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Local order in liquid and amorphous Cs-Sb

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We have investigated the effects of local order on the density of states and the conductivity of liquid and amorphous Cs-Sb alloys as a function of concentration. By using a numerical Monte Carlo technique that treats the local atomic environment correctly, we show that the very sharp minimum in the conductivity that has been reported in the liquid near the Cs_3Sb stoichiometry can be explained by a local-order-induced gap in the density of states if a very high degree of local order is assumed. Although we find a substantial degree of charge transfer, ~0.6 electron/Cs atom, this charge transfer is far from complete, in agreement with the analyses of a variety of other types of experimental results. In the concentration region 30–50 at. % Sb, we find that the presence of Sb^--Sb^- covalent bonds, indicated by neutron-diffraction measurements, can accurately account for the measured conductivity which varies from ~50 to ~100 $(\Omega\,\mathrm{cm})^{-1}$. The strong temperature dependence of the conductivity in this concentration region can then be understood in terms of the dissociation of these bonds. By also applying our model to amorphous Cs-Sb, we explain the differences between the measured conductivities of the liquid and amorphous alloys.

I. INTRODUCTION

Liquid alloys have been found to exhibit a wide range of local atomic arrangements and types of bonding.[1] Because the concentration of liquid alloys can be varied continuously, many effects can be observed in liquids that cannot be studied in solids. Alloys composed of metals with large differences in electronegativity have yielded particularly interesting results. Many of these have been found to undergo metal-nonmetal transitions as a function of concentration. These transitions usually involve transfer of electronic charge between different types of atoms. Although atoms in liquid alloys have no long-range order, they can and do develop local order. Charge transfer and local order can enhance each other, resulting in dramatic changes in the transport, magnetic, and thermodynamic properties of these alloys. Many of these interesting effects are found in liquid alloys containing alkali metals. Some of the alkali-metal alloys are highly ionic and have metal-nonmetal transitions similar to those that occur in molten salts in the metal-rich regime. A typical alloy of this type is Cs-Au, which was investigated extensively some years ago.[2,3] Others have been found to contain rather long-lived ionic complexes. For instance, recent experiments[4] and theoretical work[5,6] in liquid KPb have confirmed the existence of the previously proposed,[7] tetrahedral, Pb_4^{4-} ions similar to those found in solid KPb.

One of the most interesting liquid alloy systems is Cs-Sb. Measurements of the conductivity[8] as a function of alloy composition indicate that at a temperature of 750 °C there are two distinctly different regions in which alloys exhibit nonmetallic behavior: the first is a very narrow region near 25 at. % Sb where the conductivity drops below 10 $(\Omega\,\mathrm{cm})^{-1}$, and the other is a broad region from ~35 to ~50 at. % Sb where the conductivity is ~60–100 $(\Omega\,\mathrm{cm})^{-1}$. Since the experiments were only carried out on concentrations up to 50 at. % Sb, it is not known how far this latter region extends into the Sb-rich region. Liquid Sb itself is metallic. Some information about the atomic structure has been available from a variety of experiments[8–11] that have been performed and from some previous theoretical work.[12] The fact that the conductivity drops to a minimum right at the stoichiometric concentration Cs_3Sb is reminiscent of the behavior of strongly ionic liquids. There is also a large volume contraction in liquid Cs-Sb (Ref. 8) in this concentration region which is similar to the behavior of Cs-Au. However, measurements of the magnetic susceptibility[8] and Knight shift,[9] and estimates based on measured mixing enthalpies[10] indicate that the bonding is not completely ionic and some sort of mixed bonding has been postulated. Previous theoretical work,[12] using a mean field approach, had shown that charge transfer and local order could produce a deep minimum in the conductivity at 25 at. % Sb, but the calculated width of the minimum was broader and the charge transfer was larger than those found experimentally.

In the 35–50 at. % Sb region, there is strong experimental evidence for the formation of relatively long-lived Sb^--Sb^- covalent bonds. The most direct evidence for this comes from neutron-diffraction measurements[11] that show an additional peak in the pair-correlation function at 2.8 Å in this concentration region. This distance is identical to the covalent Sb-Sb bond length in the solid compound CsSb, whose structure contains spiral Sb chains.[13] Spiral chains are characteristic of the chalcogenides, which have four valence *p* electrons. The chain structure in solid CsSb is indicative of the formation of Cs^+ ions and Sb^--Sb^- covalent bonds. Other evidence for the existence of some long-lived Sb^- complex in this concentration region comes from NMR experiments,[10] which show a large reduction in the *s* electron density at the Cs nucleus in this concentration region indicating that charge transfer occurs. In addition, although the experimental sensitivity was clearly sufficient, the investigators were never able to detect an Sb NMR signal. They attributed this to the effect of fluctuating quadrupole interactions resulting from the presence of long-lived molecular groups. No calculations of the conductivity of Cs-Sb in this concentration region have been reported to date.

In addition to the experiments that have been carried out on the liquid Cs-Sb alloy system, measurements of the conductivity of amorphous Cs-Sb have been reported over a wide concentration range by Avci and Flynn[14] and by Swenumson and Even.[15] These measurements were performed on samples prepared by co-evaporation on substrates cooled to liquid-helium temperature. Neither group found any indication of the sharp minimum that was reported in the conductivity in the liquid system near Cs_3Sb. Both groups found rapid metal-nonmetal transitions at higher Sb concentrations, one group[14] at ~45 at. % and the other[15] at ~35 at. %. (Avci and Flynn[16] have discussed the discrepancy between these two sets of measurements.) Although these results are quite different from those found in the liquid alloys, one expects the atomic interactions to be quite similar in the amorphous and liquid states. Therefore, any theoretical treatment of the conductivity in the liquid alloys should also yield reasonable agreement with the experimental results for the amorphous alloys if the differences in local order are taken into account.

Because experimental measurements that have been carried out on liquid and amorphous Cs-Sb imply that several different types of local order and bonding exist in these alloy systems in different concentration regions, we found Cs-Sb to be a particularly interesting system to investigate theoretically. The information derived from the variety of experiments that have been performed on the liquid and amorphous alloys put severe constraints on the types of models that can successfully describe them. Since the conductivity of liquid Cs-Sb remains very low ($<600\ \Omega^{-1}\mathrm{cm}^{-1}$) over the entire concentration range, 20–50 at. % Sb, the electrons are strongly scattered and have a very short mean-free path throughout this region where dramatic changes occur. For this reason, we believed that the key to understanding the behavior of these materials was a proper treatment of the local atomic configurations. This meant that we needed to go beyond the mean-field approach that had been used previously.[12] In this paper we report the results of calculations carried out using a numerical Monte Carlo technique to describe accurately the local environments of the Cs and Sb atoms.

II. MODEL

In order to understand the behavior of liquid Cs-Sb in the two concentration regions where it exhibits minima in its conductivity, we started by considering a random binary alloy, $Cs_{1-x}Sb_x$, described by the simple tight-binding Hamiltonian

$$\mathcal{H}=\sum_i \varepsilon_i c_i^\dagger c_i+\sum_{i\neq j} t_{ij} c_i^\dagger c_j \ , \tag{1}$$

where i and j must be nearest neighbors for the hopping integral t_{ij} to be nonzero. The site energy ε_i can have one of two possible values, $\varepsilon_{\mathrm{Cs}}$ or $\varepsilon_{\mathrm{Sb}}$, depending on which type of atom occupies site i. Using this Hamiltonian, we calculated the density of states and the conductivity as a function of the concentration x of Sb in the alloy, selecting the types of neighbors of individual atoms using a Monte Carlo method.[17,18] We assumed that the Fermi level of the alloy lies in an energy region dominated by the 6s electrons of Cs and the 5p electrons of Sb and neglected any contributions from other states.

The density of states $n(\varepsilon)$ is give by

$$n(\varepsilon)=(1/\pi)\langle A_{ii}(\varepsilon)\rangle \ , \tag{2}$$

where $A_{ij}(\varepsilon)\equiv -2\,\mathrm{Im}G_{ij}(\varepsilon+i\eta)$ is the spectral density for the electronic Green function $G_{ij}(\varepsilon+i\eta)$, and the angular brackets denote a configurational average over the site energies. Following the work of Girvin and Jonson,[17] and Jonson and Franz,[18] we used an approximate equation for the two-site contribution to the dc conductivity:

$$\sigma_{ij}(\varepsilon)=(Ze^2/6\pi\hbar)(N/\Omega)^{1/3}t_{ij}^2 \times\langle A_{ii}(\varepsilon)A_{jj}(\varepsilon)-A_{ij}(\varepsilon)A_{ji}(\varepsilon)\rangle \ . \tag{3}$$

Z is the number of nearest neighbors and N/Ω is the density of sites. If one neglects thermal smearing at the Fermi level, Eq. (3) can be derived from the Kubo expression under the assumption that the electron mean-free path is very short. The full conductivity $\sigma(\varepsilon)$ can be written as a product of $\sigma_{ij}(\varepsilon)$ and a correction that represents hops to sites other than i and j. Thus $\sigma_{ij}(\varepsilon)$ represents a lower bound for the full conductivity. Under strong scattering conditions, the mean-free path is short, all position summations (for example, over j for fixed i) converge very rapidly, and the correction is of order unity.[17] Even though Eq. (3) explicitly involves only two sites, the spectral density function depends on the self-energy of all the sites, and thus is capable of describing Anderson localization where appropriate. The full conductivity is calculated by averaging over the two-site contributions.

To calculate the properties of Cs-Sb in concentration regions where charge transfer and ionic behavior are important, we introduce the standard chemical short-range-order parameter σ_{sr}, which is used to describe correlation in the occupation of neighboring sites. In terms of σ_{sr}, the probabilities of an Sb atom being surrounded by an Sb or a Cs atom are given, respectively, by

$$P_{\mathrm{SbSb}}=x+(1-x)\sigma_{\mathrm{sr}},\quad P_{\mathrm{SbCs}}=(1-x)(1-\sigma_{\mathrm{sr}}) \ , \tag{4a}$$

and the same probabilities for a Cs atom are

$$P_{\mathrm{CsSb}}=x(1-\sigma_{\mathrm{sr}}),\quad P_{\mathrm{CsCs}}=(1-x)+x\sigma_{\mathrm{sr}} \ . \tag{4b}$$

The average atomic configuration is thus determined by the x and σ_{sr}. Note that when $\sigma_{\mathrm{sr}}=0$, neighboring sites are completely uncorrelated, corresponding to the random case. Ionic liquids, where a given atom is more likely to be surrounded by the opposite type of atom, are described by $\sigma_{\mathrm{sr}}<0$. In this case, the range of possible values for σ_{sr} is

$$-x/(1-x)\le\sigma_{\mathrm{sr}}\le 0 \quad \text{for } x\le\tfrac{1}{2}\ , \tag{5a}$$

$$-(1-x)/x\le\sigma_{\mathrm{sr}}\le 0 \quad \text{for } x\ge\tfrac{1}{2}\ . \tag{5b}$$

We also wished to investigate $\mathrm{Cs}_{1-x}\mathrm{Sb}_x$ in the concentration region where Sb^--Sb^- covalent bonds are expected to be important. To do this we introduced a second parameter, f, the fraction of Sb atoms in covalent bonds. Sb^- has the same electron configuration as the chalcogenide Te, which has occupied orbitals $(5s)^2(5p)^4$. In Te two p electrons occupy bonding orbitals and form covalent bonds with two neighboring atoms, while the other two p electrons occupy nonbonding orbitals (a "lone pair") with antiparallel spins. This electron configuration favors covalently bonded spiral chains. Covalently bonded spiral Sb^- chains occur in solid CsSb,[13] and neutron-diffraction experiments[11] have indicated that they are present in liquid CsSb as well. To form Sb^- ions, the Cs atoms must give up their valence electrons. The resulting Cs^+ ions then help stabilize the Sb^--Sb^- bond.

In our calculations, we assumed that the energy levels corresponding to occupied levels in covalent bonds lie well below the Fermi level, while the antibonding levels lie well above the Fermi level, so that neither needs to be included in the conduction band. The conduction band then consists of the two $6s$ states of Cs and only those $5p$ states of Sb that are not participating in covalent bonds. Because of this the number of states per atom in the calculated conduction band varies with f, and the average number of states per atom in the conduction band is given by $6(1-f)x+2(1-x)$.

III. NUMERICAL TECHNIQUE

Following the work of Watson,[19] the self-energy Δ_i, which describes hops away from site i, can be written as a sum of terms each corresponding to a nonrepeating path in the lattice. In this work, we kept only the first term of the sum. This approximation, often called the Cayley-tree approximation, turns the regular lattice into a Bethe lattice, which has no closed loop paths. For random-alloy systems in which electrons are strongly scattered, this approximation makes calculations in these complex materials feasible and has been shown to be reasonably good.[20]

With the Cayley-tree approximation, the self-energy can be expressed simply[18] as

$$\Delta_i=\sum_{j=1}^{Z} t_{ij}^2(\varepsilon-\varepsilon_j-\Delta_j^f)^{-1}\ , \tag{6}$$

$$\Delta_j^f=\sum_{k=1}^{K} t_{jk}^2(\varepsilon-\varepsilon_k-\Delta_k^f)^{-1}\ , \tag{7}$$

where $K=Z-1$ is the connectivity of the Bethe lattice. Here Δ_i indicates all hops from site i, and Δ_i^f indicates only hops in the forward direction.

Adapting techniques developed previously[17,18] for monovalent atoms to polyvalent Sb atoms, we calculated the self-energies using a self-consistent technique.[21] Briefly, for each energy, we began with separate ensembles of complex site energies for Cs sites and Sb sites; we typically used 200 values for each. (Using larger ensembles would smooth the curves shown in Figs. 1–4 somewhat, but would not significantly change any of our results.) The initial values of the imaginary parts of the self-energies must be chosen to be negative. With this constraint, the initial values do not affect the final numerical results. From one of the ensembles, we then randomly chose a self-energy corresponding to a particular site (which might be a Cs or an Sb site), chose its K forward neighbors randomly to be either Cs or Sb according to the average probability distributions of Eqs. (4a) and (4b), chose the self-energy of each neighbor randomly from the appropriate ensemble, recalculated the self-energy according to Eq. (7), and replaced the original value of the self-energy with the new value. This process was repeated until the self-energies in the ensembles had been replaced a sufficient number of times to reach a stable state. We found that 8000 repetitions was usually sufficient since the convergence is very rapid.

In terms of the self-energies defined above, $G_{ii}(\varepsilon)$ and $G_{ij}(\varepsilon)$ can be written as

$$G_{ii}(\varepsilon)=[\varepsilon-\varepsilon_i-\Delta_i(\varepsilon)]^{-1}\ , \tag{8a}$$

$$G_{ij}(\varepsilon)=G_{ii}(\varepsilon)t_{ij}[\varepsilon-\varepsilon_i-\Delta_i^f(\varepsilon)]^{-1}\ . \tag{8b}$$

From these, the density of states and the energy-dependent conductivity can by obtained by calculating the spectral density functions and taking the required averages. To calculate the measured conductivity, $\sigma(\varepsilon_F)$, we needed to determine the Fermi level. We did this by integrating the density of states as a function of energy from the bottom of the conduction band up to that energy (ε_F) for which the integral equaled the number of electrons present.

The important parameters used in these calculations are given in Table I. The site-energy difference, $\varepsilon_{\mathrm{Cs}}$-$\varepsilon_{\mathrm{Sb}}$, was taken from Ref. 12. This was held constant throughout all of our calculations, although it is expected to shift somewhat due to the charge transfer between Cs and Sb atoms. We did carry out some tests to determine the effects of shifts in the site energies, and these are discussed below. The hopping integrals, t_{CsCs} and t_{SbSb}, were taken to be constants and were derived from the bandwidths of the pure liquid metals. The value for t_{CsSb} was taken to be slightly larger than the geometric mean of the values of the pure materials.[12] The correction was included to take account of the rather sizable volume

TABLE I. Model parameter for Cs-Sb alloys.

	Parameters	Values used
Site energy difference (Ry)		
	$\varepsilon_{\mathrm{Cs}}-\varepsilon_{\mathrm{Sb}}$	0.17
Hopping integrals		
	t_{SbSb}	0.061
	t_{CsCs}	0.014
	t_{SbCs} (t_{CsSb})	0.036

contraction that occurs in these alloys between the concentrations of 20 and 70 at. % Sb.[8] The number of nearest neighbors was set equal to eight in all of our calculations.

IV. NUMERICAL RESULTS

Using the numerical technique and the parameters described above, we calculated the density of states and the conductivity as a function of energy throughout the conduction band for a range of Sb concentrations and different degrees of chemical short-range order and Sb^--Sb^- covalent bonding. For liquid Cs-Sb, we were particularly interested in two concentration regions, one around 25 at. % Sb where a very sharp minimum in the measured conductivity occurs and the other around 50 at. % Sb where a broad minimum is found.[8] It should be noted that our calculations are expected to give physically meaningful results only in the region $\varepsilon \approx \varepsilon_F \pm 0.1$ Ry (1 Ry = 13.6 eV), since our model excludes all but the Sb $5p$ and the Cs $6s$ states. In addition, the approximations described above are only expected to yield good results under conditions of strong scattering. Thus our results are best when the conductivity of the alloy is very low. For Cs-Sb this includes all of the regions in which we are particularly interested, namely, the regions where unusual types of local chemical order occur.

Figure 1(a) and 1(b) show the calculated density of states as a function of energy for an Sb concentration of 26 at. % with and without local chemical order. From a comparison of Figs. 1(a) and 1(b), it can be seen that including a high degree of local order opens up a large gap in the density of states. We choose to show the 26 at. % Sb results because it is at this concentration that, in our numerical calculations, the Fermi level passes through the gap as can be seen in Fig. 1(b). We investigated the possible discrepancy between our calculated results that places the minimum conductivity at 26 at. % Sb and the experimental results that show it to be between 25 and 26 at. %.[8] (Figure 3 of the paper by Redslob, Steinleitner, and Freyland[8] indicates that the minimum occurs at ~25.5 at. % while the text mentions 25 at. %.) We found that increasing the site energy, ε_{Cs}-ε_{Sb}, causes the

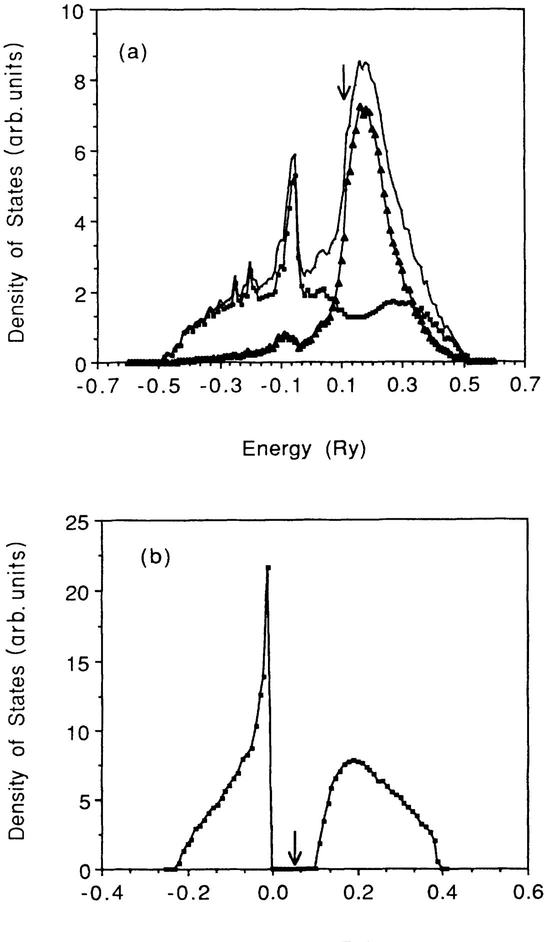

FIG. 1. Calculated density of states as a function of energy for 26 at. % Sb for (a) $\sigma_{sr}=0$ and (b) $\sigma_{sr}=-0.35$. The arrows indicate the positions of ε_F. In (a), the curve with triangles is the density of states for Cs atoms, the one with squares is for the Sb atoms, and the line shows the total density of states.

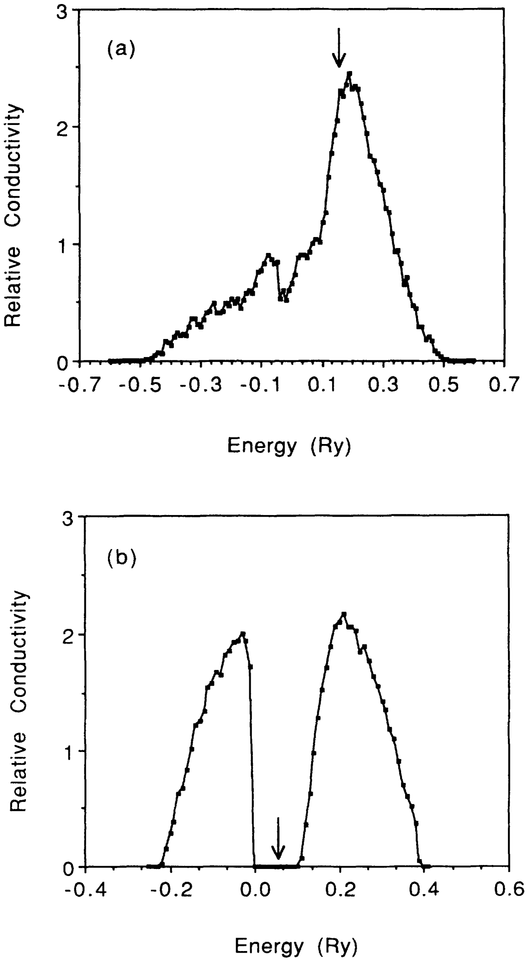

FIG. 2. The relative conductivity as a function of energy for 26 at. % Sb for (a) $\sigma_{sr}=0$ and (b) $\sigma_{sr}=-0.35$. The arrows indicate the positions of ε_F.

minimum conductivity to move toward 25 at. %. Although we took ε_{Cs}-ε_{Sb} to be constant in our calculations, we realize that charge transfer will cause this site-energy difference to vary somewhat. Such shifts in site energies are probably sufficient to account for any discrepancy in the location of the conductivity minimum.

Figure 1(a) shows the density of states of the Sb and the Cs atoms individually as well as the total density of states. It can be seen that transfer of electrons from the Cs atoms to the Sb atoms occurs even in the random case. We obtained a value of 0.4 electron/Cs atom (1.2 electrons/Sb atom) for the charge transfer in the random case and 0.6 electron/Cs atom (1.8 electrons/Sb atom) for the highly ordered alloy of Fig. 1(b).

Figures 2(a) and 2(b) show the relative conductivity as a function of energy for the same two cases as Figs. 1(a) and 1(b). The results given in Fig. 2(b) indicate that the ordered alloy would be an insulator at this concentration. At slightly lower Sb concentrations the Fermi level lies on the left shoulder of the peak on the right, while for slightly higher concentrations the Fermi level drops to the right shoulder of the peak on the left. Thus our results predict very rapid changes in $\sigma(\varepsilon_F)$, the measured conductivity, in this concentration region.

Our results for the density of states of the equiatomic alloy are given in Figs. 3(a) and 3(b). The results shown in Fig. 3(a) are for the simple random alloy. For those shown in Fig. 3(b), we assumed that 60 at. % of the Sb atoms were participating in Sb^--Sb^- covalent bonds and thus had their valence electrons removed from the conduction band. The sharp peak just to the left of ε_F corresponds to Sb atoms that are surrounded entirely by Cs atoms. The sharpness of this peak is unphysical and is caused by the use of constant hopping integrals in our numerical calculations.

Figures 4(a) and 4(b) give our results for the relative conductivity as a function of energy for the same two cases as Figs. 3(a) and 3(b). From a comparison of Figs. 4(a) and 4(b), it can be seen that the formation of covalent bonds causes a large decrease in $\sigma(\varepsilon_F)$.

Figure 5 summarizes our results for $\sigma(\varepsilon_F)$ in $\Omega^{-1}\text{cm}^{-1}$ in the region around 25 at. % Sb for three different values of σ_{sr}, while Fig. 6 summarizes our results in the region around 50 at. % Sb for five different

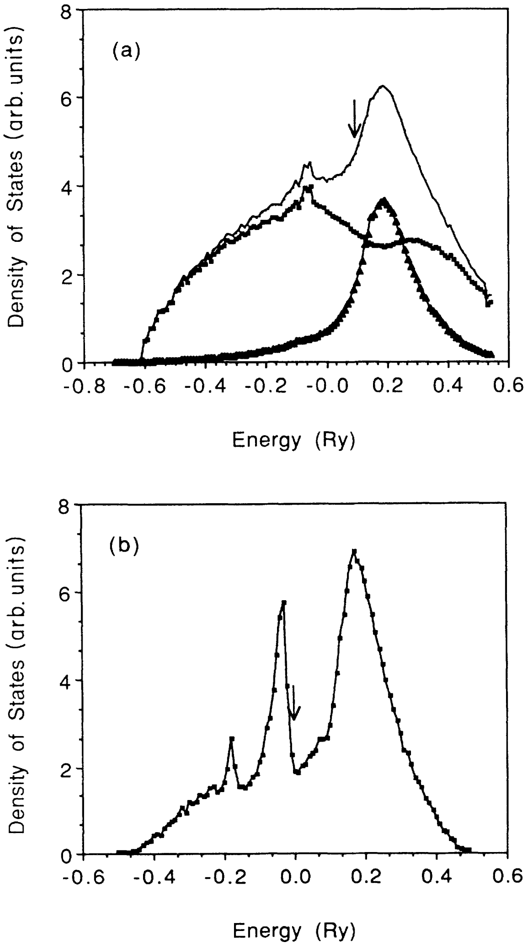

FIG. 3. Calculated density of states as a function of energy for 50 at. % Sb for (a) $f=0$ and (b) $f=0.6$. The arrows indicate the positions of ε_F. In (a), the curve with triangles is the density of states for Cs atoms, the one with squares is for the Sb atoms, and the line shows the total density of states.

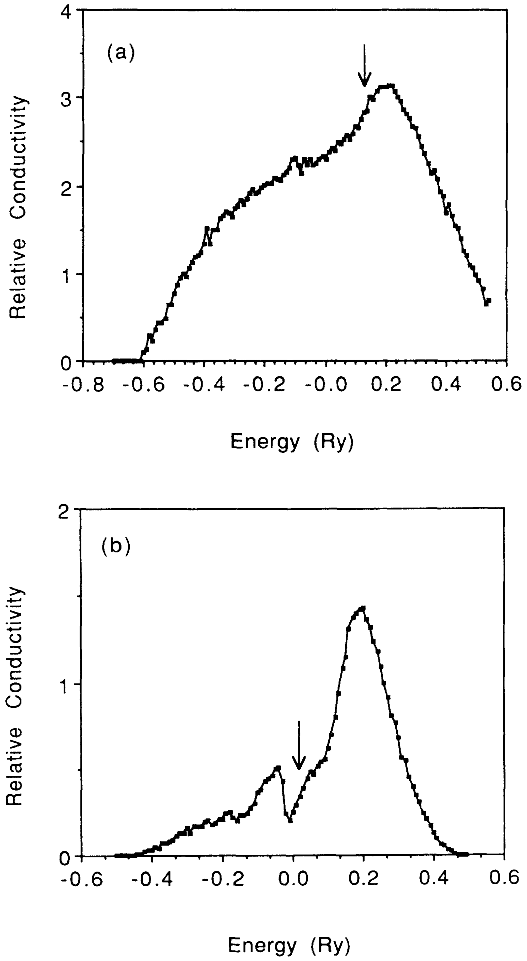

FIG. 4. The relative conductivity as a function of energy for 50 at. % Sb for (a) $f=0$ and (b) $f=0.6$. The arrows indicate the positions of ε_F.

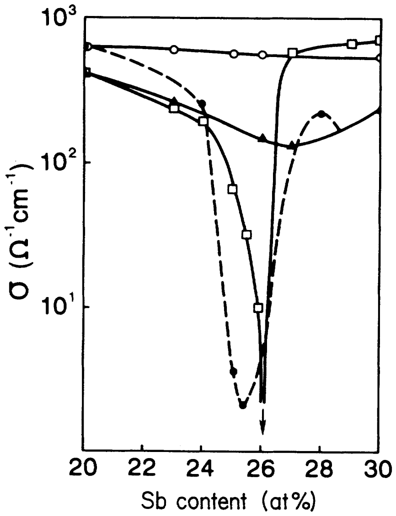

FIG. 5. The conductivity as a function of Sb concentration. The solid curves are calculated results: $\sigma_{sr}=0$, open circles; $\sigma_{sr}=-0.25$, solid triangles; $\sigma_{sr}=$ the maximum value for each concentration, open squares. The dashed curve shows the experimental results for $T=750\,^{\circ}\mathrm{C}$ (Ref. 8).

values of f. For a value of $f=1$, the Sb contribution to the conduction band would be reduced to zero. In that case the Fermi level would lie in the Cs band and move down the low-energy side of this band as the Sb concentration was increased. At an Sb concentration of ~42 at. %, the Fermi level would move into the localized states in the tail of the Cs band and the conductivity would go to zero.[22] In the next sections, we discuss the implications of the results described in this section.

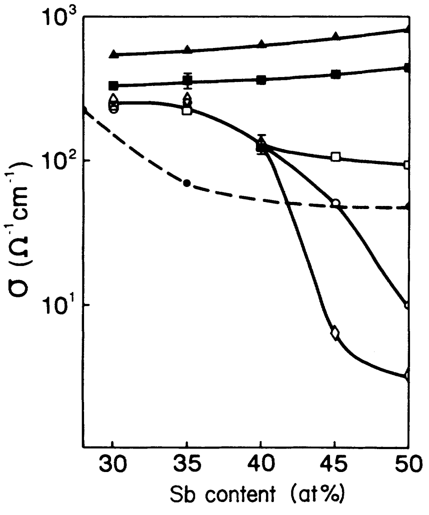

FIG. 6. The conductivity as a function of Sb concentration. The solid curves are calculated results: $f=0$, solid triangles; $f=0.3$, solid squares; $f=0.6$, open squares; $f=0.7$, open circles; $f=0.9$, open diamonds. The dashed curve shows the experimental results for $T=750\,^{\circ}\mathrm{C}$ (Ref. 8).

V. DISCUSSION

A. The Cs_3Sb concentration region

Our results for the conductivity in this region are in good agreement with the measured values (see Fig. 5) and show that the sharp minimum in the conductivity that occurs as a function of concentration near the alloy, Cs_3Sb, can be explained by a model that includes a very high degree of local chemical order. This high degree of local order causes a gap in the density of states to develop and the drop in conductivity occurs when the Fermi level passes through this gap. The extreme narrowness of the concentration region where the measured conductivity remains below 200 $(\Omega\,\mathrm{cm})^{-1}$ indicates that there are few localized states in the gap. Our calculations also yielded few localized states when the degree of local order was taken to be quite high. The inclusion of local order causes the charge transfer from Cs atoms to Sb atoms to increase from ~0.4 to ~0.6 electron/Cs atom, but even with the maximum possible order the charge transfer is far from complete and the system is only partially ionic. Thus our results are in agreement with measurements of the magnetic susceptibility[8] and Knight shift[9] in liquid Cs_3Sb. Neither of these measurements could be explained by a pure ionic model. In addition, our calculated charge transfer for the highly ordered alloy agrees very well with the value calculated by Robertson (0.6) for solid Cs_3Sb.[23]

Even with a high degree of local chemical order, however, our results did not fully reproduce the measured conductivity found in the region near Cs_3Sb. Three main differences between the measured (solid circles) and calculated results (open squares) can be seen from Fig. 5: the concentrations at which the conductivity minima occur differ by ~1/2 at. % (this was discussed above), and our calculations overestimate the sharpness of the metal-nonmetal transition on the side of the minimum with >25 at. % Sb and underestimate the sharpness of the transition on the side with <25 at. % Sb. The disagreement on the >25 at. % Sb side can be shown to be a direct result of taking the hopping integrals (t_{ij}'s) to be constants. To explain fully the very rapid change in the measured conductivity on the <25 at. % Sb side, we need to postulate changes in the degree of local chemical order in this region. Earlier work of Franz, Brouers, and Holzhey[12] gave an indication that such changes occur. In that paper, the local order was treated in the mean-field approximation, the entropy of the system was calculated, and the degree of local order was then determined by minimizing the free energy. The authors found that for low Sb concentration ($x<0.2$), zero local order was predicted. However, between 20 and 25 at. % Sb, a strong tendency for the system to order developed and maximum order produced the minimum free energy. A high degree of order continued to be favored up to a concentration of ~35 at. % Sb, at which point zero local order was once again predicted. From the results reported in this paper, it can be seen that the tendency toward a high degree of local order occurred only when the Fermi level was in the region in which this local order could produce an energy gap. This is not surprising, since it is well known that the opening of a gap in the density of states at the Fermi level lowers the energy of the system, and thus stabilizes the gap. In the work of Franz, Brouers, and Holzhey,[12] the Fermi level remained in the gap region from ~20 to 30 at. % Sb because the mean-field theory technique used in that work smeared out the density of states curves. In our current work, which correctly treats the local atomic environment, the Fermi level passes through the energy gap very quickly as a function of concentration, in fact, in a concentration range of ≤ 1 at. % of the system is highly ordered.

It can be seen from the curves in Fig. 5 that including rapid changes in local order as the Fermi level passes through the energy gap would cause our calculated conductivities to be in even better agreement with the experimental measurements. Our results for the conductivity would then follow a curve similar to that with $\sigma_{sr}=0$ (open circles) up to an Sb concentration of ~24 at. %, at which point, as the local order increased rapidly, it would cross over to a curve similar to that with open squares (maximum local order). Such rapid changes in local order as a function of concentration would also explain why Dupree, Kirby, and Freyland[9] had such trouble obtaining reproducible NMR results in this region.

It should be pointed out, however, that it would be surprising to find in a liquid, except at temperatures at or just above the melting point, the very high degree of local order needed to reproduce accurately the measured dip in the conductivity. The melting point of Cs_3Sb is reported to be 725 °C while the conductivity was measured at 750 °C.[8] This raises the question as to whether the CsSb phase diagram and, in particular, the melting point of Cs_3Sb might be in error. Recent measurements have shown that the melting point of Na_3Sb is considerably higher than reported earlier.[24]

It is important to note the large temperature dependence found in some of the measurements made in the concentration region near Cs_3Sb. From Fig. 3 of Ref. 8, it appears that the sharp minimum in the conductivity that occurs at 750 °C has become greatly diminished by a temperature of 900 °C. Although not as dramatic as this, the increase with temperature exhibited by the magnetic susceptibility[8] in the 25 at. % Sb region is quite large. Rapid changes such as these are strong indications that local order is decreasing as the temperature increases. It is not surprising that the very high degree of local order that is required for the metal-nonmetal transitions that occur near Cs_3Sb cannot be maintained as the temperature is raised well above the melting point. As the local order decreases, the gap in the density-of-states curve diminishes quickly, which causes the local order to decrease even further. This "positive feedback" can cause rapid changes in the conductivity. The magnetic susceptibility is affected more directly by the charge transfer than the local order. The charge transfer will also decrease as the temperature rises. Our calculated value for the difference in charge transfer between an alloy with maximum local order and a random alloy is 0.2 electron/Cs atom. We believe that this change in the charge state of the ions is sufficient to cause the measured temperature dependence of the susceptibility.

It is interesting to compare our results for Cs-Sb near the 25 at. % Sb concentration to those for CsAu, the prototype ionic liquid-metal alloy. Both exhibit dramatic metal-nonmetal transitions at stoichiometric concentrations that are caused by charge transfer and local order. The main difference in the form of the measured conductivities is that the transition in Cs-Sb is much sharper than that in Cs-Au. Our calculations show that the charge transfer in the transition region is less complete (~60 at. %) in Cs-Sb than in Cs-Au (~75 at. %).[25] This is not surprising when one considers the very large repulsive forces that would exist between the Sb^{3-} ions that would be formed if full charge transfer took place. Our results indicate that even the formation of $Sb^{1.8-}$ ions, which our calculations predict for Cs_3Sb, is not energetically favorable unless the alloy can develop into a highly ordered state. In Cs-Au such large ionic repulsive forces never exist since both have valence 1. Thus the difference in the valence states of Au and Sb seems to be the major cause of the differences observed between the metal-nonmetal transition observed at 25 at. % Sb and that in Cs-Au.

B. The CsSb concentration region

In our model, we attribute the broad dip in the conductivity above 30 at. % Sb to the formation of relatively long-lived Sb^{-}-Sb^{-} covalent bonds. As stated above, the most direct evidence for the formation of these bonds comes from neutron-diffraction studies[11] that show a peak in the pair-correlation function at 2.8 Å that exactly correlates with the Sb-Sb bond length of the Sb spiral chains in solid CsSb.[13] This peak, although not visible at 25 at. % Sb, is quite evident at 35 at. % and is quite large at 50 at. %. Because the neutron-diffraction measurements at the two concentrations were done at different temperatures, it is difficult to learn much from a comparison of the size of the peaks. Our results (see Fig. 6) indicate that to reproduce the general form of the measured conductivity at 750 °C, at least 60 at. % of the Sb atoms would need to be covalently bonded at any instant of time, while the results at 600 °C would require ~70 at. %. We think that these fractions are roughly consistent with the size of the peaks observed in the neutron-diffraction experiments. Whether or not such high degrees of covalent bonding actually occur in liquid CsSb depends on the energetics of the system. It is probable that just above the melting point, long Sb^{-} chains exist and that the average length of these continually decreases as the temperature is increased. The rapid increase of the conductivity with temperature in this concentration region[8] is a clear indication that some ordered structure exists and is dissociating.

For $Cs_{1-x}Sb_x$ in the Sb-rich regime, there are insufficient Cs atoms to supply the necessary electrons to ionize all of the Sb atoms. The maximum fraction of Sb ions that can form in this region is $x/(1-x)$. Here either new covalent structures must form or the Sb valence electrons will go into the conduction band. We know of no experimental results for $Cs_{1-x}Sb_x$ at these concentrations. Some indication of what may be occurring can be deduced from measurements of the activity coefficient in K-Sb alloys.[26] These yield a Darken excess stability which peaks at the equiatomic concentration and falls to half maximum at about 62 at. % Sb. If Cs-Sb alloys behave similarly, it would appear that no new covalently bonded Sb structures are formed in the Sb-rich region.

C. Amorphous Cs-Sb alloys

As mentioned above, the conductivity of amorphous Cs-Sb alloys as a function of concentration has been measured by Avci and Flynn[18] and by Swenumson and Even.[15] Neither group found any indication of the type of metal-nonmetal transition that occurs in the liquid system with 25 at. % Sb. Both found rapid transitions at higher Sb concentrations, one[14] at ~45 at. % and the other[15] at ~35 at. %. We believe that our calculations can help to explain these results. We have shown that the sharp minimum in the conductivity that occurs in liquid Cs_3Sb results from the fact that if the system can develop a high degree of local chemical order, it will lower its energy by the formation of a gap in its density of states at the Fermi level. The important point is that the liquid alloy is free to rearrange itself to achieve this lower-energy state, while the amorphous system is not. The amorphous samples, which are formed by coevaporation on substrates held near liquid-He temperature, are expected to have a nearly random distribution of Cs and Sb atoms. Although the forces acting on an atom as it approaches the substrate will have some small effect on exactly where it sticks, there is no way to generate the order required for a metal-nonmetal transition such as the one that occurs in liquid Cs_3Sb. Of course, it is also possible that concentration fluctuations in the amorphous samples might have smeared out the very sharp metal-nonmetal transition seen in the liquid samples.

Although the local order and the behavior of the liquid and amorphous Cs_3Sb alloys are quite different, we were interested in investigating whether the metal-nonmetal transition observed in the amorphous alloys at higher Sb concentrations could be caused by the same type of covalent bonding that we believe occurs in liquid alloys in the 35–50 at. % Sb concentration range. If the formation of Cs^+ ions and Sb^--Sb^- covalent bonds is energetically favored in the liquid state then it should be in the amorphous alloys as well. The occurrence of Sb^--Sb^- covalent bonds does not require a highly ordered state, but only that Sb atoms that are nearest neighbors find Cs atoms nearby. Even at low temperatures, the atoms should be able to rearrange themselves slightly to achieve a near-optimal covalent bond length. To see whether a random system could produce a sufficiently large number of covalent bonds to cause a metal-nonmetal transition, we carried out a bond-site percolation calculation for a simple cubic model alloy with periodic boundary conditions. With the concentration of the alloy determining the average fraction of Cs and Sb atoms, we randomly distributed these atoms on the sites of the lattice. To simulate the formation of chains, we forced each Sb to bond with nearest-neighbor Sb atoms up to a maximum of two bonds per atom. We then counted the number of Sb atoms with no bonds (singles), with one bond (chain ends), and two bonds (interior to the chains). Our results are shown in Fig. 7. It can be seen that the number of singles declines rapidly as the Sb concentration increases and drops to less than 10 at. % at a concentration of 40 at. % Sb. We counted Sb atoms with one and two bonds separately because it is possible that the chain ends might act as weakly conducting sites. The number of doubly bonded Sb atoms increases monotonically with Sb concentration, going from ~60 at. % at a concentration of 0.35 to ~75 at. % at 0.50. From Fig. 6, it can be seen that this change would have a dramatic effect on the conductivity. Thus in the region that the measured resistivities of the alloys is increasing rapidly, the fraction of covalently bonded Sb atoms is passing through the region where our calculations indicate that this should indeed be happening. Of course in amorphous alloys, once the covalently bonded chains form, they would remain indefinitely, unlike those in the liquids that are continually breaking and reforming.

How realistic are the results of this simple percolation model? The assumption of a lattice should have no effect on the results; it only simplifies the calculation. The dominant factor in the calculation is the number of nearest neighbors. The desire to use a simple-cubic-lattice structure forced us to use six nearest neighbors. An Sb atom in an amorphous structure probably has the choice of more than six neighbors with which it can bond. Increasing the number of neighbors increases the fraction of Sb atoms that can form covalently bonded chains. In addition, although we placed the Sb atoms at random sites in the lattice, it is possible that, during the growth of the samples, they will locate preferentially at sites that allow covalent bond formation, if such sites are available locally. Both of these factors would indicate that we undercounted the fraction of covalently bonded Sb atoms. On the other hand, it is probable that some Sb atoms that we have counted as covalently bonded will not form such bonds, either because the electron transfer from nearby Cs atoms is incomplete or because they are

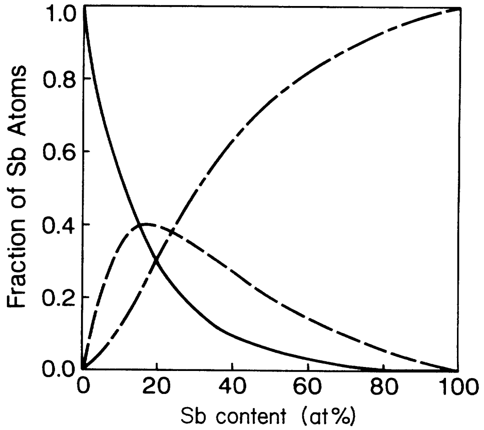

FIG. 7. The fraction of Sb atoms with different types of bonding as a function of Sb concentration: solid curve, Sb atoms with no covalent bonds; dashed curve, with one covalent bond; long-dashed–short-dashed curve, with two covalent bonds.

unable to achieve the optimum bond length. Because all of these factors tend to cancel each other, we believe that our simple calculation gives a reasonable estimate, and that Sb$^-$-Sb$^-$ covalent bonds can account for the metal-nonmetal transition seen in amorphous Cs-Sb alloys.

VI. CONCLUSIONS

We have investigated the effects of local order on the density of states and conductivity of liquid and amorphous Cs-Sb alloys. By using a model that treats the local atomic environment correctly, we have shown that the very sharp minimum in the conductivity that has been observed in liquid alloys near 25 at. % Sb can be explained by a local-order-induced gap in the density of states. This gap opens when it coincides with the Fermi level as it does at this particular concentration. Although we have found a substantial degree of charge transfer (~ 0.6 electron/Cs atom) under these conditions, this charge transfer is far from complete, in agreement with the analyses of a variety of other types of experiments. The results reported here using a Monte Carlo technique are in much better agreement with experimental measurements in this concentration region than the previous work that used a mean-field method.

As the concentration of Sb is increased beyond 25 at. %, the local order is expected to decrease and the importance of Sb$^-$-Sb$^-$ covalently bonded chains to grow. Whether such relatively long-lived complexes occur at lower Sb concentrations is unclear, but at concentrations >30 at. % Sb, they have been observed in a number of experiments, and their effect on the conductivity is substantial. While the measured conductivity rises very steeply with Sb concentration from a value of ~ 2 $(\Omega\ \mathrm{cm})^{-1}$ at 25 at. % Sb to a value of several hundred $(\Omega\ \mathrm{cm})^{-1}$ at 28 at. % Sb, above 28 at. % it begins to fall again. It then remains quite low up to 50 at. % Sb, the highest concentration measured. Our conductivity calculations show that our model, which assumes that at any instant of time a large fraction of Sb atoms are participating in Sb$^-$-Sb$^-$ covalent bonds, is consistent with this behavior. The strong temperature dependence of the conductivity in this concentration region can then be understood in terms of the dissociation of these bonds.

By applying our model to amorphous Cs-Sb, we have explained the differences between the conductivities of the liquid and amorphous alloys. The absence of a metal-nonmetal transition in the amorphous alloys near Cs_3Sb is due to the fact that, at the low temperatures at which the experiments were performed, the atoms are trapped in nonequilibrium positions and cannot achieve the high degree of local chemical order necessary for this type of transition. We believe that the metal-nonmetal transition that takes place in amorphous alloys at higher Sb concentration is caused by the formation of Sb$^-$-Sb$^-$ covalent bonds similar to those found in the nonmetallic state in liquid Cs-Sb in the 35–50 at. % Sb range. This is possible because even at low temperatures Sb atoms can shift their positions sufficiently to achieve optimal covalent bond lengths with neighboring Sb atoms.

The Cs-Sb alloys system is particularly interesting because of the variety in the type of bonding that takes place as the concentration is varied. Other Sb–alkali-metal alloys probably exhibit a similar range of behavior, and it is unfortunate that many fewer experiments have been performed on these. Measurements of the concentration-dependent conductivity of Na-Sb (Ref. 8) have been carried out and indicate covalent bonding is less important here than in Cs-Sb. This gives a hint that the size of the Cs$^+$ ion may be particularly advantageous for assisting in Sb covalent bond formation. More recent experiments indicate that K dimers may be forming in Sb-rich K-Sb.[26] Investigations of the structure of Na-Sb or K-Sb by neutron diffraction would help to clarify these structures and might well uncover others.

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