work.[15] The solid line drawn in Fig. 3 is the theoretical prediction given by Kosterlitz and Thouless. It is clear that the data from all the different experiments are in good general agreement with the theoretical prediction and therefore provide strong support for the Kosterlitz-Thouless picture of the phase transition in the two-dimensional superfluid.

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Metallic Glasses of Oxidized Rubidium and Cesium

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Metallic glasses of the alkali metals Rb and Cs containing 13–20 at.% oxygen have been obtained for the first time by rapid cooling ($\sim 10^2$ K/s) of liquid samples. An investigation of the electronic and structural properties leads to the conclusion that a chemical bonding model is more appropriate for these glasses than a free-electron model. Strongly bonded ionic clusters are responsible for the enhanced tendency for glass formation.

A large number of metallic glasses have recently been obtained by quenching of the liquid state.[1] The enhanced glass formation has been explained with three different models on the basis of (i) packing of hard spheres,[2] (ii) chemical bonding effects,[3] and (iii) the influence of conduction electrons.[4] The general validity of models (i) and (ii) has been questioned,[3,5,6] but so far, there seems to be no experimental evidence which rules out model (iii) in any special system. The nonexistence of alkali metal glasses has been accepted as an additional proof for the validity of model (iii).[7] It should be noted that the proposed models are not contradictory. The range of applicability of each model can be explored only by investigating new metallic glass systems.

We report on the first metallic glasses of alkali metals stabilized by oxygen. Rubidium and cesium can be obtained in the amorphous state by addition of ~16 at.% and 14–20 at.% oxygen, respectively.

The phase diagrams[8] of the systems Rb/O and Cs/O are illustrated in Fig. 1. The shaded areas mark the composition range where glasslike states can be obtained by quenching molten samples in liquid nitrogen (0.15 g substance in glass capillaries with 2 mm diam). It should be pointed out that this procedure leads to exceptionally low cooling rates of 10^2 K/s. Considerably lower cooling rates are sufficient to drive oxidized Rb/Cs alloys into the amorphous state.

The amorphous nature of the samples is verified by x-ray diffraction. With rubidium, the quenched samples always contain a small amount of crystalline substance (Rb or Rb_9O_2) which becomes larger when deviating from the indicated region of concentration. The glassy state as well as the metallic character[9] of the quenched samples is also reflected in the electrical resistivity ρ (see Fig. 2) measured by a probeless eddy-current technique.[10] The temperature dependence of ρ is typical for amorphous metals: The resistivity of the melt corresponds to an extrapolation of the resistivity in the amorphous state with the $Cs_{0.82}O_{0.18}$ sample. The lower value of the resistivity in the amorphous sample $Rb_{0.87}O_{0.13}$ is due to the above-mentioned crystalline portion. A small irreversible maximum of the resistivity at the glass temperature is known from many other metallic glass systems[10] but is much more pronounced in this case.

It is well established by Hall-effect measurements of Kendall[11] that oxygen dissolved in liquid cesium removes two electrons per oxygen atom from the conduction band to form an O^{2-} ion. The same holds for crystalline Rb and Cs suboxides as has been shown by photoelectron spectroscopy.[12] Both the very narrow $2p$ band of oxygen and its small binding energy as well as the measured surface plasmon frequencies are in accordance with the assumption of formation of O^{2-} ions. These facts suggest that for the amorphous state the number of free electrons can be calculated by assuming each alkali metal atom to contribute one electron whereas two electrons are trapped by each oxygen atom. This leads to an average number of conduction electrons per atom, $z_{\mathrm{eff}} < 1$, corresponding to a lower value of $2K_F$ compared to the pure alkali metals; $2K_F$ represents the diameter of the Fermi sphere. Figure 3 shows the structure factor of amorphous $Cs_{0.8}O_{0.2}$ measured by x-ray scattering. It is representative for the other amorphous samples. Oxidation of the alkali metals shifts the main peak in the structure factor as measured in the liquid metal to a larger value of the wave vector because of the 20% contraction of the metal-metal distances around the O^{2-} ions.

An additional peak at 0.73 $\mathrm{\AA}^{-1}$ develops in the oxidized alkali metals. This peak corresponds to pair correlations of ~10.5 Å, which can be interpreted as distances between the centers of neighboring ionic clusters. The value of $2K_F$ indicated in Fig. 3 is calculated using the structural information[13] on crystalline Cs_4O with a 3% larger volume of the amorphous phase and two

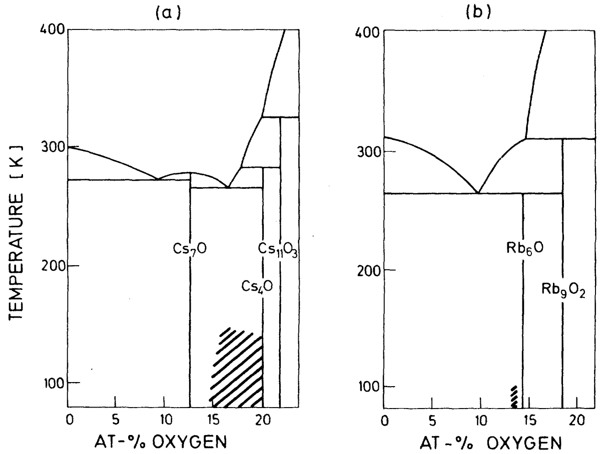

FIG. 1. Metal-rich parts of the phase diagrams of (a) Cs/O and (b) Rb/O. The shaded areas indicate the glass-forming regions.

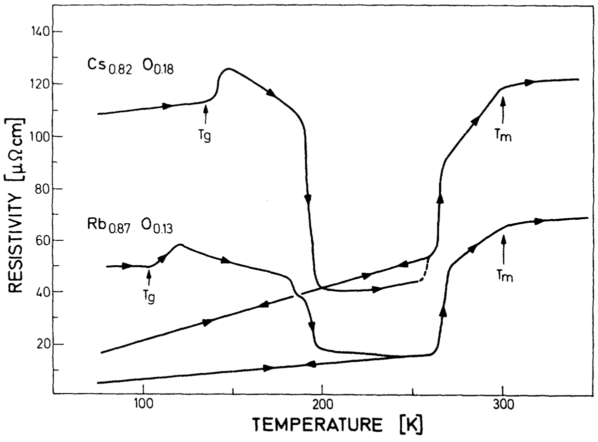

FIG. 2. Temperature dependence of the electrical resistivities of two representative quenched samples of oxidized alkali metals. T_g and T_m mark the glass and melting temperatures, respectively. Arrows on the curves indicate the direction of the temperature variation.

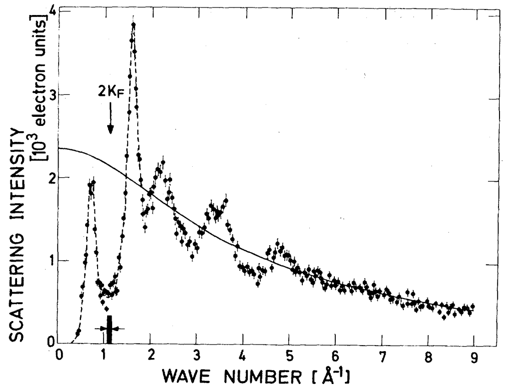

FIG. 3. Scattered x-ray intensity of an amorphous sample $Cs_{0.8}O_{0.2}$ measured at 110 K, the standard deviation is indicated by the error bars. The solid line is the mean-square scattering factor $0.8\, f_{Cs^+}{}^2 + 0.2\, f_{O^{2-}}{}^2$. The large arrow marks the position of $2K_F$ for $Cs_{0.8}O_{0.2}$. The horizontal bar represents the range of values $2K_F$ for compositions of samples which can be obtained as glasses in the Cs/O system.

free electrons per formula unit. $2K_F$ is located near the minimum between the first two peaks of the structure factor. The same is true for the whole composition range in the Cs system, where the amorphous state can be obtained, and it holds for the Rb system, too. Obviously, the essential condition of model (iii) $2K_F \sim 2K_p$ (K_p is the wave number of the main peak in the structure factor) is not obeyed in the amorphous oxidized alkali metals. On the contrary, these materials represent the first examples where an amorphous state of a monovalent metal is achieved by *lowering* the number of free electrons.

In the described alkali metal systems the quenching to the amorphous state is possible due to the low crystallization temperature of the melt. This condition occurs because of the low-lying eutectic temperature in the Cs/O system as frequently observed with glassy metal systems. In contrast to thermodynamically favored conditions in the Cs/O system, the glass-forming ability in the Rb/O system is enhanced for kinetic reasons due to a pronounced delay of crystallization. It is explained by the fact that all structures of the stable suboxide phases are characterized by the occurrence of large ionic clusters ($Cs_{11}O_3$ and Rb_9O_2).[8] In the process of crystallization, first these clusters have to be formed and then to be arranged in a crystal lattice. If time is too short to complete these complicated steps, the melt will solidify in a glassy state. This phenomenon is clearly related to the strong chemical bonding between the oxygen and the metal ions which also causes the volume contraction and heat evolution when oxidizing liquid rubidium or cesium. Thus, in our view, model (ii) provides the appropriate description for the glasses of oxidized alkali metals. However, the chemical bonding in these substances is *nondirectional,* in contrast to the covalent nature of bonding in many other glasslike systems. A complete investigation of the electrical properties of oxidized alkali metals will be described elsewhere.[14]

As a concluding remark we should like to mention the problem of ambiguity in the usual calculation of z_{eff}. The actual values of z_{eff} have been measured in a few systems only.[15] When calculating $z_{eff} = c_1 z_1 + c_2 z_2$ where the c_i's are the concentrations and the z_i's the valencies of the alloy elements it is generally accepted that a main group element contributes all its valence electrons whereas the contribution of a transition-metal component is usually assumed as 0.5–1 as in the pure metals. For example, in the case of $Ni_{0.8}P_{0.2}$, z_{eff} is estimated to be 1.4 assuming 0.5 electrons/atom to be donated from nickel and 5 electrons/atom from phosphorus.[16]

If this schematic procedure is applied, e.g., to the O-stabilized glass $Rb_{0.86}O_{0.14}$, the Rb atoms should donate one and the O atoms six electrons to the total number of free electrons, leading to an average number of 1.7 electrons per atom. Now the condition $2K_F \sim 2K_p$ is fulfilled. Definitely, z_{eff} calculated in this manner constitutes the *average valence-electron* concentration, but is *not* related to the number of *conduction electrons.* Does z_{eff}, then, have some other significance?

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Optical Properties of Amorphous Metallic Alloys

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The optical properties of amorphous films of $Au_{1-x}Si_x$ alloys were studied in the spectral range from 0.01 to 6.2 eV as a function of composition in the range $0.13 \leq x \leq 0.50$. Because the electronic relaxation times are extremely short, Drude behavior dominates the entire spectrum. The onset energy of interband transitions increases on alloying with Si. In comparison with pure gold a dramatic decrease in strength of the transitions from the *d* bands to the Fermi surface is observed in all the alloys.

We report the first study of the optical properties of amorphous metallic alloys from which we obtained information about the high-frequency behavior of the carriers and about the onset of interband transitions in these materials. A knowledge of the electronic structure is clearly important, especially in light of the importance that it might play in the glass-forming ability of some alloys.[1,2] Also this is the first time, to our knowledge, in which the optical properties have been studied where the collision frequency, $1/\tau$, is much larger than the onset frequency of interband transitions. This gives rise to a dramatic change in the optical spectrum from that seen for the pure elements.

For this study, we chose the systems $Au_{1-x}Si_x$ because the optical properties of crystalline and liquid Au are understood; in particular, it is known that in both liquid and solid the onset of interband absorption is associated with transitions from the *d* bands to the Fermi level.[3-5] The phase diagram of the Au-Si alloys is simple, with a deep eutectic at $x = 0.185$. The samples were prepared by getter sputtering in argon in the form of films 200–400 nm thick, deposited on cooled (77 K) sapphire substrates. It was possible to prepare and study the films in the amorphous form over a broad range of compositions with $x > 0.12$, whereas the bulk glass can be prepared only for compositions close to the eutectic. There are good reasons to believe that the atomic arrangement in the films is almost the same as in the bulk glass; this was shown for the Pd:Ge systems near the eutectic composition.[6] The resis-