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Comments

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Comment on metal-insulator transitions in Cs alloys

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Recent measurements of metal-insulator transitions in Cs-based alloys are compared, and the interpretations of the data are discussed.

Of all the pure metals Cs has the lowest conduction electron density. Cs alloys, therefore, offer an opportunity to examine systems in which Coulombic interactions play a particularly important role. In probing these effects Avci and Flynn[1,2] (AF) examined solid-state metal-insulator transitions in the seven systems Cs-I, Cs-Te, Cs-Sb, Cs-Sn, Cs-Au, Rb-Br, and Na-Sn, in addition to the two systems Cs-Xe and Rb-Kr reported by Phelps, Avci, and Flynn (PAF)[3] and Phelps and Flynn (PF).[4] Three further systems, Cs-Ag, Cs-Cd, and Cs-In, explored by AF in this survey, exhibited no significant signs of metal-insulator transitions.[1,2] Optical measurements on the systems Cs-Xe and Rb-Kr,[3,5,6,7] Cs-I and a variety of other alkali-halogen systems[8] and Cs-Te (Ref. 9) revealed optical excitation channels specifically characteristic of the second component, particularly in the dilute alloys. All the above work necessarily involved alloys quench condensed onto substrates held at liquid-He temperatures, since the random solid alloys are all thermodynamically unstable. Investigations of conductivity in *liquid* Cs-Au and liquid Cs-Sb have also been reported.[8,10]

Papers describing reinvestigations of three of these twelve systems have recently been published: Cs-Xe by Swenumson, Leutwyler, and Even (SLE),[11] and Cs-Au and Cs-Sb by Swenumson and Even (SE).[12,13] These workers omit significant comparisons with the earlier work. They also offer somewhat disparate commentaries on the origins of the metal-insulator transitions. One purpose of this paper is to provide the necessary comparisons and to show that they are informative. The second purpose is to emphasize certain basic physical characteristics of the transitions reported in Refs. 1–4.

Figure 1 compares the AF data for Cs-Au (solid circles) with the SE data (open circles) for the same system. The latter were digitized by Autotrol from enlarged photographs. They are as accurate as needed for the present purposes of approximate comparison. The SE reinvestigation apparently confirms the earlier AF work rather well, including the large resistivity of quench-condensed Au and the conductivity anomaly near the 50% composition. A principal conclusion is thus that the technique of quench condensation has developed to the point at which the main features can be reproduced from one laboratory to another even on tricky alloy systems, such as Cs-Au, which are found to undergo thermal evolution at ~ 20 K (AF). We return below to a mention of the discrepancies that remain between the two data sets.

The second case, Cs-Sb, is shown in Fig. 2, with

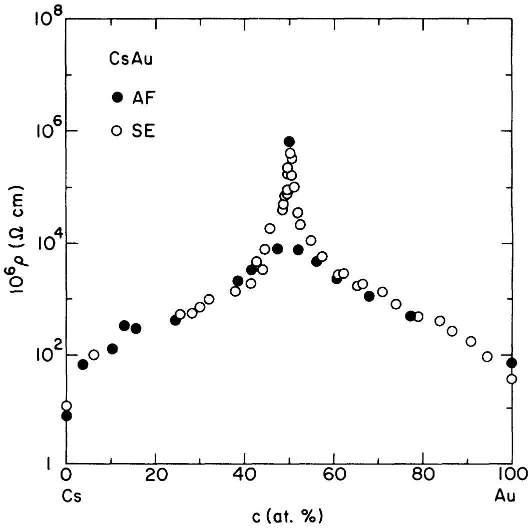

FIG. 1. Resistivity of Cs-Au alloys according to Avci and Flynn (solid circles, Ref. 2) and Swenumson and Even (open circles, Ref. 12).

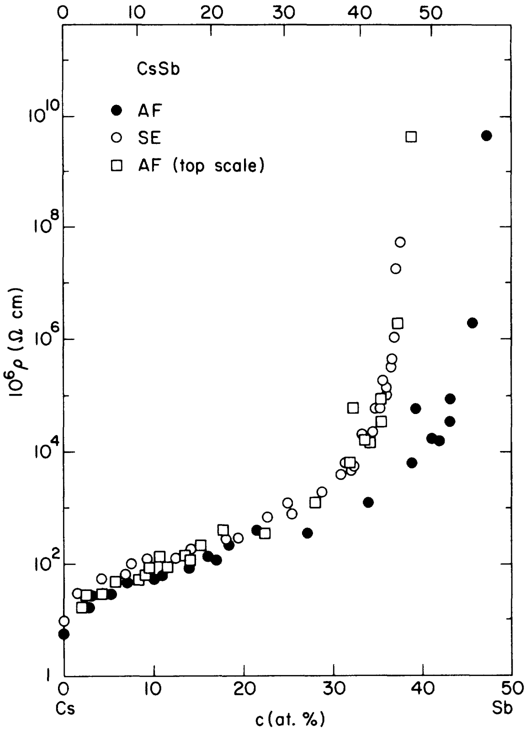

FIG. 2. Resistivity of Cs-Sb alloys according to Avci and Flynn (solid circles, Ref. 2) and Swenumson and Even (open circles, Ref. 13). The solid squares show the AF data replotted using the composition scale at the top of the graph.

closed circles and open circles again marking AF and SE measurements, respectively. The lower concentration scale is pertinent to both data sets as published. Open squares show the AF data replotted with the concentration scaled by a factor of 0.82 in conformity with the concentration scale at the top of the figure. The two data sets now match entirely through the composition range of the transition. It is possible that a calibration error in the molecular-beam intensity occurred in one or both experiments, the result otherwise being in very good agreement. A check of our records has revealed no obvious error. A second, perhaps unlikely, possibility is that significantly different temperatures were employed for Sb sublimation in the two cases. This could possibly result in differing Sb, and Sb_3, molecular content of the beams, and hence differences of short-range order in the two sets of alloys.

Results for Cs-Xe by PAF (solid circles) and SLE (open circles) are replotted in Fig. 3. While the SLE measurements lie at generally higher resistances than the AF data the overall behavior of the Cs-Xe system, including the composition at which the metal-insulator transition occurs, is again reproduced quite well.

The SLE data in Figs. 1–3 may be seen to lie, fairly systematically, at higher resistivities than those of AF. It should be noted that part of this systematic difference arises as an artifact of the interpretation rather than as a result of different measured resistances. In neither the AF nor the SLE work could the film thicknesses be determined directly. AF calculate film thicknesses using a Vegard's-law approximation in which the alloy thickness is assumed to equal the sum of the thicknesses that the the two components, when crystalline, would contribute separately. In contrast, SLE assume that the materials are amorphous and therefore are ~ 1.5 times thicker than AF calculate, so that the resistivities they deduce are proportionately larger. Part of the apparent residual differences between the data sets in Figs. 1–3 are thus artifacts of the chosen interpretations.

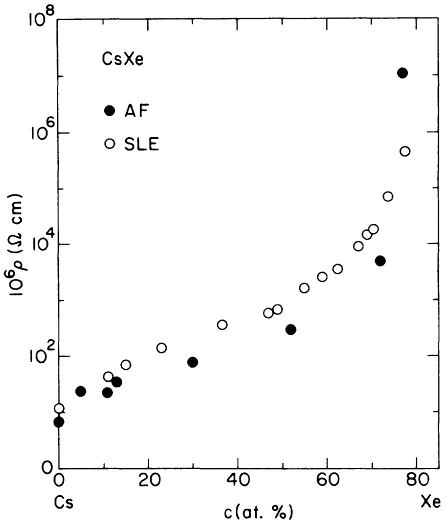

Fig. 3. Resistivity of Cs-Xe alloys according to Avci and Flynn (solid circles, Ref. 2) and Swenumson, Leutwyler, and Even (Ref. 11).

Thin films are notoriously difficult to characterize for microscopic structure even when that structure persists at room temperature. We believe that certain of the films examined by AF are crystalline and others may very probably be close to amorphous, but that accurate structural distinctions at He temperature will not be established unambiguously in the near future. Some further discussion of details will be found below in the Appendix. Fortunately, the uncertainties are largely systematic and amount to a numerical factor of order unity in conductivities which are observed to vary over many orders of magnitude, as shown in Figs. 1–3. Such uncertainties have little or no significance for the rich qualitative structure of residual resistivities, phase transition, and temperature-dependent resistivity behavior reported for these alloy systems in the survey by AF.

One experimental point that appears worth mentioning concerns the widths of the metal-insulator transitions. AF report a transition in Cs-Xe (Fig. 3) which has about the same width as those they report for Rb-Kr, Rb-Br, Cs-I, Cs-Te, Cs-Sn, Na-Sn, and Cs-Sb (for example, the data near the transition of Cs-Sb in Fig. 2 match the variation of the AF data for Cs-Xe in Fig. 3 very closely), whereas the SLE data for Cs-Xe show a much slower variation of resistivity with composition there (see Fig. 3). The AF data appear to identify a sharper anomaly near 50 at.% Cs-Au, also, than that of SE. A number of experimental artifacts that could possibly *broaden* observed transitions include (i) inhomogeneous alloys due to deposition geometry; (ii) imperfect sample masking, leading to metal paths at the sample edges (see AF for description); and (iii) saturation of resistance measurement capability (SLE state for Cs-Xe that "The values ... diverge sharply beyond the measurement capability at the Cs atomic fraction $x = 0.23$"; cf. Fig. 3). In connection with point (i) we draw attention here to the large resistance and very large temperature dependence (see AF) of the AF sample at 50 at.% Cs-Au. The lower resistance and lesser temperature dependence of the SE alloys could be explained if the SE materials were inhomogeneous.

Some brief comments about the qualitative chemical origins of the observed conductivity transitions appear to be warranted. All these effects arise from the Coulomb interaction. Ordinarily, only a single aspect of the physical behavior changes rapidly near a given transition. However, quite a number of alternative Coulomb-induced effects are able to cause rapid changes of conduction near some critical configuration of the system. Interest centers on a determination of the mechanism which operates in particular systems.

In the case of Cs-Au, conduction near 50 at.% is caused by carriers introduced in the usual way[14] to accommodate charge imbalances between unequal densities of anions and cations. The crystalline equiatomic compound is a polar semiconductor, and this characteristic is clearly maintained in the melt and in the disordered material prepared by quench condensation. Accordingly, the critical property through which the Coulomb interaction induces the conductivity anomaly is the *stoichiometry.* This follows from the fact that the conduction anomaly is linked unambiguously with the 50-at.% composition of perfectly stoichiometric material (AF, see Fig. 1). It is affirmed by the remarkable similarity between the observed conductivities in the melt[9] and in the quench-condensed solid.[12] Apparently the carrier density and the carrier mobility must both be largely athermal or else their temperature dependences are mutually compensatory.

Our purpose now is to point out once more that alloys such as Cs—rare-gas and Cs-halogen mixtures are qualitatively different from Cs-Au. The energy required, for example, to transfer an electron from Cs to Xe in the alloy must be 3—5 eV, much as in a vacuum. In the insulating regime this wide-gap material must confine electrons to Cs-occupied sites alone. To bring this important point into sharp focus we should term materials of this type *persistently heterogeneous.* This correctly indicates that halogen ions or rare-gas atoms remain compact and maintain their chemical identities across the entire phase diagram of the alkali—rare-gas or alkali-alkali halide phase diagram. Also, the oribitals are bound at energies which are remote from those of the alkali component.

Unlike Cs-Au, such materials undergo conductivity transitions at compositions having no special stoichiometric significance. By definition, also, an ideal persistently heterogeneous system undergoes no chemical change which could possibly induce conductivity transitions. No Mott transitions[15] can occur because the conduction orbitals are always confined to specific chemical sites, having the same local electron densities. Similarly, the idea of *bulk* Anderson localization[16] is made inapplicable by the sharp localization introduced in the electron wave function by each heterogeneity. Instead, the only property which varies rapidly with composition at the observed transitions is the topology of nearest-neighbor interconnections. Since conduction can only take place through alkali orbitals, conduction requires that unbroken sequences of alkali orbitals extend from one end of the material to the other. This is also the criterion for percolation.[17] It is therefore satisfactory that the observed conductivity transitions take place near compositions appropriate for percolative transitions, as observed by PAF and AF.

In their comments to the contrary, SLE and SE appear to overlook the chemical facts. No complete theory is available to describe the quantum mechanics of percolative conduction on an atomic scale through persistently heterogeneous systems. SLE discount the influence of the topological constraints in Cs-Xe because, they conclude, neither the power-law behavior at the transition nor the critical composition itself conforms precisely to the predictions of *macroscopic* models of percolation. However, the observed temperature-dependent conductivities near the transition already establish that classical, macroscopic models are not adequate. Very recently, theoretical models of quantum hopping have appeared.[17] These include bond disorder appropriate, for example, to models of Cs-Xe or Cs-I (AF). There is an interesting indication that Anderson-type localization and conductivity loss may occur in the infinite cluster before the absolute limit set by the requirement of percolative connectivity is reached. These matters remain for future clarification. Certain experimental refinements, also, will be needed before quantitative comparison can be made with *any* theory, as the comparison of data near the transition in Fig. 3 attests.

Not much can be said at present about the conductivity transition in Cs-Sb. The systems examined by AF can be placed in an approximate sequence of behavior as follows: Cs-Xe and Rb-Kr, Cs-I and Rb-Br, Cs-Te, Cs-Sb, Cs-Sn, Na-Sn, Cs-Au, followed by the three systems Cs-In, Cs-Cd, and Cs-Ag which apparently lack the conduction anomalies and ionic characteristics found in the other alloys. There is a relatively smooth variation of properties in this sequence from the rare-gas and halogen alloys, which are persistently heterogeneous, through to Cs-Au which is controlled by stoichiometry and has the weakest observed anomaly. In the alloy systems between these limits, including Cs-Sb, the conductivity transitions have a chemically mixed character which is not well understood at present.

In alloys containing chemically dissimilar components the optical properties, also, show striking evidence of the alloy heterogeneity. What happens is that the optical excitation spectrum is strongly modified by the Coulomb interaction. In less heterogeneous systems the photon absorption is presumed to create an electron and a hole which are delocalized and independent. Persistently heterogeneous systems, to the contrary, yield spectra resembling a superposition of two contributions which are separately characteristic of the two component elements. There is a direct analogy here with the "persistence" and "amalgamation" of exciton spectra in insulating alloys as discussed, for example, by Onodera and Toyozawa.[18] Our measurements on alkali-metal–rare-gas, alkali-metal–halogen, and alkali-metal–chalcogen systems clearly reveal persistent spectra of this type for deep levels. The important recent development is the discovery that shallow levels in such simple materials as Li-Mg and Ag-Cd are quite strongly heterogeneous in their optical behavior.[19] For example, in the optical spectrum of alloys containing a little Mg in Li, the main feature, between 1 and 5 eV, is the Mg $3s^2 \rightarrow 3s3p$ resonance, which exists in the alloy as an electron-hole pair bound together at a Mg site by the Coulomb interaction. Moreover the resonance can be traced across the entire phase diagram to pure Mg where it has long been regarded as the interband transition near 0.6 eV.[20] Thus, the alloy spectrum is strongly influenced by the Coulomb interaction between carriers, in a way which has not previously been recognized.

Given careful ellipsometric determinations of $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ it is still possible in a simple case such as that of Li-Mg to resolve the dilute alloy spectra approximately into terms arising from single-particle and plasmon components, modeled by Drude theory, superposed on the persistent two-particle, impurity-specific features and their shakeoff sidebands.[19] As the concentration is increased the impurities occur, by chance, in pairs, multiplets, and so forth, each with its own spectrum. Also, as the host metal becomes fragmented by intervening heterogeneities, the simplified notions of a single carrier relaxation time and a single plasmon mode become unrealistic. As a result, it is not possible at present to interpret the optical spectrum of even a moderately heterogeneous system such as Li-Mg other than in the dilute alloy regime. Even then, careful fitting of accurately determined ϵ_1 and ϵ_2 is needed to separate Drude terms from persistent features in the low-energy region.

These complexities must be borne in mind in connection with the optical data obtained by SLE and SE to probe conductivity behavior in Cs alloys. There are two areas in which caution appears advisable. First, the Li-Mg system is probably less heterogeneous than any of the twelve alloy systems examined by AF. Certainly it is less so than the three alloy systems reinvestigated by SLE and SE, namely Cs-Xe, Cs-Au, and Cs-Sb. Therefore the excitation spectra of these systems must be regarded as complicated mixtures of single-particle and element-specific properties which vary from one site to the next in the alloy. Second, only the optical-absorption coefficient of the alloys, rather than ϵ_1 or ϵ_2, was measured by SLE and SE, and estimates of the dielectric function were obtained by fitting the 0.5–5-eV absorption spectrum to several damped oscillators. These procedures are not fully reliable for quantitative work, particularly when ϵ has singular behavior immediately outside the range of the measurements, as is necessarily the case with metals.

It is likely that the optical data of SLE and SE nevertheless retain a qualitative significance and do reflect the general conductivity behavior of the materials. Much more caution is, however, needed in connection with specific deductions made from the optical data by SLE and SE about the precise locations of metal-insulator transitions in these systems. To us it seems unlikely that either the particular data employed, or the degree of available understanding of optical properties in chemically heterogeneous alloys, could possibly support such specific conclusions.

ACKNOWLEDGMENTS

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APPENDIX

Careful structural studies will be required before the structure even of pure metals quench condensed at liquid-He temperatures becomes well understood. AF measured 25 and 65 $\mu\Omega$ cm for pure Ag and pure Au, while SE measured 35 $\mu\Omega$ cm for Au, both using their respective procedures to estimate thickness. These values are comparable with the liquid-state resistance[21] near the melting point of 17 $\mu\Omega$ cm for Ag and 31 $\mu\Omega$ cm for Au, which suggests that the materials are amorphous. However, S. Durbin in our laboratories has recently measured resistivities up to 150 $\mu\Omega$ cm for quench-condensed Cu, which is much greater than the liquid-state resistance of 20 $\mu\Omega$ cm. Detailed investigations are needed because these materials are known to follow columnar growth patterns under some circumstances.[22] It is still noteworthy that the Cs resistivity of 7 $\mu\Omega$ cm (AF) and ~ 12 $\mu\Omega$ cm (SLE) is very much *smaller* than the liquid-state resistance of ~ 37 $\mu\Omega$ cm. Therefore quench-condensed pure Cs certainly cannot be prepared amorphous, in contradiction with the conclusion of SLE. Elsewhere these authors argue that impurity additions ~ 5 at.% stabilize the amorphous state. A change from polycrystalline to amorphous in this range is hard to reconcile with the linear changes of residual resistance with composition in the 0–10-at.% range observed by AF, and with the fact that the observed residual resistances are similar to those observed in liquid and crystalline alkali alloys,[23] in which no such change can occur. In contrast to the case of Cs, quench-condensed Sb *is* amorphous,[24] as clearly stated by AF. We have not been able to understand the (sole) citation by SE of the earlier investigation of Cs-Sb by AF in connection with their statement that the loss of conductivity of Sb at low temperature occurs *because it is a semimetal.*

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