

Metal-insulator transition in rare-gas-alkali-metal thin films*

D. J. Phelps and C. P. Flynn

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

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We report measurements of the conductivity and optical absorption in KrRb and XeCs thin films through the composition range spanning the metal-insulator transition. It is argued from chemical properties of the constituents that the conductivity loss must take the form of a percolative transition. In agreement with this assignment, the optical absorption shows no discontinuous or even marked change through the transitions. "Metallic" and "excitonic" features both persist on each side of the observed transitions in the two systems. The resistivity in metal-rich alloys yields residual resistivities for rare-gas impurities close to the values expected of vacancies, and the resistivity transitions at ~ 75 at.% rare gas conform rather closely to the prediction of percolation theory.

I. INTRODUCTION

In recent years the nature of metal-insulator transitions in condensed systems has attracted much attention.¹ Correlation-induced transitions were first studied in Wigner's work² on electron localization in a dilute electron gas, and generalized by Mott³ to the case of electrons interacting with a lattice of positive point charges. A variety of alternative mechanisms lead to the loss of conduction in other cases,¹ including volume-dependent band crossings. Disorder can, for example, introduce random fields that cause localization.⁴ Finally, in some cases the possibility of charge transport in an inhomogeneous material may reduce to a percolation problem.

Percolation theory finds its correct application to those systems for which the conduction process is explicitly associated with particular randomly located volumes in the material.⁵ For example, a mixture of macroscopic particles, some insulating and some conducting, exhibits a macroscopic metal-to-insulator transition as the proportion of insulating particles is increased.⁶⁻⁸ Microscopic questions, concerning, for example, Coulomb correlations, do not enter into the description of this transition, for it is presumed that two neighboring metallic particles support a current flow when they are in mechanical contact. The conductivity of the material in particular cases is determined only by topological properties concerning the distribution of conducting material in the matrix.⁹ A mixture becomes substantially conducting when the density of metal exceeds some critical value for which chains of successive metal particles thread their way unbroken through the solid. Conductivity is lost when the density of unbroken chains becomes infinitesimal. No microscopic analogs of the macroscopic percolative process have hitherto been identified with certainty.

Metal-rare-gas mixtures have been viewed as¹⁰⁻¹⁴ suitable systems for study in the search for Mott transitions. The affinity of the noble-gas atoms is only slightly negative, and these species, when interposed between metal atoms, thus provide relatively inactive material with which to space alkali atoms. Their dielectric constant is not large, so they present a minimal perturbation on the metal valence states. In this deceptive light the rare-gas-alkali-metal mixtures appear to offer a close approximation to the ideal conditions under which a Mott-type transition may emerge.

It is worth mention here that the structure of alkali-metal-rare-gas mixtures is not ideally suited to fundamental studies of conductivity transitions—a disadvantage apparently common to most alternative systems. In the first place, the materials are thermally unstable and must therefore be prepared and maintained at low temperature throughout their useful lifetimes.¹⁵ Thermal manipulation of the samples to anneal defect structures created during deposition is not possible as the atomic species segregate. Furthermore, the coordination numbers of the components are not known. At high temperatures the alkali metals are bcc but they are known to undergo slow transformations to hcp at low temperatures. A phase transition must therefore take place before the fcc structure of gas-rich mixtures can prevail, presuming that the samples are microcrystalline. The position of this transition remains uncertain; light rare gases can undergo a fcc to hcp transition induced by impurity additions as small as 1 at.%.¹⁶ Imperfect resolutions of these several difficulties may possibly have influenced the results of early measurements taken on these interesting systems.¹⁰⁻¹²

The resistance transitions in¹⁰ ArNa and¹¹ ArCu have been previously studied. Abrupt losses of conductivity were observed, but the samples were

not well characterized. Excitonic features in the optical spectra of very thin XeHg films have been discussed,¹² but the observations do not seem relevant to the phenomena reported here and in Papers I and II for KrRb and XeCs mixtures. All these results have been interpreted in terms of Mott-type transitions.^{13,14}

In what follows we shall suggest, to the contrary, that known chemical properties of the constituents make the existence of a Mott-type conductivity transition extremely unlikely in alkali-metal-rare-gas alloys. Rather, these materials provide a paradigm of percolative processes on an atomic scale. The conductivity and optical absorption results presented in this paper appear to confirm that a percolative transition occurs as the density of alkali-metal atoms is increased.

It is argued that the core field of the alkali metal provides the dominant structure-determining force in these systems. Optical studies¹⁷⁻¹⁹ show that the excitation spectra of alkali atoms at dilution in rare-gas hosts are perturbed, but not to any unusual degree, by the embedding lattice. The dielectric constants of the rare gases are not large, and the alkali *s* states do not spread after the manner of donor levels in semiconductors. The first *s* → *p* transition of alkali impurities appears as a triplet, and this evidence for Jahn-Teller distortion in the excited state conforms to a pattern established in other systems, e.g., the *F* center in Cs salts.²⁰ Signs of alkali-metal clustering evident in the concentration dependence point to the requirement of low temperatures throughout the sample lifetimes. From a structural viewpoint, however, the important feature is that the low-lying alkali levels are not greatly perturbed and the impurity wave functions must remain much like alkali-atom wave functions, with the impurity atom occupying a hole in the rare-gas lattice.

The opposite limit, in which rare-gas atoms exist at dilution in alkali-metal hosts, has been discussed in Papers I (Ref. 21) and II (Ref. 22), and this limit both provides fresh insight into the

general structure of more complex mixtures and allows the deduction that the conductivity transition must resemble the idealization of percolation theory. The principal point is that *conduction electrons do not penetrate throughout the impurity cells* even in the metal-rich limit. They are excluded from much of the atomic cell whenever the positive ion is missing, as is well known for vacancies.^{23,24} The negative affinity of rare-gas atoms can only enhance this dominant effect of the alkali-atom core field. In mixtures containing larger proportions of rare-gas atoms, a hypothetical electron gas spread through the entire volume has a smaller kinetic energy while the strength of the ion fields remains largely unchanged. Thus the effective confinement of alkali valence states in the alkali cells must be maintained as the rare-gas atoms become more numerous, as sketched for various concentrations in Fig. 1. A close connection between the electron-gas distribution in random mixtures and the topology of the percolation problem emerges clearly from these sketches.

For the percolation analogy to become complete two conditions must be satisfied. First, it is necessary that charge can pass between near-neighbor alkali atoms that form a conducting chain and, second, that an interposed rare-gas atom breaking the chain reduces the conductivity to zero. Since the conduction-electron density falls almost to zero in the center of a vacant alkali-metal cell,²³ the overlap between alkali *s* states separated by a rare-gas atom must be greatly reduced and conduction processes indeed strongly inhibited, if not reduced entirely to zero. It also seems likely that chains of near-neighbor alkali atoms can conduct electrical charge. The bond energies *B* of homovalent diatomic alkali-metal molecules are known to bear a strong relationship to the cohesive energy *E_c* of the pure alkali metal.²⁵ In fact, the relationship $E_c = (1.7 \pm 0.2)B$ interconnects these quantities, and attests to an invariant nature of the metallic interaction.²⁴ It therefore seems very probable that the alkali

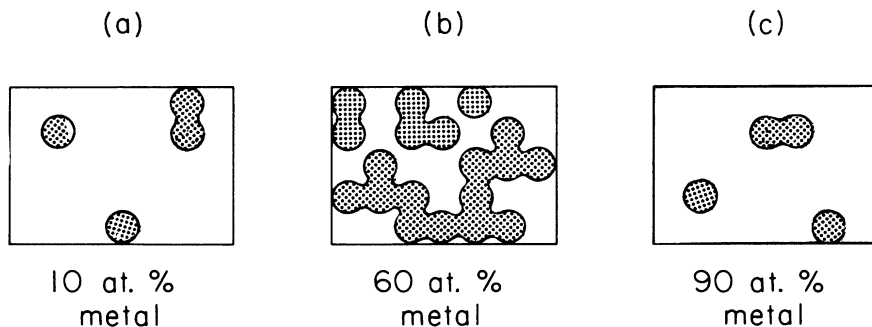


FIG. 1. Sketch showing the alkali-atom valence-electron distribution in alkali-metal-rare-gas mixtures of various compositions. The diagrams have only a schematic significance. They indicate a strong similarity with the metal distribution in a macroscopic percolative mixture.

valence electrons are free to move throughout the volume of contiguous alkali-metal cells, and that a single strand of neighboring alkali atoms can support a current flow. In this case macroscopic percolation theory should provide a reasonable approximation to the topology of microscopic current flow in alkali-metal-rare-gas mixtures. A precise justification of this simplified view must, of course, await future theoretical studies.

In the Sec. II we describe some additional experimental matters and then turn in Sec. III to the presentation of the results obtained in optical absorption and resistance measurements on thin KrRb and XeCs films. The paper concludes with a discussion of these results and their relationship to percolation processes in Sec. IV.

II. APPARATUS

Resistance and optical-absorption measurements were made on samples deposited onto modified LiF substrates. Silver electrodes were evaporated onto the LiF in the pattern shown in Fig. 2. It was found, in practice, that silver does not bond satisfactorily to LiF. The difficulty was remedied by first evaporating ~ 100 Å of aluminum, followed by several thousand angstroms of silver, through the mask defining the electrode pattern. Excellent bonds were obtained in this way, and it proved possible to attach current and potential leads to ridges of indium soldered down the centers of the electrodes, as shown in Fig. 2. The smallest film resistance studies were $\sim 1 \Omega$, and compared to this value the electrode resistance proved negligibly small. At the same time, the electrode area remained small enough to allow optical measurements to proceed as described in Paper I of this series.

Samples were prepared by simultaneous evaporation of pure metal and alloy films onto the substrate and electrodes. No difficulty with electrical contact between the films and electrodes was encountered at any time. Care was taken to ensure that the current and potential leads could not cast shadows on the film. Shadows in the film evapora-

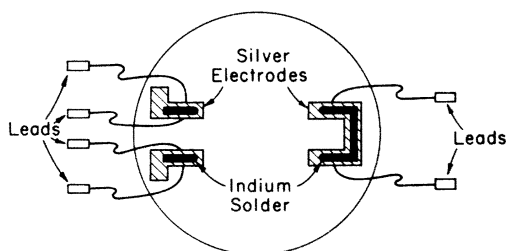


FIG. 2. Electrode pattern and lead connections on LiF substrate.

tion were deliberately created between the two sample halves and around the circular perimeter of the sample holder, in order that each sample half was electrically isolated from the other and from the copper substrate holder. Four-terminal resistance measurements could therefore be made on both the reference and alloy halves of the film. These were converted into resistivities using the known number densities of atoms on the substrate halves. For this purpose, the film thicknesses were calculated using Vegard's law (additivity of the constituent molar volumes) and the influence of film shape on resistance was evaluated to all necessary accuracy by analog methods using silver electrodes painted on resistance paper.

As stated in Paper I, great care was taken to calibrate the evaporation system in order to obtain absolute atom densities on the substrate. Rare-gas capillary leaks provided flow rates reproducible to 5%, as functions of gas overpressure, in calibration runs spaced over the course of many months. The metal evaporation was accurately monitored throughout the preparation of each sample. As a result, the densities of species in the films were known to absolute accuracies of 7% or better and the relative densities from one run to the next with much higher precision, probably $\sim 2\%$. One complication that could influence both optical and electrical measurements was examined with some care. The gas leak was closer

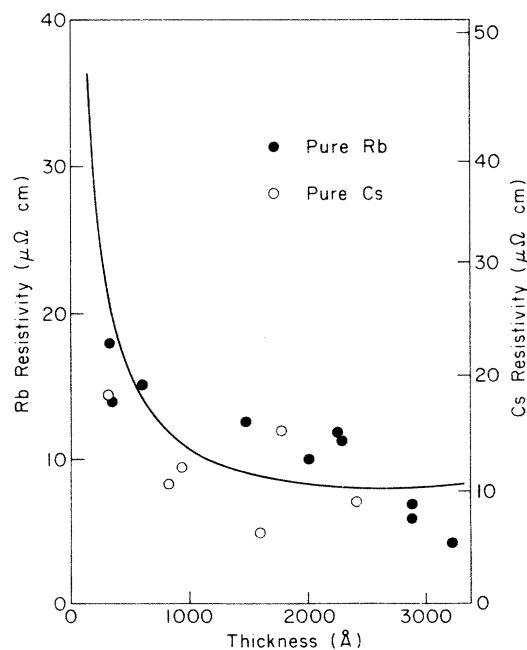


FIG. 3. Resistivities of Rb and Cs thin film as a function of film thickness. The solid line shows a best fit to the standard resistance variation for ideal thin films.

to the sample than, and set off-axis from, the metal evaporation path (to avoid shadowing) with the consequence that the rare gas density was not perfectly uniform over the sample. For optical measurements, which employed the full sample area, we estimate that this variation was reflected in the following composition inhomogeneities at the stated metal concentrations: 75-at.% metal, ± 2 at.%; 50-at.% metal, ± 4 at.%; 25-at.% metal, ± 2 at.%. It will be evident from the observed rather slow evolution of the optical spectra with composition that this inhomogeneity has a negligible effect on the optical densities. For resistance measurements the effective inhomogeneity is greatly improved, since a fraction of the substrate area in between the electrodes carries the major current. The gas leak was set off-axis between the electrodes in order to maximize homogeneity there, and the inhomogeneities pertinent to resistivity measurements are at most half those that describe the optical results. We shall see in what follows that the metal-insulator transitions are observed at ~ 25 -at.% metal, for which the relevant sample inhomogeneity is $\sim \pm 1$ at.%.

III. RESULTS

In Fig. 3 the observed resistivities of the *reference* halves of the KrRb samples are shown as a function of film thickness. Substantial defect densities are present in these pure metal samples, since the observed resistivities are comparable with expected room-temperature values rather than low-temperature values. Detailed comment on these residual resistance effects appear later in this section. For the moment it suffices that the scatter of the points reflects the reproducibility of the defect densities in the samples. This scatter is small compared with the impurity-induced resistivity change discussed below, thereby establishing the validity of the alloy resistivities on which our present interest centers. The line passing among the points represents a fit of the well-established theory for anomalous resistance effects²⁶ to the data. A noticeable increase of the resistivity with decreasing film thickness, present in the data, does conform in a reasonable way to the increase expected when the electronic mean free path becomes comparable with or exceeds the sample thickness. Small metal densities were used for gas-rich samples in these studies, and since the mean free path is greatly reduced by large rare-gas concentrations, the anomalous resistance effects must exert a negligible influence on the resistances of the alloy samples. For this reason we neglect corrections for anomalous resistance effects in the alloy resistivities reported

below.

The resistivities of KrRb and XeCs alloys are presented as a function of alloy composition in Fig. 4. Note that both the resistivity and concentration scales differ by small factors for the KrRb and XeCs alloys, in order to emphasize the very similar trends of the two sets of data. Clearly, the resistivity measurements probe a common property of the two alloy systems. In what follows two features of these results are central: First, the variation of resistivity with composition in the metal-rich materials and, second, the large resistance increase that takes place when the metal density is reduced to ~ 25 at.%.

The observed resistivities in the metal-rich alloys both establish the random nature of the short-range order in the samples and confirm the model of ground-state impurity structure described in Paper I. A discussion of the latter point is deferred until Sec. IV. It is well known in the theory of metallic alloys that the residual resistance increases linearly with impurity concentration in the metal-rich limit because randomly placed impurities in effect scatter the conduction elec-

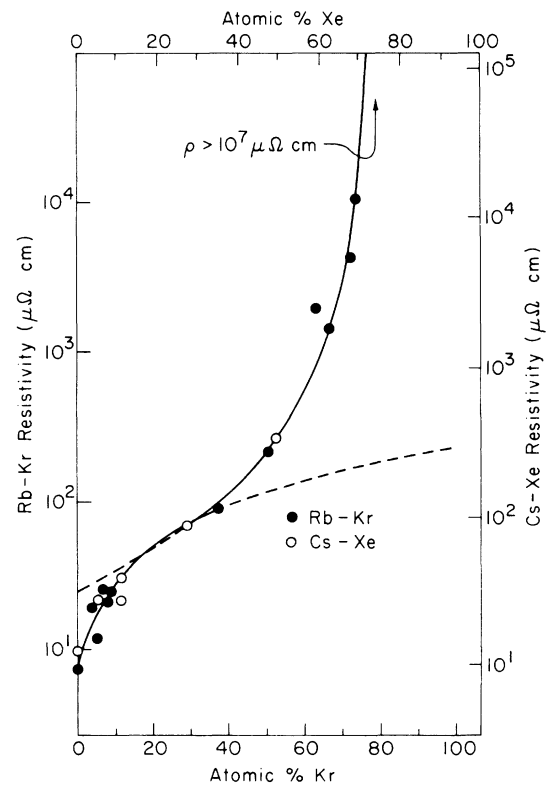


FIG. 4. Resistivities of RbKr and CsXe thin films shown as functions of rare gas concentration. Note that the resistivity and composition scales differ for the two alloy systems.

trons independently.²⁷ Any segregation of the impurities into clusters causes a marked reduction of residual resistance. The solid line drawn through the data from 0- to ~40-at.% impurity concentration in Fig. 4, and its broken extrapolation to higher impurity concentrations, indicates the expected linear variation of resistivity with composition. The theoretical line does provide a very satisfactory description of the data, thereby demonstrating that the impurities do indeed scatter electrons in a sensibly independent fashion. The data show no evidence for clustering effects, thereby attesting to the satisfactory nature of the techniques adopted for sample preparation.

In this connection it should be mentioned that the optical absorption measurements presented in Papers I and II lend strong support to the belief that these dilute alloys possess a random arrangement of the two species among the lattice sites. Most noteworthy is the fact that the absorption spectrum tends, in the dilute limit, to a limiting form that bears no direct relationship to the absorption of condensed rare-gas phases. Rather, the absorption threshold takes precisely the value expected of rare-gas atoms isolated in the alkali-metal host lattice. The simple functional dependence of the sharp pair-peak amplitude on composition in more concentrated alloys is also consistent with the belief that the random short-range order persists in passing from metal-rich to gas-rich positions of the phase diagram.

An observed increase in resistivity by many orders of magnitude marks the metal-insulator transition in both the KrRb and XeCs mixtures. The apparatus sensitivity limited the measurements to samples having resistivities less than $10^7 \mu\Omega \text{ cm}$. As may be seen in Fig. 4, the transitions in the two systems take very similar forms, with transition compositions estimated by method discussed in Sec. IV at 78-at.% Kr in KrRb and 73-at.% Xe in XeCs alloys.

No marked changes in optical absorption were observed at the metal-insulator transitions in either system. Figure 5 shows, by way of example, the absorption cross section per Kr atom in KrRb mixtures spanning the metal-insulator transition at ~78-at.% Kr. The broad absorption, associated in metal-rich alloys with metallic screening, was shown in Paper II to persist for impurity concentrations up to ~50-at.% Xe in K. In Fig. 5 these same features are shown for Kr impurities in Rb to undergo a continuing diminution at higher concentrations, but they nevertheless remain clearly visible in the spectra of KrRb mixtures containing only 10-at.% Rb. We have traced the final disappearance of these features in the composition range 0-10-at.% metal. Figure 6

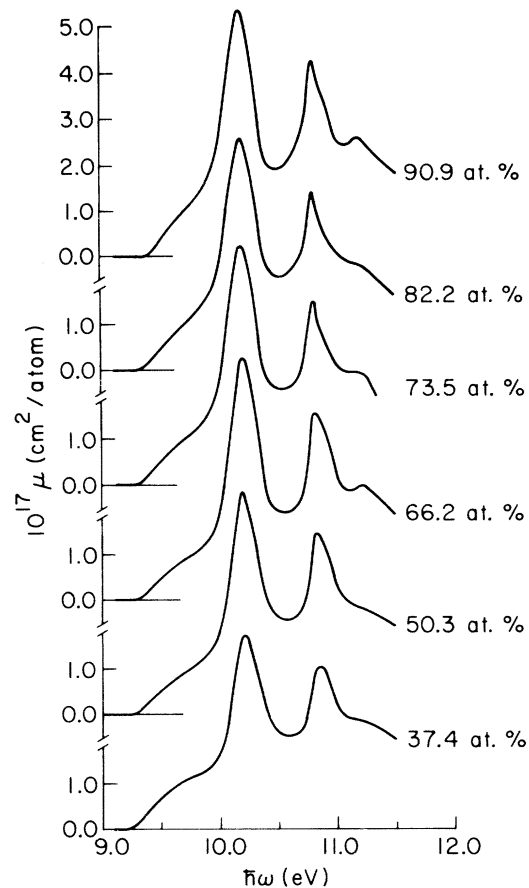


FIG. 5. Optical absorption per Kr atom in thin RbKr films spanning the composition of the metal-insulator transition.

shows the spectrum of Xe in Xe-rich XeCs mixtures. A residual broadening of the low-energy threshold is still evident when only 4-at.% Cs remains present in the solutions. An added oscillator strength in the high-energy tail of the lowest Xe exciton suggests that the major effect is merely a broadening of this strong resonance line.

Both the "metallic" threshold features and the pair peaks are visible over almost the entire composition range of these alkali-metal-rare-gas mixtures. However, the energies at which the features occur vary significantly with alloy concentration. The observations are summarized for the KrRb system in Fig. 7. The threshold E_t shifts to higher energies with increasing rare-gas concentration, in much the same way the XeK threshold shifts (see Paper II). At the same time, the two pair peaks shift to lower energies, and to about the same extent for the two lines, in the dilute KrRb alloys. For rare gas concentrations exceeding about 10-at.% Kr the location of the pair peaks stabilizes and these features pass as c

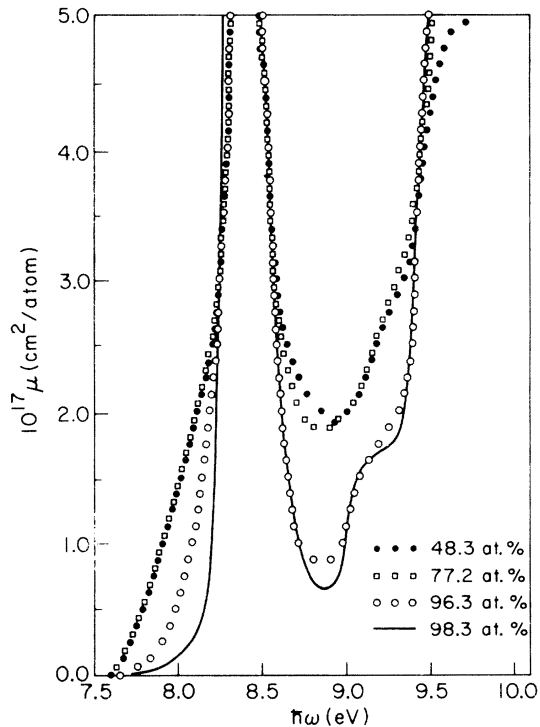


FIG. 6. Optical absorption per Xe atom in thin CsXe films, showing how the "metallic" absorption threshold finally disappears as the Cs concentration becomes sufficiently small.

→ 100 at. % into the two lowest excitations of pure solid Kr. In this gas-rich limit, the threshold absorption weakens and the incidence of absorption at E_t shifts noticeably to higher energies into the low-energy wing of the lowest exciton line.

IV. DISCUSSION

A. Resistivity in the dilute limit

The observed residual resistivity in the dilute limit contains quantitative information concerning impurity structure that we now examine. The line passing near the points for $c \approx 40$ -at. % rare gas, and its broken extrapolation to larger c in Fig. 4, represents different resistivities for the KrRb and XeCs systems because slightly different axes are employed there for the two systems. In the two cases the resistivities are

$$\rho = 7.4 + 2.18c \mu\Omega \text{ cm (KrRb)}$$

and

$$\rho = 12.3 + 2.77c \mu\Omega \text{ cm (XeCs)} .$$

For the two systems, the rare-gas residual resistivities are determined in this way as $2.2 \pm 0.4 \mu\Omega \text{ cm/at. \%}$ (Kr in Rb) and $2.8 \pm 0.5 \mu\Omega \text{ cm/at. \%}$

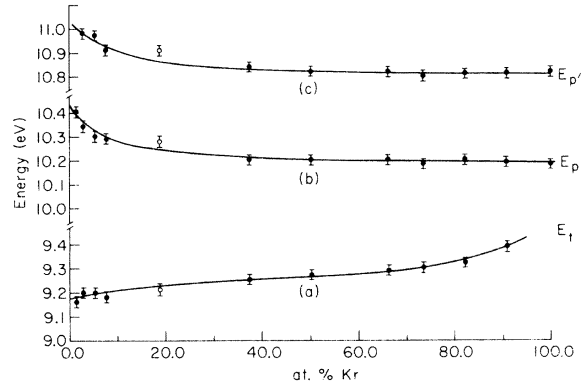


FIG. 7. Energy at which various features of the RbKr absorption spectrum appear, shown as functions of rare-gas concentration. The threshold energy E_t and the energies E_p and $E_{p'}$ of the first two pair peaks are shown.

(Xe in Cs). To within a precision of $\sim \pm 1 \mu\Omega \text{ cm}$, the resistivities for $c \rightarrow 0$ represent both the best extrapolation of data for $c > 0$ and the observed resistivity of the *reference* halves of the samples. These latter results therefore provide specific information concerning the defect structure in pure evaporated alkali-metal films. They also indicate that interaction effects between the defect and impurity resistances are negligible.

It is not possible to calculate the residual resistances accurately from first principles because relaxation causes large and imperfectly predictable effects on the scattering cross sections. However, one can easily show that the observed resistivities are consistent with the model proposed in Papers I and II. If the electronic structures of rare-gas impurities do resemble neutral atoms occupying relaxed vacancies, then the scattering of conduction electrons at the Fermi level should be largely unaffected by the impurities. For this reason the residual resistivities should fall close to the values for relaxed vacancies in the alkali-metal host lattices. There exist at present no reliable measurements of vacancy resistance in Rb and Cs, but the principal features are common to vacancies in all monovalent metals and simple scaling of the resistivities observed for noble-metal hosts should provide reasonable estimates. For this purpose the best-known case is that of Au, in which vacancies contribute a resistance of $1.5 \pm 0.3 \mu\Omega \text{ cm/at. \%}$.²⁸ The resistivity scales among host lattices as k_F^{-1} , with k_F the Fermi wave vector.²⁸ For Rb and Cs, respectively, this leads to vacancy resistivities of 2.6 ± 0.5 and $2.8 \pm 0.6 \mu\Omega \text{ cm/at. \%}$. Clearly, the agreement with the observed residual resistances (2.2 and $2.8 \mu\Omega \text{ cm/at. \%}$) is all that could be hoped for. The resis-

tance measurements therefore lend strong support to the ground-state rare-gas structures described in Papers I and II.

Less can be said with certainty about the residual resistance observed in pure metal samples. For the present purposes the main points are that this contribution is reproducible, is independent of film thickness within the existing uncertainties, and has no detected interaction with the impurity resistance. It doubtless arises from defect structure within the films in the form of grain boundaries, point defects, longer-range inhomogeneity, or even, as an extreme case, actual amorphous coordination of the constituents. Of these alternatives the first seems to be ruled out, at least for presumed grain sizes comparable with the film thickness, both by the magnitude of the resistivity and its independence of film thickness (Fig. 3). If we presume that KrRb and XeCs support similar defect structures under the experimental conditions of these experiments, then the observed resistivities provide an interesting comparison with the observed room-temperature resistivities of bulk Rb and Cs. The observed residual resistances of 7.4 and 12.3 $\mu\Omega\text{cm/at.}\%$ fall in a ratio of 0.60 while the room-temperature resistances²⁹ of 12.5 and 20.0 $\mu\Omega\text{cm/at.}\%$ fall in a ratio of 0.63. To the degree that random static atomic displacements resemble a superposition of phonon amplitudes, these results suggest that the metal-rich samples may contain a substantial disorder in the near-neighboring coordination. It remains possible, however, that the resistivity arises mostly from point defects (e.g., vacancies or interstitials) or longer-range distortions in microcrystalline samples.

B. Metal-insulator transition

The resistivities of KrRb and XeCs mixtures are shown in Fig. 4 to undergo transitions to essentially insulating values at concentrations corresponding to approximately 78- and 73-at.% rare gas in the two systems. The methods by which these compositions were determined are discussed below. A precursor of the transition is visible some 25 at.% before the critical composition is reached. In most random alloys containing two metallic species the residual resistance is observed to fall *below* the linear extrapolation of the dilute limit trend at relatively small solute concentrations, and to pass through a maximum near 50 at.%.²⁶ The reasons for this behavior were first explained by Nordheim in terms of scattering by deviations from an average potential.²⁷ In contrast, the data of Fig. 4 exhibit a protracted approximate linearity extending up to $c \sim 40\text{-at.}\%$

rare gas. This effect no doubt arises from the particular chemical properties of the rare-gas impurities, and may itself be regarded in some sense as a precursor of the metal-insulator transition observed at $\sim 75\text{-at.}\%$ rare gas.

Consider now the resistance transition itself and the way it reflects the percolative origins of conductivity in the transitional region. To this end we first note that in the region where the resistivity rises rapidly with composition, with $\rho \sim 10^3 \mu\Omega\text{cm}$, the mean free path offered to the average alkali valence electron is reduced to interatomic dimensions. As the hopping distance thus deduced from free-electron estimates becomes so small, we conclude that such theories have no relevance to the observed resistivities in the rare-gas-alkali-metal mixtures. At the same composition ($\sim 60\text{-at.}\%$ rare gas) the average metal atom retains several metal neighbors and there exists no short-range impediment to charge flow between successive atoms with strongly overlapping valence orbitals. A gross modification in the density of states at E_F , caused by one-electron average band structure effects, also appears most unlikely in view of the random nature of the alloys. These considerations therefore serve to refocus attention on the topology of current flow as the cause of the observed major breakdown in long-range conductivity.

The macroscopic percolative transition is characterized by (i) the concentration of metal required for conductivity; and (ii) the form of the resistance variation with composition through the transition region. Both properties can be determined from our results, and both have been studied for macroscopic percolative transitions, so a comparison is possible. Some complication occurs in connecting the microscopic and macroscopic parameters, but the results do lend convincing support to the belief that the transition is percolative. The critical composition will be discussed first.

The critical composition c_c at which conductivity emerges in mixtures of uniform metallic spheres immersed in an embedding dielectric, has been studied by Scher and Zallen.⁸ These authors find that for both two- and three-dimensional arrays (the one-dimensional case being trivial) there exist a critical metal density that is independent of geometrical complexities. Their results make it clear that, regardless of the lattice in which the metal balls are packed, the *volume* fraction occupied by the metal spheres is 0.15 at the composition for which long-range conduction is established. Since it is the topology of intermetallic contacts that matters, the empirical result holds whether the dielectric is regarded as a continuum or as a set of spheres. Consequently,

this result finds a direct application to the present experiments, provided that an effective inter-atomic distance between metal atoms providing metallic conduction can be defined.

It is likely that metal atoms occupying nearest neighboring sites are able to pass charge in the rare-gas-metal mixtures of interest here, but that an intervening rare-gas atom reduces conduction to much smaller values. In practice, we have employed the hard-sphere radii of alkali atoms in their liquid phases, and a packing fraction of 0.45 in the mixtures, to deduce the appropriate volume fraction c_v of metal atoms in the samples at the metal-insulator transition. One finds in this way

$$c_v = 0.14 \text{ (KrRb)}$$

and

$$c_v = 0.17 \text{ (XeCs)} .$$

These deduced values are in very satisfactory agreement with the empirical result $c_v = 0.15$ found for all lattice structures by Scher and Zallen.

Two further comments about these results seem worthwhile. First, the criterion $c_v = 0.15$ is independent of lattice geometry and the results are therefore not likely to be influenced to a major degree by any phase changes that occur in passing from pure metal to pure rare gas. Nor should the emergence of amorphous structures under the experimental conditions have a strong bearing on the interpretation. Second, the notions of atomic radius and of the "fractional volume of metal" lack precision when applied in general to microscopic systems, but a tight confinement of alkali valence electrons to alkali cells does make the atomic system bear a close *geometrical* similarity to the ideal macroscopic percolation problem. The results therefore lend some support to our model of the geometrical characteristics of the valence electron distribution.

The resistance variation with composition on the metal-rich side of the transition offers further insight into the topology of current-carrying paths near the metal-insulator transition. Computer studies by Kirkpatrick of conductivity through randomly broken lattices of resistors revealed that the conductivity falls in proportion to $(\sigma - \sigma_c)^s$ for *bond* densities σ close to σ_c , with σ_c the critical concentration of random conductors.³⁰ The exponent s takes the value $s = 1.6 \pm 0.1$ for a cubic lattice of randomly broken conductances. These results have been revised by Adler *et al.*,³¹ who show that the appropriate form is $(c - c_c)^{-2}$ when the resistance is expressed in terms of atomic concentrations c , with c_c the critical concentration. Two difficulties bar a direct application of these results to the present systems. First, there

is no direct evidence to show that the *computed* results are independent of lattice geometry, and their applicability in the present context remains uncertain. It seems likely, however, that different lattices support similar percolative transitions. After all, the density of conducting paths connecting two volumes may be obtained as an exercise in the theory of nonintersecting random walks, and probably reduces to descriptions in terms of bulk properties in much the way diffusion problems do. For this reason it seems quite possible that the general form of the computed transition is insensitive to the chosen lattice structure as, indeed, proves to be the case for the critical volume of metal in the approach discussed above.

No specific resolution is offered for the second difficulty, which concerns the degree to which charge flow among atomic centers can possibly be simulated with microscopic fidelity by networks of conductors. If conduction took place along independent extensive chains of single-atom links then the chain shape and atomic polarization effects might both be adequately contained in the resistor analogy. As Fig. 8 shows, however, the complexity of the chains for the actual density of metal atoms near the transition makes the model a good deal less satisfactory. However, a coarse geometrical similarity does remain, and the model does give a good account of the critical composition. For this reason we have compared our results to the predictions of the network model.

The results of this comparison are shown in Fig. 4. The solid line and its broken extrapolation to small rare-gas concentration represents a fit of the power law

$$\rho = \rho_0 (c_t - c)^{-s}$$

to the observed resistivities. This fit was employed in practice to determine the critical rare-gas composition $c_t = 78\text{-at.}\%$ Kr in Rb and $c_t = 73\text{-at.}\%$ Xe in Cs quoted above. The fit also

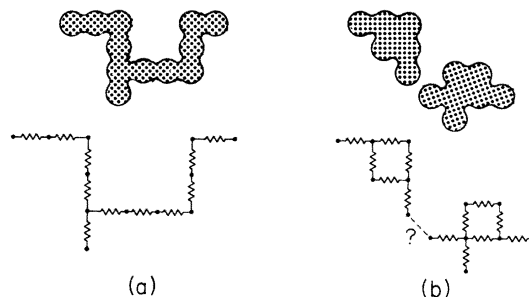


FIG. 8. Resistor analogy to conduction along chains of metal atoms appears plausible for simple chains of near neighbors as in (a), but has a less apparent ability for the more complex chain shown in (b).

yields the exponent $s = 2.1 \pm 0.5$, which may be compared with the value $s = 2.0$ determined by Adler *et al.*³¹ for the cubic network of resistors.³²

In surveying these results we may note that the fit to the results for percolation in a resistive network is rather satisfactory, although the available data are insufficient to determine either the functional form or the exponent with high precision. Thus, the expected similarity to a percolation process extends both to the critical composition and to the form of the resistivity change in rare-gas-alkali-metal mixtures. It may be remarked that previous investigations of ArNa and ArCu mixtures have identified sharp transitions at larger metal concentrations than those obtained here. Effects of this type may possibly originate in composition inhomogeneities that break the conduction paths between the electrodes.

C. Rare-gas absorption spectra near the transition

The nontransport properties of media exhibiting microscopic percolative transitions have not previously been studied either theoretically or in the laboratory. We shall therefore take this opportunity to comment, in general, on the properties these systems are expected to have, before turning to discuss the observed optical absorption at high-photon energies. Of course, any quantitative description is sensitive to the particular components contained in the material. Our qualitative remarks are relevant only to the general trends produced by the particular nature of the electron gas distribution described in Sec. I.

Both the electronic specific-heat coefficient γ , and the electronic susceptibility χ_e of the metal valence electrons (each regarded as molar quantities) may be expected to decrease with increasing rare-gas concentration. The dilute limit may be understood quantitatively from the discussion by Flynn and Lipari.³³ These authors calculate the reduction of state density at E_F consequent upon the addition of high valence impurities. One cannot expect, however, that either γ or χ_e fall to zero at the critical composition c_c . At c_c the average metal atom is in contact with many others through successive near-neighbor bonds and only the long-range conductivity is eliminated by eventual breaks in the chains. Accordingly, the free-atom valence levels remain spread into bands and the electronic system maintains low-energy excitations and spin-reversals even through c_c . At the gas-rich limit the alkali atoms are isolated and their susceptibility must take the Curie-law form. This leads to a low-temperature residual electronic susceptibility even in the concentration range $c_c < c < 1$. In the case of the low-temperature specific heat the Fermi gas heat capacity must give way with

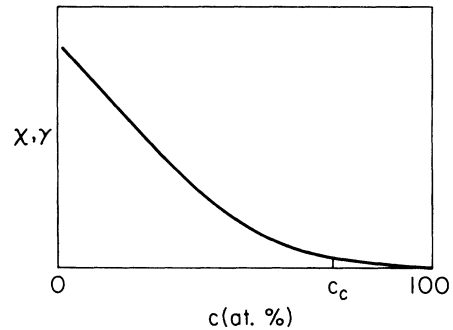


FIG. 9. Sketch showing schematically how the coefficient γ of the electronic specific heat, and the electronic susceptibility χ_e at low temperatures, should vary with composition in alkali-metal-rare-gas alloys.

decreasing metal concentration to Schottky anomalies associated with spin interactions among small clusters. Typical qualitative variations of χ_e and specific heat γ with concentration c are sketched in Fig. 9.

The electron-gas excitation spectrum also determines the frequency-dependent dielectric function $\epsilon(q, \omega)$ at low energies and hence the long-wavelength optical properties of these materials.³⁴ Only the value of $\epsilon(q, \omega)$ as the wave vector $q \rightarrow 0$ is greatly modified by the loss of long-range conductivity, and we expect that this feature of the dielectric function alone marks the metal-insulator transition by a discontinuity. The excitation spectrum, for example, is expected to show no other abrupt modifications as the mean chain length decreases. $\epsilon(q, \omega)$ must maintain a partially metallic form whenever q exceeds the reciprocal mean chain length and ω exceeds the mean excitation energy.

It is for entirely analogous reasons that the rare-gas spectra shown in Figs. 5 and 6 are so insensitive to the loss of long-range conduction at the critical composition c_c . Each rare-gas atom interacts with an inhomogeneous environment which remains part metallic and part insulator on each side of c_c . Features associated with a coupling of the excitation to each type of material therefore also persist with no marked discontinuity. From this viewpoint the observations merely establish that the value of $\epsilon(q, \omega)$ for $q \rightarrow 0$ and $\omega \rightarrow 0$ has little influence on the optical spectrum at $\hbar\omega \sim 10$ eV, and confirm the belief that locally metallic features persist on the insulating side of the percolative transition.

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