins is also observed [13]. The features just described are not observed in the crystalline near-stoichiometric alloy [14], for which no evidence is found for excess localized paramagnetic centres.

At what value, y_M , of y does a composition-induced insulator-metal transition (I-MT) occur in the liquid alloy? Experimentally one would like to answer this via electrical conductivity measurements, but the experiments [2-5] are of necessity performed at elevated temperatures ($T \sim 600^\circ\text{C}$) and precise sample control is demanding; an unambiguous answer is difficult to obtain. Previous conductivity studies [2-4] suggest an I-MT around $y_M \sim 0.21$ (where $\sigma_{\text{dc}} \sim 450 \Omega^{-1} \text{cm}^{-1}$ from recent measurements [5]), and it is worth noting that the work of Avcı and Flynn [50], and Swenumson and Even [51], on amorphous $\text{Cs}_y[\text{CsAu}]_{1-y}$ in the temperature range $T \sim 5\text{-}20$ K suggests an I-MT around $y \sim 0.3$. The above NMR results [13] are certainly consistent with localized electronic states for $y \lesssim 0.07$; and at $y = y_C \simeq 0.07$, $\sigma_{\text{dc}} \simeq 130 \Omega^{-1} \text{cm}^{-1}$ [5] which is sufficiently below any reasonable estimate of σ_{min} that we expect $y_M > y_C$. (Further, as argued physically later, we do not think it reasonable to infer an I-MT from the onset of a diminution in K or χ_{ep} below a linear dependence on y characteristic of free-spin- $\frac{1}{2}$ Curie law paramagnetism.) All one can say with some confidence is that y_M probably lies somewhat in excess of y_C .

7.1. Qualitative considerations

We first attempt a qualitative account of the observations from the viewpoint of the present work, involving an interplay between disorder and the effects of electron correlation. Referring to figure 1, we pointed out that a fraction, f_- , of cation sites will have effective coulombic site energies lying below the lower edge of the unperturbed conduction/cation band, extending somewhat into the gap region. As a rough order of magnitude estimate, we find from the MSA $F(V_{M;iC})$ with parameters appropriate to $\text{Cs}_y[\text{CsAu}]_{1-y}$ at low y for the temperature range $T \sim 600\text{-}800^\circ\text{C}$, and with zero-order cation bandwidths $W_C^0 \sim 2\text{-}4$ eV, that f_- has a fairly small value typically in the range 1-10%.

Regardless of the precise means of modelling, we expect pseudoparticle states in the low-energy edge of the conduction band DOS to be localized, mainly by the effects of the coulombic site disorder. For relatively small amounts of excess Cs, we thus expect physically that the $N_e = N_{\text{Cs}} - N_{\text{Au}}$ excess electrons will occupy such localized states, centred around cation sites with the lowest coulombic site energies—those sites whose local ionic environment is energetically most favourable in terms of

the local coulombic fields experienced by the electrons. The system would therefore be insulating.

That, however, is only part of the problem—for the greater the tendency is towards coulombically induced localization of the excess electrons, the greater the extent to which electron–electron interactions will act to prevent double occupancy of the relevant states. That is, in consequence of disorder-induced charge localization, the excess electrons at sufficiently low concentration will be highly correlated, electrons of the opposite spin being effectively precluded from an occupied spatial region by the effects of electron–electron interactions (both on-site and inter-site in general). For sufficiently small excess Cs concentrations, we thus envisage the occupied pseudoparticle states in the edge of the conduction band to be essentially non-overlapping and singly occupied by electrons. In consequence, it follows that in such a low- y domain the paramagnetic spin susceptibility per cation site, χ_{ep} , will follow a free spin- $\frac{1}{2}$ Curie law, i.e.

$$\chi_{ep} = \frac{\mu_0 \mu_B^2}{kT} \frac{N_e}{N_{Cs}} = \frac{\mu_0 \mu_B^2}{kT} y. \quad (7.1)$$

Both χ_{ep} and hence the Knight shift, K , should thus be proportional to y in $Cs_y[CsAu]_{1-y}$, as observed for $y < y_C \sim 0.07$ [13]. We add that arguments based on disorder alone are unlikely to suffice: if electron correlation effects were irrelevant, we would expect essentially doubly occupied pseudoparticle states, leading to a Pauli paramagnetism for the excess electrons with an expected y dependence $\chi_{ep} \sim y^{1/3}$.

To point up the above, note that we do *not* assume the localized pseudoparticle states occupied by the excess electrons at low y to be atomically localized on single cation sites: the states may, and in general will, extend over several such sites. To obtain (7.1) we simply require y sufficiently small that the localization lengths ξ_λ of the occupied pseudoparticle states are small compared to the mean separation between the excess electrons, so the singly occupied states do not overlap each other in space. Provided this is the case, a free-spin- $\frac{1}{2}$ Curie law paramagnetism for the excess electrons will result, as it would for the case of genuine ‘atomic’ localization; for this reason, we refer to the y domain in which a free-spin- $\frac{1}{2}$ Curie law paramagnetism results as a quasi-atomic regime [39].

These arguments have a further implication. The smaller the localization length, ξ_λ , of a pseudoparticle state, the greater the extent to which electron correlation effects are enhanced, suppressing double occupancy of the state. Physically, we expect ξ_λ to increase with increasing pseudoparticle state energy, tending to infinity as a mobility edge is approached from below. Further, with increasing population of the conduction band (increasing y), the mean separation between the excess electrons will decrease. The free-spin- $\frac{1}{2}$ Curie law paramagnetism symptomatic of the quasi-atomic regime is indicative of the excess electrons being in non-overlapping singly occupied localized states; and erosion of this behaviour as y is further increased will occur when some of the occupied pseudoparticle states overlap each other in space. From the above, this process will begin to occur when the occupied states are still localized; that is still in the insulating domain, below the critical y_M at which Fermi level pseudoparticle states become extended over a finite fraction of the macroscopic system ($\xi_F \rightarrow \infty$) and the transition to a metallic state occurs. We thus expect $y_M > y_C$ where y_C is the excess Cs fraction at which the paramagnetic susceptibility begins to deviate below a free-spin- $\frac{1}{2}$ Curie law paramagnetism. (Quantitatively,

however, all we can say is that $y_C \sim 0.07$ is compatible with the rough estimate of $f_- \sim 1-10\%$.)

7.2. The quasi-atomic limit

To see the origins of the quasi-atomic regime from a specific model, we consider a simple one-band description of the conduction band (cf equations (2.8), (2.1b,c)):

$$H_C = H_{TB}(\{\epsilon_{iC}\}) + H_{\text{intra}} \quad (7.2)$$

$$H_{TB} = \sum_{i,\sigma} \epsilon_{iC} n_{i\sigma} + \sum'_{i,j,\sigma} T_{ij} C_{i\sigma}^\dagger C_{j\sigma} \quad (7.3a)$$

$$H_{\text{intra}} = \sum_i U n_{i\uparrow} n_{i\downarrow}. \quad (7.3b)$$

As in (2.8b), $\epsilon_{iC} = \epsilon_C + V_{M;iC}$ includes the coulombically generated site disorder; and the sums now run over cation sites only, with $T_{ij} = T(|\mathbf{R}_{iC} - \mathbf{R}_{jC}|)$ and the on-site Hubbard U referring to cation sites. H_C is just a simplification of the model H considered in (2.8a), for if one-electron hybridization matrix elements $\{T_{ij}^{AC}\}$ are neglected H is separable, $H = H_A + H_C$, with H_A pertaining to the anion/valence band and H_C as above. The simplification is physically reasonable provided conduction band pseudoparticle states are primarily associated with the cation sites, but we make it largely for convenience: much of what follows can be extended with labour to the full H .

The disordered Hubbard model H_C can clearly be canonically transformed [52, 53] from a site basis to a representation in terms of the exact eigenstates $\{|\Psi_\lambda\rangle\}$ of the Hamiltonian in the $U = 0$ non-interacting limit (i.e. the disordered tight-binding Hamiltonian (TBH), $H_{TB}(\{\epsilon_{iC}\})$), with basic operators $C_{\lambda\sigma}^\dagger$ and $C_{\lambda\sigma}$. Specifically,

$$C_{\lambda\sigma}^\dagger = \sum_i a_{i\lambda} C_{i\sigma}^\dagger \quad C_{\lambda\sigma} = \sum_i a_{i\lambda}^* C_{i\sigma} \quad (7.4)$$

where $a_{i\lambda}$ is the coefficient of the site atomic orbital $|i\rangle$ in the expansion of the TBH eigenstate $|\Psi_\lambda\rangle$ with energy E_λ : $|\Psi_\lambda\rangle = \sum_i a_{i\lambda} |i\rangle$. This leads to

$$H_C = \sum_{\lambda,\sigma} E_\lambda n_{\lambda\sigma} + \sum_{\lambda,\nu,\mu,\tau} U_{\lambda\nu\mu\tau} C_{\lambda\uparrow}^\dagger C_{\nu\uparrow} C_{\mu\downarrow}^\dagger C_{\tau\downarrow} \quad (7.5a)$$

$$= \sum_{\lambda,\sigma} E_\lambda n_{\lambda\sigma} + \sum_\lambda U_\lambda n_{\lambda\uparrow} n_{\lambda\downarrow} + (\text{terms excluding } \lambda = \nu = \mu = \tau) \quad (7.5b)$$

where

$$U_{\lambda\nu\mu\tau} = U \sum_i a_{i\lambda}^* a_{i\nu} a_{i\mu}^* a_{i\tau}. \quad (7.5c)$$

In particular, $U_\lambda \equiv U_{\lambda\lambda\lambda\lambda}$ is given by

$$U_\lambda = U \sum_i |a_{i\lambda}|^4 \equiv UL(E_\lambda) \quad (7.6)$$

where $L(E_\lambda)$ is the inverse participation ratio (IPR) for a TBH state of energy E_λ , which vanishes for an extended state and is finite for a localized state, with $[L(E_\lambda)]^{-1}$ a rough measure of the number of sites participating in the state. The interplay between disorder and correlation is thus evident in $U_{\lambda\nu\mu\tau}$ in general, and U_λ in particular, for the latter is an effective 'on-state' Hubbard- U for a TBH state of energy E_λ ; and its magnitude is determined by the extent to which the state is localized, increasing for more strongly localized states.

We now consider the system at a low filling fraction $y = N_e/N_C$ such that, for $U = 0$, only a small fraction of TBH conduction band 'tail states' are occupied in the non-interacting ground state. The non-interacting ground state thus consists of TBH states doubly occupied up to an energy $E_F^0(y)$. This is illustrated in figure 3 which shows schematically the lower region of the conduction band DOS in the $U = 0$ non-interacting (TBH) limit, denoted by $D_C^{(0)}(E)$ (full curve). A region of TBH states is assumed localized by the effects of disorder, with a mobility edge E_{mob} separating the localized and extended portions of the spectrum as shown. And y is assumed sufficiently small that the occupied TBH states are quite strongly localized (with $E_F^0(y) \ll E_{mob}$), so such localized states will typically not overlap in space.

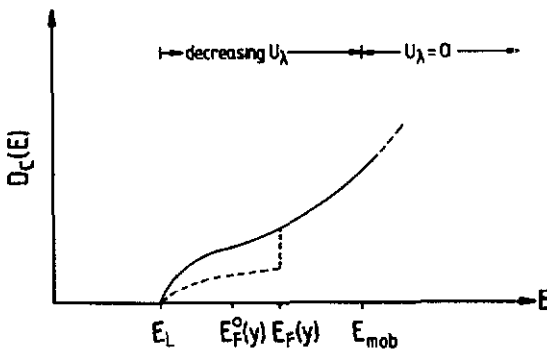


Figure 3. Schematic illustration of the lower region of conduction band DOS appropriate to small y in the $U = 0$ non-interacting TBH limit ($D_C^{(0)}(E)$, full curve); E_{mob} denotes a mobility edge, and $E_F^0(y)$ the $U = 0$ Fermi level. $D_C(E)$ appropriate to the interacting Hamiltonian equation (7.6) is also shown (broken curve) together with corresponding Fermi level $E_F(y)$, under conditions detailed in text.

We now envisage 'switching on' the on-site electron-electron interactions embodied in the Hubbard U , regaining the full H_C , equation (7.5). Terms in (7.5b) over and above the diagonal on-state U_λ interaction, such as spin-flip exchange terms of form

$$U \sum_i \sum_{\substack{\lambda, \nu \\ (\nu \neq \lambda)}} |a_{i_\lambda}|^2 |a_{i_\nu}|^2 C_{\lambda\uparrow}^+ C_{\nu\uparrow} C_{\nu\downarrow}^+ C_{\lambda\downarrow}$$

involve on-site overlap of distinct TBH states, embodied in $|a_{i_\lambda}|^2 |a_{i_\nu}|^2 (\nu \neq \lambda)$. The argument that strongly localized TBH states will typically not overlap in space implies that if λ and $\nu (\neq \lambda)$ are such a pair, then $|a_{i_\lambda}|^2$ and $|a_{i_\nu}|^2$ will not typically both be appreciable. As a first approximation, therefore, and given our consideration of

small y , we retain only the first two terms of (7.5b) yielding

$$H_C \simeq \sum_{\lambda, \sigma} E_\lambda n_{\lambda\sigma} + \sum_{\lambda} U_\lambda n_{\lambda\uparrow} n_{\lambda\downarrow}. \quad (7.6)$$

We note that (7.6) is also the approximation to a half-filled ($y = 1$) topologically disordered Hubbard model used by Kamimura and coworkers [52, 53] to describe the intermediate density regime of doped semiconductors. Equation (7.6) is formally similar to H_C appropriate to the true atomic limit $\{T_{ij}\} \approx 0$ (see (7.2) and (7.3)), but with site energies replaced by the eigenenergies of the disordered TBH, and with the on-site U replaced by on-state U_λ s; (hence 'quasi-atomic' limit). TBH states well below the mobility edge are quite strongly localized. Hence, for sufficiently large U , the corresponding U_λ are expected to be large enough to prevent double occupancy of TBH states. For the small y domain under consideration, the ground state of the interacting Hamiltonian (7.6) will thus consist of TBH states singly occupied up to an energy $E_F(y) (< E_{\text{mob}})$ as illustrated in figure 3; and, for experimentally relevant temperatures, a free-spin- $\frac{1}{2}$ Curie-law susceptibility thus results.

It is clear that these simple arguments apply to a regime of well localized states, and will certainly break down before $E_F(y)$ crosses a mobility edge and Fermi level pseudoparticle states become extended, pointing up the expectation $y_M > y_C$ discussed in the previous section.

This discussion, while instructive, is essentially qualitative. To gain a more detailed understanding of the quasi-atomic limit, and to understand even qualitative aspects of the ground-state properties of a 'simple' disordered Hubbard model, as the filling fraction y is increased through and above the quasi-atomic regime, is difficult. One possibility is a probabilistic mean-field approach to an unrestricted Hartree-Fock treatment of the on-site electron-electron repulsions, carefully avoiding a double mean-field approach to the latter (such as a disorder-averaged restricted HF approximation). Steps in this direction have recently been taken [39].

To connect a result of [39] for the quasi-atomic regime to these arguments, we note that in this small y 'singly occupied state' domain, the DOS or single-particle excitation spectrum $D_C(E) (= \frac{1}{2} \sum_{\sigma} D_{C,\sigma}(E))$ corresponding to the approximate interacting Hamiltonian (7.6) can be shown related to the non-interacting TBH spectrum $D_C^{(0)}$ by: $D_C(E) = \frac{1}{2} D_C^{(0)}(E)$ for $E < E_F(y)$, and $D_C(E) = D_C^{(0)}(E)$ for $E_F(y) < E \ll E_L + U$. This is illustrated in figure 3 (broken curve), showing the discontinuity in $D_C(E)$ at the Fermi level $E = E_F(y)$, and is essentially what is found in Siringo and Logan's [39] mean-field approach in the quasi-atomic regime. From the previous discussion the physical reason for the behaviour of the interacting single-particle excitation spectrum becomes evident: because the interacting ground state consists of states singly occupied up to the Fermi level, the energy cost of adding a hole to (removing an electron from) an occupied state λ is $E_\lambda < E_F$, but the cost of adding an electron of the opposite spin to such a state is $E_\lambda + U_\lambda > E_F(y)$. For $E < E_F(y)$ the density of single-particle excitations is thus reduced by a factor of two below the $U = 0$ non-interacting limit. In contrast, for E just greater than $E_F(y)$, we can add either an up or a down spin electron to an unoccupied state, the energy cost in either case being simply E_λ , so $D_C(E) = D_C^{(0)}(E)$.

7.3. Polaronic processes

In interpreting the experiments on $\text{Cs}_y[\text{CsAu}]_{1-y}$ in the quasi-atomic regime, we have

emphasized the role of coulombic disorder in leading to localization of pseudoparticle states in the edge of the conduction/cation band, and the consequent enhancement of electron correlation effects resulting in strong local moments and a Curie law paramagnetism for the excess electrons. There is, however, another potential consequence of disorder-induced localization; namely that the local ionic environment may distort or adjust itself to further accommodate the localized charge, leading to a possible role for polaronic effects [48]. Clearly, the more localized the occupied conduction band pseudoparticle states are—i.e. the smaller their localization lengths $\{\xi_\lambda\}$ —the greater is the potential for such processes to play a role. And, as an obvious corollary, any such effects will become less significant as the excess Cs content y is progressively increased and the occupied pseudoparticle states become less strongly localized (and ultimately extended).

The point to be emphasized is that we envisage any such processes which may be present in $Cs_y[CsAu]_{1-y}$ at low y , as being largely a further consequence of disorder-induced localization of charge in the vicinity of cation sites with the lowest coulombic site energies. We mention this because the earliest interpretation [13] of the NMR experiments on liquid $Cs_y[CsAu]_{1-y}$ in the quasi-atomic domain $y < y_C \sim 0.07$ was in terms of the liquid analogue of an F centre, motivated by analogy to the behaviour of the 'excess' electrons in alkali metal/metal-halide (M-MX) systems. The existence of F centres in the sense of electron-occupied anion vacancies is well known in the crystalline M-MXs, evidenced in a characteristic absorption band in the red or near infrared, with Mollwo-Ivey behaviour; and supported by various magnetic measurements. That these features persist [54] in $M_y[MX]_{1-y}$ melts at low y immediately suggests the veracity of adopting a generalized F centre model appropriate to a liquid—such as that studied by Senatore *et al* [55] in the limit of ∞ -dilution—in which the primary emphasis is on an electron-occupied anion vacancy in the liquid.

The behaviour of $Cs_y[CsAu]_{1-y}$ is, however, in contrast to the M-MXs. NMR experiments by Dupree *et al* [14] have ruled out the possibility of F centres in the crystalline near-stoichiometric solid; and we do not know of evidence for a characteristic absorption band in the liquid at low y . There is, however, clear evidence that disorder plays an important role in liquid caesium-gold; for on melting the solid the DC conductivity drops significantly [2-4] and, in contrast to the solid, there is clear NMR evidence [13] in the liquid alloy for strongly localized excess spins as discussed here. It is largely for these reasons that we have emphasized the primary role of coulombic disorder, with enhancement of correlation effects and possible polaronic readjustments being viewed in effect as attendant processes.

It should be remembered that these distinctions are in part a matter of degree, and that various relevant physical mechanisms are not mutually exclusive. Indeed, in their study of M-MX melts, Senatore *et al* [55] argue that there is no obvious contradiction between an F centre model and one involving Anderson localization; and suggest that the F centre bound states may be the lowest electronic states associated with an Anderson tail to the conduction band of the solution, a view previously discussed by Katz and Rice [56] for M-MX systems.

Nonetheless, as above, there does appear to be a difference in the properties of Cs-Au compared with the M-MXs. This may perhaps be connected to the fact that the stoichiometric M-MXs are large band gap materials ($\Delta E_G^0 \sim 6$ eV for CsI through to ~ 12 eV for LiF), whereas for stoichiometric crystalline Cs-Au at its melting point $\Delta E_G^0 \sim 2$ eV [12]. In the M-MX melts, electronic states for the initial excess electrons

will lie sufficiently far into the gap that they are more likely to be associated with deep trap vacancies, where the excess electronic charge primarily localizes off cation sites. For $\text{Cs}_y[\text{CsAu}]_{1-y}$ in contrast, the lowest electronic states for excess electrons will typically lie not more than ~ 1 eV ($\sim \frac{1}{2}\Delta E_G^0$) below the edge of the crystalline conduction band, and are envisaged as being more significantly associated with cation sites, commensurate with [54] the experimental mean hyperfine coupling constants for Cs in $\text{Cs}_y[\text{CsAu}]_{1-y}$ [13] as opposed to $\text{Cs}_y[\text{CsI}]_{1-y}$ [57].

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