

Electronic structure and the metal-nonmetal transition in liquid CsAu and Cs<sub>3</sub>Sb

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(Received 4 October 1982)

The electronic structure and ionicity of some alkali-gold and alkali-pnictide compounds has been calculated and used to investigate the type of chemical ordering and the nature of the metal-nonmetal transition (MNMT) in their liquid semiconducting phases. The gold compounds are found to extremely high ionicities, averaging 0.96, while the pnictides are much lower, ranging from 0.60 for Cs<sub>3</sub>Sb to 0.05 for Li<sub>3</sub>Sb. The thermochemical, structural, and transport properties of the liquid alloys are similar, but the range of composition for which *l*-CsAu is semiconducting is larger than in the other systems. This is shown to be wider than is consistent with band-filling models of the MNMT and is further evidence that the transition occurs by carrier localization at defects such as *F* centers. The pnictides and Pb alloys have more usual MNMT's and presumably *F* centers are not stable at their much lower ionicities. The unifying feature of the bonding in these systems is that the lowest valence orbital of the cation is above the highest occupied anion orbital in their free atoms. They may therefore be classed as charge-transfer compounds. However, their bonding cannot always be truly termed ionic as the net ionic charges and ionicities are often very low, as in the Li salts.

## I. INTRODUCTION

Ionic liquid semiconductors such as CsAu and Mg<sub>3</sub>Bi<sub>2</sub> are examples of systems displaying composition-dependent metal-nonmetal transitions (MNMT's).<sup>1-5</sup> CsAu is believed to be fairly ionic, Cs<sup>+</sup>Au<sup>-</sup>, and the MNMT in liquid (*l*-) Cs<sub>*x*</sub>Au<sub>1-*x*</sub> is frequently visualized in terms of "band filling," the result of  $\epsilon_F$  rising through a valence band of Au 6*s* states and a conduction band of Cs 6*s* states with increasing Cs content such that  $\epsilon_F$  sits in a semiconducting gap for  $x=0.5$ .<sup>6-9</sup> If this model applies, the isotropy of interacting *s* orbitals would make *l*-CsAu the simplest theoretical example of a composition-dependent MNMT.

Unfortunately, there is evidence that *l*-CsAu may differ from other ionic liquid semiconductors in that *F* centers and other defects of the solid state may also be stable in its liquid phase and dominate its MNMT. Nuclear magnetic resonance (NMR) found direct evidence of carrier localization in the semiconducting phase around  $x=0.5$ .<sup>10</sup> However, the NMR relaxation time of electrons due to excess Cs showed them to be localized not on atom-centered orbitals, but rather between several sites, perhaps six, as at *F* centers (electrons trapped at anion vacancies in the ionic lattice). If this is so, the MNMT in

*l*-CsAu can no longer be modeled in terms of the filling of a one-electron density of states and the effects of special defect states must be included.<sup>11</sup>

In the present paper we contrast the MNMT in the major ionic liquid semiconductors in terms of the composition dependence of their conductivities, their local structures and calculations of their electronic structures given here. We show that the effect of disorder on the spectra of one-electron states places very general constraints on the compositions where the conductivity passes through the minimum metallic value. This causes similarities between the composition dependence of the conductivities in those systems obeying the band-filling model. The wider semiconducting region of CsAu is noted and used as additional evidence for *F* centers. *F* centers have been shown to be stable in *l*-CsAu and the MNMT has been discussed in terms of their Hubbard bands.<sup>11</sup> The band-filling model is found to apply to other ionic liquid semiconductors. The stability of *F* centers clearly depends on sufficient local ordering and a highly ionic electronic structure. The electronic structure of alkali-gold salts and (I)<sub>3</sub>-V compounds is calculated here by tight-binding (TB) methods. The ionicities of the gold salts are found to be extremely high while the pnictides are much lower. Local structure and transport measure-

ments are then discussed in the light of our interpretation of the band-filling model and our calculations, and are used to classify the order in these systems.<sup>12,13</sup> The electronic structure of the Mg salts has already been given.<sup>12</sup>

## II. BAND-FILLING MODELS OF THE METAL-NONMETAL TRANSITION

Before discussing particular ionic semiconductors, it is appropriate to consider in some detail an idealized model of the MNMT in these materials. The composition dependence of the conductivity in each system shows a pronounced minimum around the stoichiometric composition. The absolute minimum conductivity does not concern us so long as it lies below about  $10^3 \Omega \text{ cm}$ . Rather, we show that if the width of the dip is defined at its minimum metallic conductivity, then it serves to classify the MNMT in ionic semiconductors.

An idealized ionic liquid semiconductor  $M_xX_{1-x}$  can be defined as having complete chemical ordering at its stoichiometric composition  $x=0.5$ . As  $x$  moves away from 0.5 the proportion of unlike neighbors can still be kept high by allowing the coordination number to vary. The electronic structure of the idealized alloy consists of an anionlike valence band and a cationlike conduction band.<sup>12,13</sup> Following Figs. 1(a)–1(e), as  $x$  increases from 0 to 1.0,  $\epsilon_F$  moves from the center of the valence band through the pseudogap at  $x=0.5$  to the center of the conduction band. The corresponding changes in the conductivity  $\sigma$  depend on the width of the pseudogap and the disposition of the localized states. Mobility edges separate the extended, bandlike states from the localized tail states. Generally, mobility edges lie 10–15 % into the band for typical values

of disorder potential. As  $x$  varies and  $\epsilon_F$  moves from the valence band to the conduction band (Fig. 2),  $\sigma$  passes through the minimum metallic conductivity  $\sigma_m$  whenever  $\epsilon_F$  passes through a mobility edge.<sup>1</sup> This gives the deep dip in  $\sigma$  below  $\sigma_m$  for compositions near  $x=0.5$ . Movements of  $\epsilon_F$  dominate any changes in band shapes around  $x=0.5$  if the ionic model holds. Therefore if the width of the conductivity minimum is defined to be at  $\sigma_m$  then it is limited to a small range of compositions, at most  $0.45 < x < 0.55$ .

The width of the semiconducting region is relatively independent of the system because the energy range of localized states depends very generally on disorder. If a large density of states were to appear in the pseudogap due to defects, similar considerations would apply to these states and part of the defect band would become extended if the density of states became too large. The band-filling model of the MNMT transition only breaks down if the electrons are no longer independent or if the ionic model itself breaks down. If lattice relaxation occurs at the defects, forming polaronic defect states, then this is a source of localization in addition to disorder. Inward ionic relaxation is an essential feature of  $F$  centers and is crucial to their stabilization in  $I$ -CsAu.<sup>11</sup> A larger density of localized states is now possible and  $\sigma$  can stay below the  $\sigma_m$  further away from stoichiometry. Of course, the ionic model also may break down due to covalent-bond formation, as in  $\alpha$ - $\text{Mg}_x\text{Sb}_{1-x}$ .<sup>13</sup>

Thus, the conductivity minimum should be defined in terms of its width at  $\sigma_m$ . Theoretically,  $\sigma_m$  depends on coordination and, although rather undefined, it is about  $10^3$ – $10^4 \Omega \text{ cm}$ .<sup>1</sup> The temperature coefficient of resistance changes sign as  $\epsilon_f$  passes through a mobility edge and may be used as an alternative.

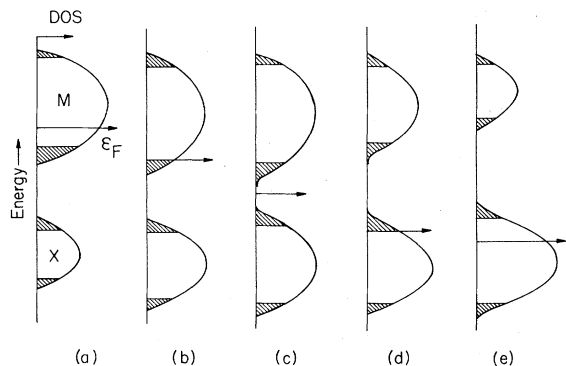


FIG. 1. Position of  $\epsilon_F$  as the cation concentration increases in the band-filling model of a MNMT in a liquid semiconductor alloy  $M_xX_{1-x}$ ; (a)  $x \approx 1$ , (b)  $\epsilon_F$  crossing the valence-band mobility edge, (c)  $\epsilon_F$  in the pseudogap,  $x \approx 0.5$ , (d)  $\epsilon_F$  crossing the conduction-band mobility edge, (e)  $x \approx 0$  shading denotes localized states.

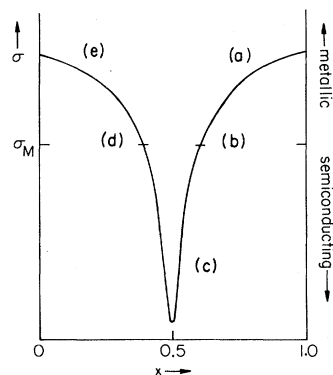


FIG. 2. Conductivities corresponding to Fig. 1; (a) metallic cation-rich regime, (b) passing through MNMT, (c) semiconducting regime, (d) passing through MNMT, (e) metallic anion-rich regime.

### III. THE BAND STRUCTURE OF ALKALI-GOLD SALTS

The electronic structure of the crystalline compounds is calculated as a reference for a discussion of the liquids. CsAu has the CsCl structure in which each ion has eight unlike-ion neighbors and six like-ion second neighbors. The TB band structure is found by fitting the results of a self-consistent pseudopotential calculation,<sup>14</sup> of those available.<sup>14-16</sup> The fitting process is similar to that used for many semiconductors.<sup>17-21</sup> Algebraic expressions are derived for the band energies at points of high symmetry in the Brillouin zone and equated to their pseudopotential values. In the present fit, Cs *s*, *p*, and *d* states and Au *s* and *p* states are included. In covalent solids first-neighbor interactions are often sufficient to give an accurate representation of the lower bands. However, for very ionic materials their effects are greatly reduced, and the effects of the like-atom second-neighbor interactions begin to dominate.<sup>20,21</sup> Both types of interaction are included in the present fit. It has been found that the two-center TB interactions scale with bond length within many different series of compounds.<sup>18</sup> This scaling is assumed to hold in the alkali-gold salts and is used to derive bands for the lighter members. The resulting bands for KAu should be metallic or semimetallic,<sup>22,23</sup> and this is included as a final constraint in the fitting process. Further details are given in the Appendix.

The bands and densities of states (DOS) for CsAu are given in Fig. 3. Similar bands and DOS are found for RbAu and KAu but with decreasing gap. The parameters used are given in Table I, and the calculated gaps and ionicities are given in Table II. The single valence band of CsAu has a maximum at point R, a minimum at point  $\Gamma$ , and is almost entirely Au *s*-like. The localization of valence charge around the anion is also found in charge-density

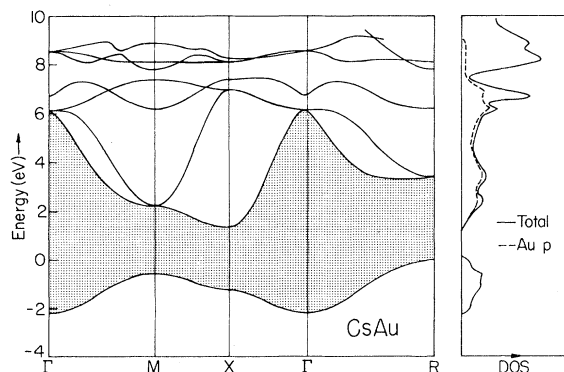


FIG. 3. Band structure, total and partial Au DOS for CsAu.

plots.<sup>14</sup> The shape of the DOS compares well with that seen in photoemission.<sup>23,24</sup> The gap is indirect. The conduction band has a minimum at point X and a subsidiary minimum at point R. It is mainly Au-*p* like, as may be seen from the Au *p* partial DOS, also shown in Fig. 3.<sup>25</sup> There is some Cs *s* admixture at point X and a small Cs *d* admixture at point R. Most ionic salts with a completed octet of electrons have a cation *s* lower conduction band. The alkali-gold salts have only two electrons per formula unit and are therefore "electron deficient." The electron-deficient compounds are seen to have a gap between anion states while electron-excess compounds such as PbI<sub>2</sub> or GaSe have a gap between primarily cation states.<sup>20</sup>

An ionicity  $f_i$  was defined as the charge on the cation. The values found, 0.97, 0.96, and 0.94 for CsAu, RbAu, and KAu, respectively, are extremely high and reiterate the observation that the Cs two-electron salts are the most ionic metal alloys known.<sup>11,26</sup> These ionicities are much greater than those found using Pauling electronegativities<sup>27</sup> or from the core-level shifts seen in photoemission.<sup>24</sup> A consequence of these very high ionicities is that 75% of the overall valence-band width is due to the Au-Au *ss* $\sigma$  interaction and only 25% to the Cs-Au *ss* $\sigma$  term.<sup>25</sup> If one compares CsAu and CsI, which have anions of similar radii, it is interesting that a band gap of about 10 eV is required in CsI to give an ionicity as high as that in CsAu. The high ionicities of the gold-alkali salts are possible and can coexist with small or negative gaps because of the unusual form of the "covalent" gap in two-electron systems. The overall covalent gap<sup>28</sup> is small over large parts of the zone because of a cancellation of phase factors in the Cs-Au *ss* $\sigma$  interactions, and so the zone-averaged total gap is dominated by its ionic component.

### IV. Cs<sub>3</sub>Sb AND OTHER Pnictides

The structure of Cs<sub>3</sub>Sb is related to that of the NaTl or B32 lattice. In NaTl, the Na and Tl atoms are each arranged in two interpenetrating, diamond sublattices so that each atom has four like neighbors on the same sublattice and four unlike neighbors on the other sublattice [Fig. 4(a)]. The pnictides are formed by placing Cs atoms on all the Na sites and distributing the Sb atoms and remaining Cs atoms on the Tl sites [Fig. 4(b)]. In Li<sub>3</sub>Sb the Li and Sb atoms on the second sublattice have a zinc-blende-like ordering,<sup>29</sup> whereas in Cs<sub>3</sub>Sb both ordered and disordered arrangements have been noted.<sup>29-31</sup> Only the ordered lattice is considered here. There are two types of cation site: Cs<sub>I</sub>, with both cation and anion neighbors and Cs<sub>II</sub> sites with only Cs<sub>I</sub>

TABLE I. TB interactions and interatomic distances in Å for CsAu; those for the other Au salts are found by scaling as  $d^{-2}$ .

	$r$ (Å)	$V(ss)$	$V(sc,pa)$	$V(sa,pc)$	$V(pp\sigma)$	$V(pp\pi)$
Cs-Au	3.69	-0.24	-0.53	-0.25	0.65	-0.15
Cs-Cs	4.26	0	0	0	0.15	0
Au-Au	4.26	-0.136	-0.33	-0.33	1.0	-0.1
	$r$ (Å)	$\epsilon_c^s$	$\epsilon_c^p$	$\epsilon_c^d$	$\epsilon_a^s$	$\epsilon_a^p$
CsAu	3.69	6.2	7.8	9.2	-0.82	5.0
RbAu	3.54	5.8	7.5	9.5	-0.90	4.9
KAu	3.38	5.45	7.35	9.9	-0.97	4.8

neighbors. The electronic structure of  $B32$  compounds is frequently compared to that of diamond because if NaTl is considered to be ionic,  $\text{Na}^+\text{Tl}^-$ , then the  $\text{Tl}^-$  ions possess four electrons and lie on a diamond lattice with the possibility of covalent bonding.<sup>32</sup> However, explicit calculations of their electronic structures find that the atoms are almost neutral, so this analogy is incorrect.<sup>33,34</sup> Similarly, the pnictides are sometimes incorrectly referred to as covalently bonded on a Cs-Sb sublattice by analogy to zinc blende.<sup>27,30,32</sup>

Tight-binding band structures for the pnictides have been calculated in an attempt to find whether the bonding should be classed as covalent or ionic. As described in more detail elsewhere,<sup>35</sup> the bands were calculated by scaling their interactions from a fit to the bands of LiAl (Ref. 33), a  $B32$  compound. The interactions are listed in Table III. Each subcell in the  $B32$  or the  $\text{Li}_3\text{Sb}$  lattices is a body-centered cube, in which the second neighbors are only 15% more distant than the first. Therefore both types of interactions were included in the calculation. The ionicities  $f_i$  were calculated in terms of the atomic charge on the cation  $Q$ , as  $f_i = Q$ . The ionicities were also calculated for a number of pnictides whose crystal structures are actually hexagonal, so that their values would be available for a discussion of the liquids (Table II). The ionicities of the pnictides span a wide range, from 0.60 for  $\text{Cs}_3\text{Sb}$  to 0.05 for  $\text{Li}_3\text{Sb}$ .

The bands of the  $B32$  compounds resemble those of Si, particularly the valence band. The pnictide bands in Figs. 5 and 6 similarly resemble those of

the zinc blendes. The valence band consists of a lower narrow anion  $s$  band and a wider anion  $p$  band at the top of the valence band. This peak is calculated to be 2.2 eV wide, as in photoemission.<sup>36</sup> The  $p$  bands of  $\text{Li}_3\text{Sb}$  are much wider at 5.6 eV. The minimum gap was calculated to be 2.4 eV in  $\text{Cs}_3\text{Sb}$  compared to 1.6 eV experimentally, and 1.4 eV in  $\text{Li}_3\text{Sb}$ . The lowest conduction band is of cation  $s$  states.

Note that the large number of cation-cation first-neighbor contacts does not necessarily wipe out the band gap, as it is primarily due to differences in orbital energy. In the pnictides the cation  $s$  orbital always lies above the highest occupied anion orbital, so there is always some charge transfer even if the ionicities are low. If a charge-transfer compound is defined in terms of orbital energies in this way, then it provides a common definition of these liquid semiconductors which ionicity failed to do.

## V. NATURE OF THE LIQUIDS

In this section the differences in the MNMT's in the various systems are discussed and related to their local bonding. Initially, we review our understanding of ordering in the systems in the light of the band calculations as the prevailing bonding character in many systems is not fully settled.

Evidence for compound formation in liquids is usually based on three types of data: thermochemical, structural, and transport data.<sup>2-4</sup> Ionic ordering is confirmed thermochemically if there is a large molar volume contraction with respect to the ele-

TABLE II. Nearest-neighbor bond length, calculated ionicity, and minimum gap for various gold and pnictide salts.

	CsAu	RbAu	KAu	$\text{Cs}_3\text{Sb}$	$\text{Cs}_3\text{Bi}$	$\text{Na}_3\text{Sb}$	$\text{Na}_3\text{P}$	$\text{Li}_3\text{Sb}$	$\text{Li}_3\text{Bi}$
$r$ (Å)	3.69	3.54	3.38	3.95	4.03	3.24	3.01	2.85	2.91
$f_i$	0.97	0.96	0.94	0.60	0.59	0.24	0.30	0.05	0.05
Min. gap (eV)	1.3	0.7	0.1	2.4	1.4	1.2	2.0	1.4	1.0

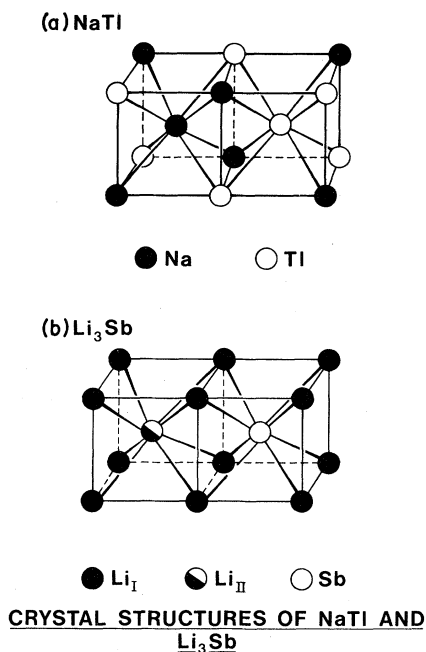


FIG. 4. One quarter of the unit cell of (a) NaTi, (b) Li<sub>3</sub>Sb.

ments and if the heat of formation is large. Covalent ordering or metallic alloying does not generally lead to a volume contraction because the covalent or metallic radii are common to the elements and the compounds, while ionic radii are much smaller than metallic radii.

The ideal structural confirmation of ionic ordering would be the measurement of the individual partial structure factors by extended x-ray-absorption fine-structure (EXAFS) or neutron diffraction on isotopically enriched samples. In lieu of this, the appearance of a prepeak in the total structure factor

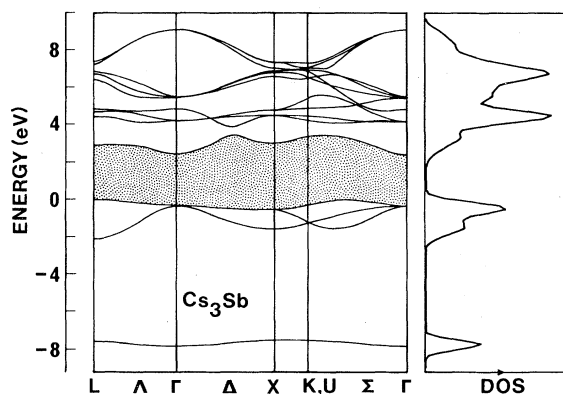


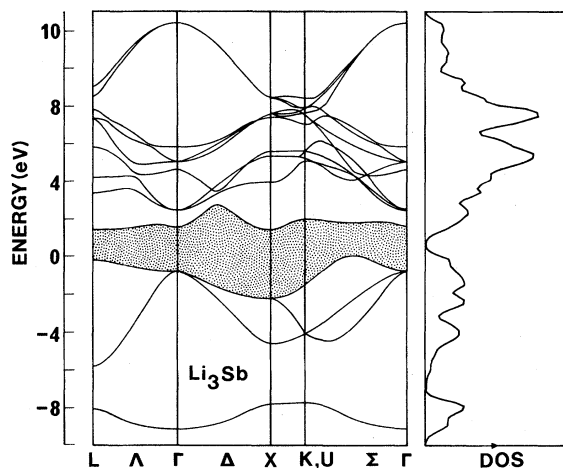
FIG. 5. Bands and DOS of Cs<sub>3</sub>Sb.

has become accepted as a signature of ionic ordering.<sup>4,37</sup> To see this consider *l*-NaCl; the total structure factor  $S(q)$  is the weighted sum of the partial structure factors  $S_{+-}$ ,  $S_{++}$ , and  $S_{--}$  for cations + and anions -. The signature of ionic ordering is that the ions arrange themselves to maximize ionic screening. This causes  $S_{++}(q)$  and  $S_{--}(q)$  to each have a large positive peak and  $S_{+-}(q)$  to be highly negative at  $q_s$  corresponding to like-ion correlations, while all three  $S_{ij}(q)$  have a positive peak at  $q_m$ , the main peak in  $S$ . The correlations at  $q_s$  largely cancel, leaving just a small prepeak before the main peak at  $q_m$  where all are in phase.

Transport data give no information on the type of ordering at stoichiometry, rather they indicate how the excess of a constituent enters the structure away from stoichiometry.<sup>12</sup> Qualitatively, in a covalent alloy each atom maintains its stable electronic configuration, such as the octet, by keeping a constant coordination at the expense of unlike-atom bonds, while ionic ordering attempts to maintain unlike-ion

TABLE III. TB interactions and interatomic distances in Å for Cs<sub>3</sub>Sb; those for others found by scaling.

	$r$ (Å)	$V(ss)$	$V(sc,pa)$	$V(sa,pc)$	$V(pp\sigma)$	$V(pp\pi)$
Cs-Sb	3.95	-0.36	-0.85	-0.58	0.81	-0.0
Cs-Cs	3.95	-0.24	-0.53	-0.53	0.70	-0.0
Cs-Sb	4.56	-0.24	-0.62	-0.22	0.64	-0.13
Cs-Cs	4.56	-0.24	-0.38	-0.38	0.64	-0.13
	$-\epsilon_c^s$	$-\epsilon_c^p$	$-\epsilon_a^s$	$-\epsilon_a^p$		
Cs <sub>3</sub> Sb	3.60	1.60	14.82	7.26		
Cs <sub>3</sub> Bi	3.60	1.60	14.16	6.98		
Na <sub>3</sub> Sb	5.14	2.20	14.82	7.26		
Na <sub>3</sub> P	5.14	2.20	17.17	8.35		
Li <sub>3</sub> Sb	5.49	2.60	14.82	7.26		
Li <sub>3</sub> Bi	5.49	2.60	14.16	6.98		

FIG. 6. Bands and DOS of  $\text{Li}_3\text{Sb}$ .

neighbors and screening at the expense of constant coordinations. Coordinations for ionic ordering depend largely on ionic radii, whether in the solid or liquid.<sup>12,13</sup> Hence the electronic structure of a crystal is a useful reference for the properties of the fully ordered liquid. The degree of ordering can then be found from thermochemical or structural data.

Idealized  $l\text{-CsAu}$  is therefore highly ionic. Experimentally, there is a large volume contraction with respect to the elements and a high heat of formation.<sup>38,39,27</sup>  $l\text{-CsAu}$  has an optical gap of 1.3 eV (Ref. 40) and ionic conductivity dominates around  $x=0.5$  (Ref. 41). A prepeak is found in the total structure factor as measured by neutron diffraction.<sup>37,5</sup>

$l\text{-Cs}_3\text{Sb}$  has been studied in far less detail experimentally. One major question has been whether  $\text{Cs}_3\text{Sb}$  should be classed as ionic or covalent.<sup>27,32,42</sup> Our calculations show that its ionicity is 0.60. However, we also find that compounds with a wide range of ionicities, 0.05–0.60, are stable in the  $\text{Li}_3\text{Sb}$  structure. One common feature of these compounds is the ordering of orbital energies and their classification as charge-transfer compounds. Structurally, there is less evidence for a prepeak in the total structure factor. As only small ionic charges were needed in a structural simulation of  $l\text{-Cs}_3\text{Sb}$  it was concluded to be not particularly ionic.<sup>42</sup> However, it is possible that  $l\text{-Cs}_3\text{Sb}$  should not have a prepeak if its local order is similar to its crystal. In such cation-rich compounds it becomes impossible to maintain only anion-cation contacts. This does not necessarily destroy semiconduction as seen earlier. When cation-cation first neighbors occur they are often at different distances to anion-cation neighbors. In the  $\text{Cs}_3\text{Sb}$  lattice, like and unlike neighbors appear at the same distance. If the liquid structure is similar,

there is less need for a strong shell structure causing the prepeak because ionic screening occurs within each shell.

The conductivity of  $l\text{-Li}_{1-x}\text{Bi}_x$  shows a minimum at  $x=0.25$ .<sup>43</sup> The crystal has an ionicity of 0.05 and a band structure similar to that of  $\text{Li}_3\text{Sb}$  in Fig. 6, but with non-negligible spin-orbit splitting.

The electronic structure of  $\text{Li}_4\text{Pb}$  has not been calculated here, but it is expected that the charge transfer is low, as in  $\text{Li}_3\text{Sb}$ , giving ionic charges of, say,  $\text{Li}^{+0.05}$  and  $\text{Pb}^{-0.2}$ . The charge distribution is then very delocalized and does not require the existence of the full  $\text{Pb}^{4-}$  ion. The conductivity shows a strong dip at  $\text{Li}_4\text{Pb}$  (Fig. 7).<sup>44</sup> Strong ordering around the Pb sites has been found experimentally,<sup>45</sup> but clearly many Li-Li contacts must occur in  $\text{Li}_4\text{Pb}$ .

$l\text{-Mg}_3\text{Bi}_2$  and  $l\text{-Mg}_3\text{Sb}_2$  were the first studied liquid semiconductors showing a MNMT.<sup>46</sup> Strong chemical ordering is suggested from the thermochemical parameters.<sup>47</sup> Their composition is such

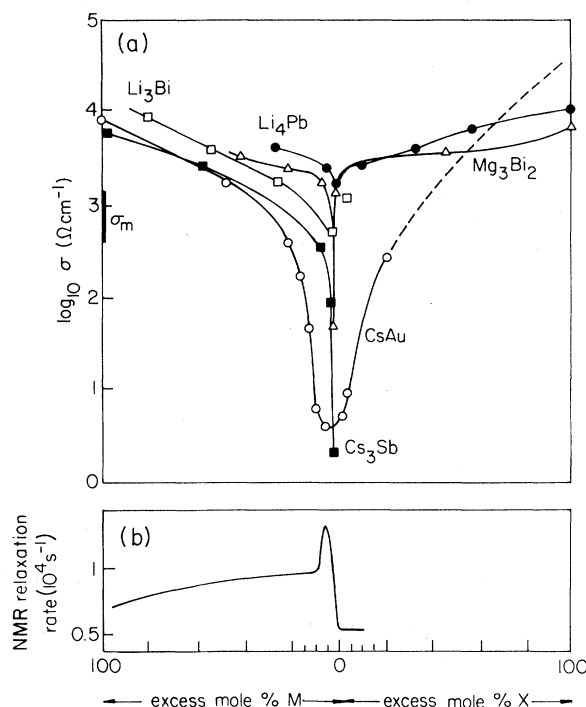


FIG. 7. (a) Conductivity vs reduced composition for various alloys  $MM'$ . For a stoichiometry  $M_mM'_n$  the  $M$ -rich alloys are  $M_x(M'_{n/m})_{1-x}$  and the  $M'$ -rich alloys  $M'_y(M_{m/n}M')_{1-y}$ , with  $x=0$  and  $y=0$  at stoichiometry (Ref. 3).  $\sigma_m$  is also shown as a line on the left; its value is ill-defined, depending on coordination and the type of disorder. The minimum of  $\text{CsAu}$  is seen to be much wider at  $\sigma_m$ . (b) NMR relaxation times for  $\text{CsAu}$  (Ref. 10) are shown below; its features are still wider than  $\sigma$  for the other alloys.

that a liquid structure is possible with only unlike-ion contacts, as in the crystals.<sup>29</sup> These liquids, therefore, have ionic ordering. Their band structures have been calculated earlier and the DOS are consistent with the charge-transfer notion.<sup>12</sup>

The composition dependences of the conductivity of liquid CsAu, CsSb, LiPb, LiBi, and MgBi alloys are plotted in Fig. 7 in terms of the reduced compositions,<sup>3</sup> such that stoichiometry always appears in the center. It is seen that the conductivity varies in qualitatively the same way for excess metal content in each system except *l*-CsAu, dropping below  $\sigma_m$ , about  $10^3 \Omega m$ , for  $\Delta x = 10\%$ . *l*-CsAu clearly has a much wider conductivity minimum than the other systems and cannot obey the band-filling model. *F* centers provides one of the few additional mechanisms of localization which is not essentially similar to the band-filling models. Electron localization at *F* centers is enhanced by strong electron-lattice coupling. When this localization is lost and the MNMT occurs<sup>11</sup> it happens at the usual value of  $\sigma_m$ . The narrower minima of the other alloy systems is evidence for the unimportance of *F* centers. Thus the conductivity curves are evidence that only *l*-CsAu possesses *F* centers. This may indicate that an ionicity of over 90% is needed for their presence in the liquid state. Only alkali-gold salts, alkali halides, and perhaps some flourites possess such high ionicities, but not the alkali pnictides. Other reasons for the breakdown of band-filling models in *l*-CsAu are difficult to accept. For instance, it is difficult to envisage excess alkali atoms not being ionized in some manner, and certainly not participating in covalent bonds in a condensed phase. The covalent option is available for the anion-rich compositions, and may occur in the alkali Sb, As, or P alloys, as in *a*-Mg<sub>3</sub>Sb<sub>2</sub>.<sup>12,13</sup>

Cs and the heavier alkalis are so electropositive that they can force many conventional metals to act as anions, as in CsAu. As solubilities are low in solid Cs, these materials are produced in the form of amorphous thin films by codeposition on *l*-He cooled substrates. The resultant films often show conductivity minima at chemically expected compositions, and sometimes over a wider range.<sup>48,49</sup> The width of these minima is not always consistent with the above theory. Further progress must await data on the local bonding in these highly nonequilibrium films.

In summary, qualitatively all the liquid semiconductor systems considered here have a large molar volume contraction and could be classified as ionic. This appears to apply even to compounds with low calculated TB ionicities. It is preferable to term these compounds charge-transfer semiconductors, whose ionicity can in some circumstances be quite

small due to the delocalization of the anion orbital. The alkali-gold alloys then stand out for their extremely high ionicities, their ability to support stable *F* centers, and their consequent wider conductivity minima. Clearly, the alkali-gold salts are the most extreme example of ionic liquid semiconductors but are atypical for these reasons.

*Note added in proof.* A band structure of CsAu, similar to that of Ref. 14, was found by D. R. Hamann and M. Schluter [unpublished; quoted by G. B. Bachelet, D. R. Hamann, and M. Schluter Phys. Rev. B **26**, 4199 (1982)]. Both these calculations underestimate the gap because they use local density screening. The difference of the MNMT in *l*-CsAu and *l*-Cs<sub>3</sub>Sb and the appearance of Sb-Sb bonds in Sb-rich *l*-Cs<sub>x</sub>Sb<sub>1-x</sub> have been noted by R. Duprec, D. J. Kirby, and W. Freyland, Philos. Mag. B **46**, 595 (1982).

#### ACKNOWLEDGMENTS

It is a pleasure to acknowledge many helpful discussions with R. Dupree, R. Evans, C. P. Flynn, P. B. Littlewood, and W. W. Warren. We also gratefully acknowledge the support of the U.S. Office of Naval Research, Grant No. N00014-79-C-0537.

#### APPENDIX

CsAu has a simple cubic *B2* lattice. Energies for the anion *s* and *p* orbitals are defined as  $\epsilon_a^s$  and  $\epsilon_a^p$ , and similarly for the cation *s*, *p*, and *d* orbitals. The first-neighbor interactions are defined as  $V(sc,sa)$ ,  $V(sc,pa)$  or  $V(sa,pc)$ ,  $V(pc,pa\sigma)$ , and  $V(pc,pa\pi)$  for the *ss* $\sigma$ , *sp* $\sigma$ , *pp* $\sigma$ , and *pp* $\pi$  interactions, respectively, with cation *c* and anion *a*. For the second neighbors they are  $V(sa,sa)$ ,  $V(sa,pa)$ ,  $V(pa,pa\sigma)$ , and  $V(pa,pa\pi)$  for anion-anion interactions, and  $V(sc,sc)$ ,  $V(sc,pc)$ ,  $V(pc,pc\sigma)$ ,  $V(pc,pc\pi)$ , and  $V(dc,dc)$  for cation to cation.

There is much less orbital mixing in the cubic lattice than in the fcc, which facilitates the fitting procedure. We first concentrate on those lower bands which have only one orbital component, as this allows the unambiguous fitting of Au-Au parameters. As point *R* the *s* band has energy

$$\epsilon = \epsilon_a^s - 6V(sa,sa),$$

and at point *M*

$$\epsilon = \epsilon_a^s - 2V(sa,sa),$$

allowing the Au *s* parameters to be set. One may extract the Au *p* parameters by a similar process; at *M*

$$\epsilon = \epsilon_a^p + 2V(pa,pa\sigma) - 4V(pa,pa\pi),$$

while the doubly degenerate band at point  $X$  has energy

$$\epsilon = \epsilon_a^p + 2V(pa, pa\sigma).$$

At  $R$  the lowest conduction level is Au  $p$  with a small Cs  $d$  admixture, which is ignored for the moment, so that

$$\epsilon = \epsilon_a^p - 2V(pa, pa\sigma) - 4V(pa, pa\pi).$$

The determination of the other parameters is less straightforward. The lowest conduction band at point  $\Gamma$  is much higher than elsewhere, and has  $d_{xy}$  character. If the Cs  $d$  orbitals are positioned so as

to reproduce this level, then they also give a number of rather undispersed bands at that energy unless many  $d$  parameters are included, which is beyond the scope of the present work. Therefore, it was decided to place the Cs  $d$  orbital just above the Cs  $s$  level and to allow them to interact only with the  $R_{15}$  level which is much lower. Most of the cation-anion parameters are set to zero. The cation-anion interactions are then set to reproduce the various bandwidths. The valence band sets  $V(sa, sc)$ , the conduction-band minimum sets  $V(sc, pa)$ , and the positions of states at points  $\Gamma$  and  $X$  set  $V(pa, pc\sigma)$  and  $V(pa, pc\pi)$ . As mentioned earlier, the bands for KAu were also constrained to be nearly metallic.

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<sup>1</sup>N. F. Mott and E. A. Davis, *Electronic Processes in Non-crystalline Materials* (Oxford University Press, Oxford, 1980).

<sup>2</sup>F. Hensel, *Adv. Phys.* **28**, 555 (1979).

<sup>3</sup>W. W. Warren, in *Advances in Molten Salt Chemistry*, edited by V. Braunstein, G. Mamantov, and G. P. Smith (Plenum, New York, 1982), Vol. 4.

<sup>4</sup>J. E. Enderby, in *Metal-Insulator Transition in Disordered Systems*, edited by D. P. Tunstall and L. R. Friedman (Scottish University Summer Schools, Edinburgh, 1978) Vol. 19, p. 425; J. E. Enderby and G. W. Neilson, *Adv. Phys.* **29**, 323 (1980); J. E. Enderby, *J. Phys. C* **15**, 4609 (1981).

<sup>5</sup>W. Martin, W. Freyland, P. Lamparter, and S. Steeb, *Phys. Chem. Liq.* **10**, 49 (1980); **10**, 61 (1980); **10**, 77 (1980).

<sup>6</sup>R. C. Kittler and L. M. Falicov, *J. Phys. C* **9**, 4259 (1976).

<sup>7</sup>J. R. Franz, F. Brouers, and C. Holzhey, *J. Phys. F* **10**, 236 (1980).

<sup>8</sup>C. Holzhey, F. Brouers, and J. R. Franz, *J. Phys. F* **11**, 1047 (1981); C. Holzhey, F. Brouers, J. R. Franz, and W. Schirmacher, *ibid.* **12**, 2601 (1982); J. R. Franz, F. Brouers, and C. Holzhey, *ibid.* **12**, 2611 (1982).

<sup>9</sup>A. ten Bosch, J. L. Moran-Lopez, and K. H. Benneman, *J. Phys. C* **11**, 2959 (1978).

<sup>10</sup>R. Dupree, D. J. Kirby, W. Freyland, and W. W. Warren, *Phys. Rev. Lett.* **45**, 130 (1980); *J. Phys. (Paris) Colloq.* **41**, C8-16 (1980).

<sup>11</sup>P. B. Littlewood, *Phys. Rev. B* **24**, 1710 (1981).

<sup>12</sup>J. Robertson, *Philos. Mag.* **39**, 479 (1979).

<sup>13</sup>J. Robertson, *Philos. Mag.* **44**, 239 (1981).

<sup>14</sup>F. Meloni and A. Balderschi, in *Recent Advances in Condensed Matter Physics*, edited by J. T. Devreese *et al.* (Plenum, New York, 1981).

<sup>15</sup>A. Hasegawa and M. Watabe, *J. Phys. F* **7**, 75 (1977).

<sup>16</sup>H. Overhof, J. Knecht, R. Fischer, and F. Hensel, *J. Phys. F* **8**, 1067 (1979).

<sup>17</sup>D. J. Chadi and M. L. Cohen, *Phys. Status Solidi B* **68**, 405 (1975).

<sup>18</sup>S. Froyen and W. A. Harrison, *Phys. Rev. B* **20**, 2420 (1979).

<sup>19</sup>J. Robertson (unpublished).

<sup>20</sup>J. Robertson, *J. Phys. C* **12**, 4753 (1979); **12**, 4767 (1979); **12**, 4777 (1979).

<sup>21</sup>S. T. Pantelides, *Phys. Rev. B* **11**, 5082 (1975).

<sup>22</sup>N. Nicholoso, R. W. Schmutzler, and F. Hensel, *Ber. Bunsenges. Phys. Chem.* **82**, 621 (1978).

<sup>23</sup>C. Norris, and L. Walden, *Phys. Status Solidi A* **2**, 381 (1970).

<sup>24</sup>G. K. Wertheim, C. W. Bates, and D. N. E. Buchanan, *Solid State Commun.* **30**, 483 (1979).

<sup>25</sup>Our results emphasize important weaknesses in previous calculations (Refs. 6–9). If only the Cs-Au  $ss\sigma$  term is included and its value fitted to the full width of the valence band, this greatly overestimates the covalence of CsAu. Additionally, the lowest band is largely Au  $p$ -like and not Cs  $s$ -like. This does not invalidate band-filling models of the MNMT. However, it does suggest that excess electrons may still reside in Au-centered orbitals which need to be included when estimating magnetic susceptibilities (Ref. 7).

<sup>26</sup>J. R. Chelikowsky and J. C. Phillips, *Phys. Rev. B* **17**, 2453 (1978).

<sup>27</sup>W. Freyland and G. Steinleitner, *Ber. Bunsenges. Phys. Chem.* **80**, 810 (1976).

<sup>28</sup>J. C. Phillips, *Rev. Mod. Phys.* **42**, 310 (1970).

<sup>29</sup>R. Wyckoff, *Crystal Structures* (Wiley, New York, 1964), Vol. 2.

<sup>30</sup>J. H. Jack and M. M. Watchel, *Proc. R. Soc. London Ser. A* **239**, 49 (1957).

<sup>31</sup>G. M. DeMunari, F. Ginsiano, and G. Mambriani, *Phys. Status Solidi* **29**, 341 (1968).

<sup>32</sup>J. Krebs, *Acta. Crystallogr.* **2**, 95 (1956); E. Zintl and G. Brauer, *Z. Phys. Chem. Crystallogr. B* **20**, 245 (1933); W. B. Pearson, *Acta. Crystallogr. Sect. B* **24**, 1415 (1968).

<sup>33</sup>A. Zunger, *Phys. Rev. B* **17**, 2582 (1978); T. Asada, T. Jarlborg, and A. J. Freeman, *ibid.* **24**, 510 (1981); **24**, 857 (1981).

<sup>34</sup>E. Parthe, *Crystal Chemistry of Tetrahedral Structures*



- (Gordon and Breach, London, 1965).
- <sup>35</sup>J. Robertson (unpublished).
- <sup>36</sup>C. W. Bates, D. D. Gupta, L. Galan, and D. N. E. Buchanan, *Thin Solid Films* **69**, 175 (1980).
- <sup>37</sup>R. Evans, and M. M. Telo da Gama, *Philos. Mag. B* **41**, 351 (1980).
- <sup>38</sup>F. Sommer, R. W. Schmutzler, B. Predel, and D. Eschenweck, *J. Met.* **32**, 3 (1980).
- <sup>39</sup>A. Kempf and R. W. Schmutzler, *Ber. Bunsenges. Phys. Chem.* **84**, 5 (1980).
- <sup>40</sup>P. Munster and W. Freyland, *Philos. Mag. B* **39**, 93 (1979).
- <sup>41</sup>R. W. Schmutzler, H. Hoshino, R. Fischer, and F. Hensel, *Ber. Bunsenges. Phys. Chem.* **80**, 107 (1976).
- <sup>42</sup>A. Copestake, R. Evans, and M. M. Telo da Gama, *J. Phys. (Paris) Colloq.* **41**, C8-321 (1981); A. P. Copestake and R. Evans, *J. Phys. C* **15**, 4961 (1982).
- <sup>43</sup>G. Steinleitner, W. Freyland, and F. Hensel, *Ber. Bunsenges. Phys. Chem.* **79**, 1186 (1975).
- <sup>44</sup>V. T. Nguyen and J. E. Enderby, *Philos. Mag.* **35**, 1013 (1977).
- <sup>45</sup>H. Ruppertsberg and H. Egger, *J. Chem. Phys.* **65**, 4095 (1975).
- <sup>46</sup>B. R. Ilshner and C. N. Wagner, *Acta. Metall.* **6**, 712 (1953).
- <sup>47</sup>J. E. Enderby, *J. Phys. (Paris) Colloq.* **35**, C4-309 (1974).
- <sup>48</sup>R. Avci and C. P. Flynn, *Phys. Rev. B* **19**, 5967 (1979).
- <sup>49</sup>R. D. Swenson and U. Even, *Phys. Rev. B* **24**, 5743 (1981).