Charge-Transfer Insulators

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Resistivities of thin-film Cs-based alloys prepared by coevaporation at He temperature reveal charge transfer to high-valence impurities. Percolative transitions to new disordered insulating phases occur as the impurity content is increased. Metallic components of resistance exceeding $3 \times 10^4\ \Omega$ are observed near the percolation thresholds.

In this Letter we report the observation of new disordered insulating phases in Cs-based alloys. These disordered materials are *charge-transfer insulators,* in which charge transfer among different chemical species reduces the conduction-electron density below that required for percolation. The lack of conduction thus arises from ionicity rather than covalency. Dilute alloys exhibit charge transfer from the host electron gas to impurity atoms. With increasing solute content, the materials undergo percolative transitions to disordered insulating phases associated with the charge transfer. In the case of Xe, I, and Te in Cs the percolative transitions occur at compositions clearly determined by the ionic forms of these species in Xe^0, I^-, and Te^{2-} configurations. The precise charge-transfer state is less evident for Sb and Sn, which fall in the region intermediate between the charge-transfer and normal states. Cs-Sn exhibits percolative transitions to a domain of the charge-transfer insulator phase bounded on either side by Cs and Sn metallic conduction in the two cases. We have observed similar phenomena in Na-based materials. These effects are believed to result from the low electronegativity of alkali-metal atoms.

The phenomenon of charge transfer to impurities in alkali alloys was proposed[1] to explain conduction-electron spin resonance[2] and susceptibility[3] effects in dilute liquid alkali alloys. For rare-gas and halogen impurities, the basic charge-transfer ideas have been confirmed by studies of the impurity-induced transport properties[4] and optical excitation spectra.[5] High concentrations of rare gases in solid alkali hosts cause a percolative transition to the expected rare-gas–rich insulating phase.[6] In addition, transport measurements in *liquid* alkali alloys reveal striking anomalies[7] at concentrations close to those of intermetallic compounds. This paper reports a systematic investigation of the electronic structure and electronic transport in disordered Cs-based alloys. The properties are rich in novel effects.

Alloys were prepared by coevaporation onto He-temperature substrates previously overlaid by a suitable electrode pattern, as described elsewhere.[4] Compositions and densities were determined by means of calibrated quartz crystals placed in the evaporation streams, and uniformity of the films was ensured by the evaporation geometry. In the case of halogen impurities, the appropriate Cs *halide* was usually evaporated as the second component, but only minor differences were observed when the molecular halogen was employed instead. Detailed previous studies of rare-gas impurities have indicated that these methods give good random mixtures.[4] The materials are thermally unstable but typically only decompose above 20 K. Two films were prepared simultaneously in all cases, one of pure Cs and one containing the same Cs content together with the second component. A consistent check on the Cs deposition was thereby made available.

The variation of resistivity with chemical composition for Cs mixed with various second components is shown in Figs. 1(a) and 1(b). These data all pertain to a test temperature of about 5.5 K. Some scatter evident in the data indicates that sample preparation was reproducible, with typical compositional uncertainties confined to the 2% level. Inset in Fig. 2 are resistivities for dilute Cs-based mixtures, showing the expected linear variation of resistance with impurity content. The chosen second components include a complete row of the periodic table: Ag, Cd, In, Sn, Sb, Te, I, and Xe; the dilute data therefore provide a fairly complete view of scattering power as a function of impurity species for the relatively simple host metal Cs. Residual resistances referred to a 1% impurity content, as deduced from the linear graphs inset in the figure, are displayed in the main figure. The composite data point clearly to charge-transfer effects and reveal the existence of charge-transfer insulator phases.

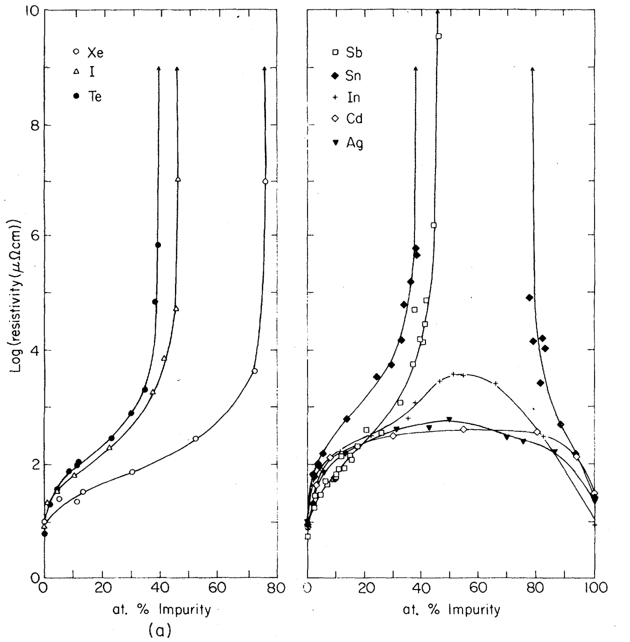

FIG. 1. Electrical resistance as a function of composition (at.% solute) for Cs-based alloys at 5.5 K: (a) Xe, I, and Te impurities; (b) Sb, Sn, In, Cd, and Ag impurities.

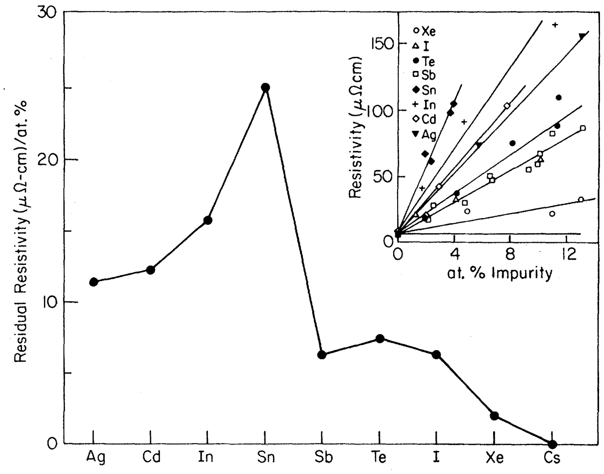

FIG. 2. The residual resistance introduced by 1% of various impurities in Cs at 5.5 K. The linear resistance variation with impurity concentration is shown as inset in the figure.

Figure 2 shows that the core- and size-difference scattering is rather large for Ag (isovalent with Cs). With increasing impurity valence the residual resistivity increases, as expected, when added *p*-wave scattering contributes significantly for In and Sn. The resistivity drops abruptly for Sb, where charge transfer becomes important, and falls off gradually from Te, through I and Xe, to zero for Cs in Cs. The abrupt drop in resistance between Sn and Sb is interpreted as mainly due to the loss in core scattering when the charge-transfer state forms. The *p* orbitals of the Sb^{3-} ion fall below the band bottom to be screened by the repulsion of conduction electrons from the impurity site. This decouples the core from the conduction band. The remaining resistivities for Te to Xe reflect scattering by the screened *repulsive* potential of the particular negative ion formed by charge transfer from the Cs conduction band to that impurity.

These observations are in excellent agreement with much earlier structure prediction (for K) by Flynn and Lipari.[1] In absolute magnitude the resistivities are also consistent with this interpretation. The core scattering for Ag and Cd has a similar magnitude to that for these elements in Na; direct phase-shift calculations have not reproduced these observations well.[8] Quantitative agreement has been established for the resistance of Xe in Cs.[4] The increase from Xe^0 through I$^-$ to Te^{2-} is consistent with the increasing size of the screening hole in the electron gas required by these negative ions. Sn and Sb clearly lie in the transitional region of the charge-transfer process. No detailed information about their structure in Cs is available, although the formation of Sn charge-transfer configurations has previously been identified by Mikolosko, Rigert, and Flynn[9] in liquid NaK hosts.

These systems exhibit novel metal-insulator transitions. It is known[4] that Xe induces a percolative transition to the insulating phase resembling that observed in macroscopic mixtures of insulating and conducting balls.[10] The similarity arises because Xe excludes conduction electrons from its cell; the conduction is associated wholly with chains of alkali atoms. Figure 1 shows that a similar transition occurs for I (impurities) at about 45 at.% I. Note that perfect charge transfer between *equal* numbers of Cs and I atoms eliminates *all* conduction electrons. Figure 1 indicates that a fractional excess of 5/50 =10% of Cs is needed to support percolation. This compares with about 25 at.% Cs needed for percolation in Cs-Xe. In Ce-Te alloys, 38 at.% of Te is evidently required to create an insulator (Fig. 1), as compared to the 33 at.% for perfect charge transfer. Clearly, the simplest model has begun to break down for Te, presumably because the Te 5*p* orbitals overlap significantly at high density.

Sn and Sb display effects having special interest; Sn, in particular, exhibits a bounded domain of the charge-transfer insulating phase. The metal-insulator transition for Sb occurs near that of I and the transition for Sn occurs near that for Te. A superficial interpretation would identify the ions as Sn^{2-} and Sb^{-} near their respective metal-insulator transitions. The actual phenomena are likely to be more complex, perhaps involving a variety of ionicities. Sn exhibits a second metal-insulator transition at low Cs content to define a bounded range of the charge-transfer insulator phase. These are random materials in which charge transfer reduces the available conduction-electron density below the percolation threshold. The Sn-rich metals show superconductivity with enhanced transition temperatures at certain compositions. No metallic conduction is observed for pure Sb films, although the crystalline material is metallic. Amorphous Sb is known to be a semiconductor.[11]

The temperature dependence of the observed conductivities near the transitions reveal further details of the conduction mechanism. Figure 3 shows how the observed conductivities vary with T^{-1} for some Cs-Sn conductors. The data are reproducible under temperature cycling through the range shown, and therefore identify electronic processes as distinct from irreversible thermal evolution of the lattice. At the lowest accessible temperatures the resistivities in Cs-rich (and Sn-rich) materials become independent of T^{-1}, thereby establishing that a metallic component of the conduction exists in the immediate neighborhood of the metal-insulator transition. This presumably arises from metal-metal links that pass through the entire material to support percolation. It is the breaking of these links with changing composition that destroys conductivity, as suggested previously for Cs-Xe.[4] The data in Fig. 3 show, in addition, that the conductivity increases significantly above 10 K, and with a larger fractional effect evident as the metal-insulator transition is approached. We interpret this as hopping charge transport that enhances conduction by cross linking the percolation chains. A hopping energy ≃ 1.6 MeV in the cross links accounts for the observed temperature dependences. Data taken near the Sn-rich percolation limit also reveal new phenomena, with resistivity maxima between superconductivity at low temperature, and hopping short circuits at high temperature.

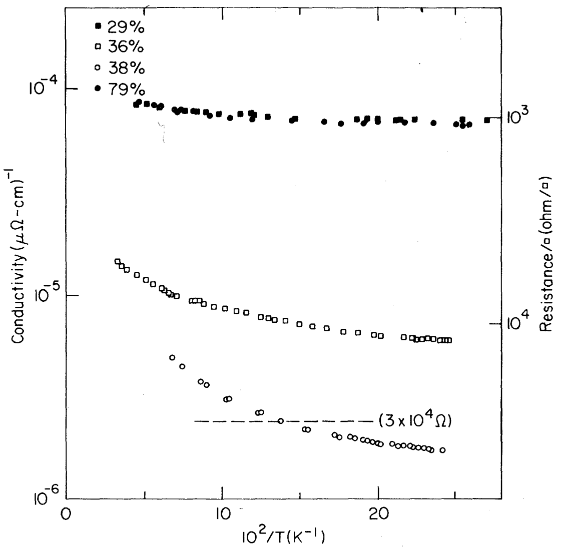

FIG. 3. The observed temperature dependence of conductivity in some Cs-Sn mixtures (concentrations given in at.%). The broken line is the theoretical limit for minimum metallic conductivity.

Metallic conduction is expected to disappear when the mean free path is reduced to the interatomic spacing. This limits metallic conduction to a resistance of about $3\times10^{4}\ \Omega$ and, for greater resistances, hopping conductivity is to be expected.[12] The argument is insensitive to film thickness. In the present experiments we find evidence for a metallic component of percolative conductance corresponding to about 1.4 times this limiting resistance (see, e.g., Fig. 3). Single conducting filaments are not limited in quite the same way, but are also said to have a maximum metallic resistance at low temperatures.[13] The percolative medium supports conductivity through few strands near the transition, and so may possess metallic resistances resembling those of single strands as much as homogeneous sheets. The precise nature of any resistance limits in these interesting systems still lacks a detailed theory.

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Electron-Phonon Contribution to Electrical Resistivity and Superconducting "*p*-Wave" Transition Temperature of Pd

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We present first-principles calculations of the electron-phonon parameters which govern transport and superconductivity in Pd. Our calculated resistivity is in good agreement with experiment. The "*s*-wave" coupling constant (or mass enhancement) is 0.41 and the "*p*-wave" coupling constant is 0.002, making the existence of observable electron-phonon–induced "*p*-wave" pairing in Pd very doubtful.

Palladium belongs to the exotic class of *d*-band elements which are neither magnetic nor superconducting. Its unusual electrical resistivity $\rho(T)$ and susceptibility $\chi(T)$ have long attracted attention. Mott[1] proposed the familiar "*s*-*d* model" to explain ρ, and invoked "Fermi smearing" to explain the T dependence of both ρ and χ. "Paramagnons[2]" have been invoked to explain the large value of χ and the absence of superconductivity. In recent years the possibility[3,4] of superconductivity with exotic pairing schemes has rekindled interest in Pd. Fay and Appel's[4] analysis of available data suggests that paramagnon coupling alone is too weak to produce "*p*-wave" superconductivity at a measurable temperature, and that the possibility of observing exotic pairing hinges on a significant attractive electron-phonon contribution. In this paper we calculate this contribution from state-of-the-art electronic band theory and experimental data. The result is a pessimistic conclusion about the possibility of exotic pairing.

The information about electron-phonon coupling necessary to calculate superconducting T_c and transport coefficients is conveniently summarized in a series of generalized electron-phonon spectral functions[5] $\alpha^2(w_a, w_b)F(\Omega)$ defined as

$$\alpha^2(w_a,w_b)F(\Omega) \equiv \frac{N_\uparrow(0)\sum_{kk'}|M_{kk'}{}^{\nu}|^2 w_a(k,k')\delta(\Omega-\Omega_{k-k'}{}^{\nu})\delta(\epsilon_k)\delta(\epsilon_{k'})}{\sum_{kk'} w_b(k,k')\delta(\epsilon_k)\delta(\epsilon_{k'})}. \tag{1}$$

Here $M_{kk'}{}^{\nu}$ is the matrix element for an electron to scatter from k to k' by a phonon of branch ν and freqnency $\Omega_{k-k'}{}^{\nu}$. The notation k is shorthand for wave number and band index $(\vec{k}, n)$ of an electron state of energy ϵ_k and velocity $\vec{v}_k$; $N_\uparrow(0)$ is the single-spin density of states at the Fermi energy. The most familiar spectral function, having weight functions $w_a = w_b = 1$, is denoted $\alpha^2F(\Omega)$ and determines the value of T_c for ordinary ("*s*-wave" or, more properly, Γ_1) pairing. Electrical and thermal resis-