sandwich, we have observed a phase transition occurring in a single film of that sandwich. Tunneling measurements have shown a second energy gap splitting off in a discontinuous fashion at this threshold and from temperature and thickness dependences we can eliminate critical-current and heating effects. At the moment we do not have a totally satisfactory theoretical explanation.

We would like to thank R. B. Kummer and M. A. Chin for advice and/or assistance with the low-temperature experiments.

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Electronic Transport in Amorphous H_xWO_3

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We report measurements of the electrical conductivity, σ, of thin amorphous films of hydrogen tungsten bronze, H_xWO_3, as a function of temperature and hydrogen/tungsten ratio, x. For $x \lesssim 0.3$ the temperature dependence of σ can be explained by the variable-range hopping model. At $x = 0.32$ an insulator-to-metal transition occurs with a minimum metallic conductance of about $5.1 \times 10^{-5}\,\Omega^{-1}$.

Considerable effort has been devoted to a study of the electron transport properties of single-crystal alkali-metal tungsten bronzes.[1-5] These are nonstoichiometric compounds of the general formula M_xWO_3, where M is the alkali metal and x the stoichiometric parameter which can vary between 0 and 1. For large x, M_xWO_3 is metallic. However, the nature of the conductivity at low x is still unclear. It is thought that a metal-insulator transition occurs below $x = 0.2$. Lightsey[1] interpreted his measurements of the x dependence of the conductivity in Na_xWO_3 in terms of a percolation threshold at $x = 0.17$. However, it was recently pointed out[4] that the existing data on Na_xWO_3 are not sufficiently refined to test models of the insulator-metal transition. Webman, Jortner, and Cohen[5] attempt to explain the transport in the bronzes in terms of a model where the metal ions cluster to form regions of MWO_3 surrounded by insulating WO_3. However, this idea has been recently criticized[4,6,7] and we shall show that it is not consistent with the results presented in this paper.

We are not aware of any quantitative transport studies on the amorphous tungsten bronzes. However, because of the ease with which x can be varied over a wide range, they are particularly well suited for a quantitative study of the metal-insulator transition. Recently there has been wide interest in these materials as the basis for

a promising new optical display device.[8]

In this Letter we present results of electrical conductivity measurements on amorphous films of H_xWO_3 over the range of x from 0 to 0.5. These measurements show, for the first time, a clear metal-to-insulator transition at $x = 0.32$. On the low-x side of this transition the temperature dependence of the conductivity is explained very well by the variable-range hopping model, thus lending support to the idea that H_xWO_3 is a homogeneous material.

Electrical conductivity measurements were made on amorphous films of WO_3 between 0.2 and 1 μm thick that were prepared by evaporation on prepared glass substrates. The dc current and voltage contacts were made through gold lands evaporated in a four-point probe configuration on the glass substrate prior to WO_3 evaporation. X-ray diffraction measurements show that the films are amorphous. As-prepared films are high-resistance transparent WO_3. These films may not be stoichiometric. Hollinger, Tran Minh Duc, and Deneuville report[9] that films evaporated from WO_3 powder are $WO_{2.7}$. The films may contain H_2O. A weak hydroxyl band is observed in ir absorption. The presence of H_2O in varying amounts may have a significant effect on the proton transport.[10,11] We have noted a wide range in the proton mobilities for films prepared under different conditions.[10] Nevertheless, the electrical conductivity varies only slightly in the as-prepared films. They are converted to H_xWO_3 by electrochromic coloration[12,13] which consists in covering the surface of the WO_3 film with dilute aqueous H_2SO_4, making an electrical contact to the acid with an indium wire, and connecting the wire through a battery to the gold electrodes underneath the film. The amount of charge injected into the film is a measure of the x value. Similarly the area under the optical absorption curve is also a measure of the x value.[14] Optical probe measurements showed a uniformity of x better than 15%. The absolute value of x is accurate to about 10%. We used films that showed the same value of x (as measured optically) before and after electrical measurements.

Figure 1 shows the electrical conductivity σ as a function of temperature for x between 0 and 0.32. The logarithm of σ is plotted versus $T^{-1/4}$. This shows that the variable-range hopping model[15] gives a good description of the transport at low x. In this model $\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}]$, where $T_0 = 16\alpha^3/kN(E_F)$. Here α is the coefficient of the exponential decay of the wave function, $N(E_F)$ is

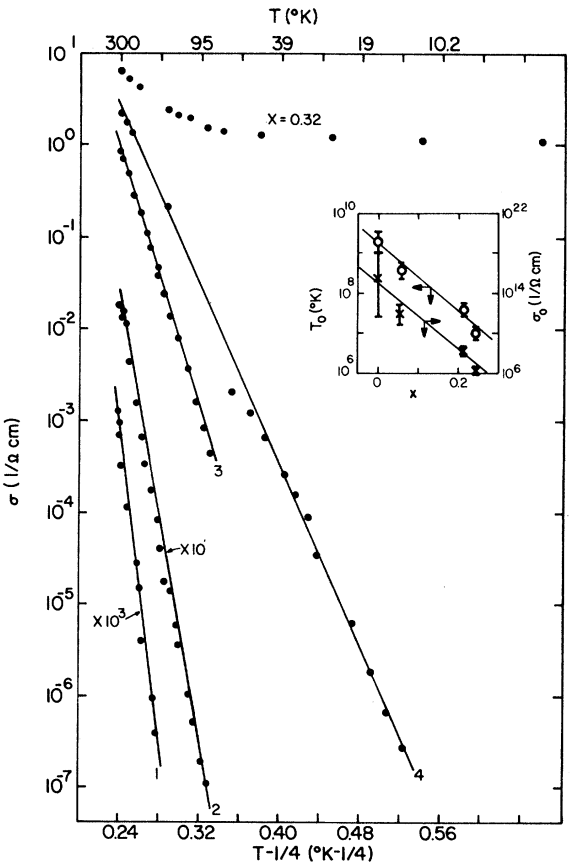

FIG. 1. The logarithm of the conductivity plotted vs $T^{-1/4}$ for amorphous H_xWO_3 films at five different x values. The inset in the figure represents both the logarithms of T_0 and of σ_0 plotted vs x. For $x = 0.32$ the film thickness is 0.51 μm; for all others it is 1 μm. For curve 1, $x = 0$, $T_0 = 2\times 10^9$°K; curve 2, $x = 0.06$, $T_0 = 4\times 10^8$°K; curve 3, $x = 0.21$, $T_0 = 4\times 10^7$°K; curve 4, $x = 0.24$, $T_0 = 9\times 10^6$°K. The notation, $\times 10$ and $\times 10^3$, means that the data points were multiplied by 10 and 10^3, respectively.

the density of states at the Fermi level, and k is Boltzmann's constant. The values of T_0 and σ_0 are displayed in the inset of Fig. 1. These data show that T_0 decreases exponentially with x.

At high values of x, variable-range hopping does not describe the transport. This is seen by the temperature dependence of σ at $x = 0.32$. Here σ decreases slightly and then is independent of temperature below about 20°K. This shows that H_xWO_3 has become metallic. This insulator-to-metal transition is best displayed in Fig. 2 where σ at 4.2 and 300°K is plotted versus x. The conductivity at 4.2°K is virtually zero at low x but at $x \sim 0.3$ it increases rapidly to a value of 38 $(\Omega\ \mathrm{cm})^{-1}$ at $x = 0.44$. The sharp onset of metallic

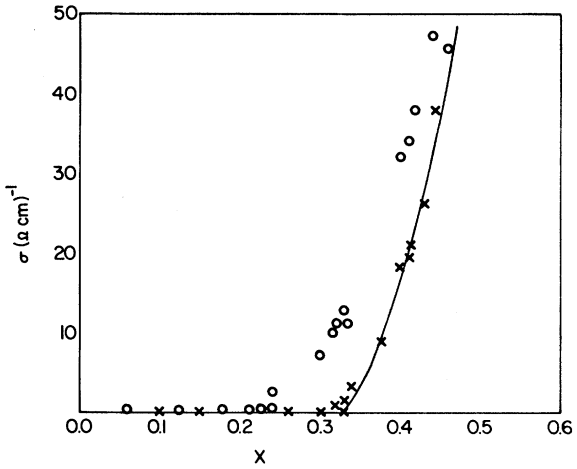

FIG. 2. The conductivity of amorphous H_xWO_3 plotted vs x at both 300 and 4.2°K. The film is 0.51 μm thick. The solid curve is a least-squares fit by the expression $\sigma = 987(x - 0.31)^{1.6}$. ○, 300°K; ×, 4.2°K.

conductivity is characteristic of a metal-insulator transition as the electrons become delocalized. Similar behavior is seen in the data for σ at 300°K. However, here σ is finite and large for values of x below that for the metal transition observed at 4.2°K. Since we do not expect the insulator-metal transition to be temperature dependent, we speculate that the finite conductivity below $x \sim 0.3$ is caused by thermal excitation from the localized states to the conduction band. That there is thermal excitation to a highly conducting state is indicated by measurements of σ above room temperature. Here σ is well described by a thermally activated process with a single activation energy E_A. However, E_A is a function of x. E_A decreases from 0.61 eV at $x = 0$ to ~0.01 eV at $x = 0.3$. A decrease in E_A with increasing x is expected as band filling raises the Fermi level.

From the magnitude of the conductivity in the metallic region we estimate the mobility to be 0.03 cm^2/V sec which is about one-sixth of the value of 0.2 cm^2/V sec determined from electron diffusion measurements on these films.[12] Presumably the mobility determined from the conductivity is lower because the conductivity averages over the mobilities of all carriers, whereas the diffusion measurement picks out those electrons with the highest mobility.

For single-crystal bronzes, where the metal-insulator transition has been studied from the metal side, the transition was described in terms of percolation theory.[1,5] However, as has been pointed out recently[4] there is as yet insufficient data to draw firm conclusions about the nature of the transition. The present data on H_xWO_3 are also insufficient to draw firm conclusions about the nature of the transition. Nevertheless, we can discuss our data in terms of the two competing views of the metal-insulator transition.[5,16] Mott[16] has argued, using the ideas of Anderson localization, that a metal-insulator transition takes place when the conductivity in the metallic region drops to a value called the minimum metallic conductivity, σ_m. This value is reached when E_F drops to the mobility edge. The value of σ_m is not known with certainty because of unknown parameters that are characteristic of the material. However, it is estimated to be within an order of magnitude of 100 $(\Omega\ \mathrm{cm})^{-1}$. If we take the conductivity for $x = 0.32$ at 4.2°K as the minimum metallic conductivity then $\sigma_m = 1\ (\Omega\ \mathrm{cm})^{-1}$ which is lower than the expected value. A recent calculation by Licciardello and Thouless[17] for a two-dimensional system shows a universal minimum metallic conductance of $3.3 \times 10^{-5}\ \Omega^{-1}$. If we express the conductivity of H_xWO_3 at $x = 0.32$ in their units we find that $\sigma = 5.1 \times 10^{-5}$ which is close to their value of σ_m. This can be taken as evidence for the Mott model of the metal-insulator transition.

Nevertheless, we should point out that the value of x for the metal-insulator transition is close to that predicted by percolation theory. Ambegaokar, Cochran, and Kurkijarvi[18] used a bond percolation model to predict a percolation threshold for amorphous materials at a critical density of 0.31. In this model each occupied site is connected to an unoccupied site by a conductor whose conductance is proportional to $\exp(-\alpha r_{ij})$, where r_{ij} is the site-to-site distance. In H_xWO_3 the situation is similar. When WO_3 is colored the electrons reside predominantly on tungsten ions forming W^{5+} ions.[11] In H_xWO_3 then, each hop is from a W^{5+} to a W^{6+} and the jump probability is proportional to $\exp(-\alpha R)$, where R is the W^{5+}-W^{6+} distance. For this bond percolation model Kirkpatrick[19] finds that above the percolation threshold the conductivity can be expressed by $\sigma = \sigma_0(x - x_c)^{1.6}$. The solid curve in Fig. 2 represents a least-squares-error fit of the data by this function with $x_c = 0.32$. This is in excellent agreement with the predicted value of 0.31. However, the data are not sufficient to distinguish the above power-law dependence of σ from a linear dependence of σ on $x - x_c$ which is predicted by the effective-medium theory.[19] It is likely that percola-

tion could occur in H_xWO_3 if an electron hops predominantly from a W^{5+} to a W^{6+} adjacent to a proton.[20] At the percolation threshold, these hops would form a continuous chain throughout the sample. Since the W^{6+}-H^+ complex would be at a lower energy than the W^{5+} no temperature dependence is expected.

We are indebted to Benjamin Abeles and Donald Licciardello for helpful discussions.

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Soft Modes in Current-Carrying Superconducting Filaments

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The dynamical stability of the current in a superconducting filament against small fluctuations of the complex order parameter and the electric potential is studied using equations based on time-dependent self-consistent mean-field theory. In the low-frequency, long-wavelength limit near the transition temperature, simple calculations are performed which predict slowing modes associated with the tendency toward resistive behavior.

The purpose of this Letter is to point out that, as the critical current is approached in a superconducting filament, certain modes of coupled motion of the order parameter and the electrochemical potential become increasingly slow. The observation of these predicted slowing modes would be interesting because they are the nucleation fluctuations for the current-driven onset of phase-slip resistivity,[1] a subject of theoretical and experimental interest.

The analysis requires a model of the dynamics, which in turn depends on physical parameters. Although the phenomenon of softening modes must be quite general, the equations describing them can be complicated. I have examined two simple sets of equations, one of which was derived for the first time in the course of this work. In both cases the main effect is the softening of diffusive long-wavelength modes. Under certain conditions the softening can affect oscillatory motions, though this last effect is likely to be small in most regions that are easily accessible experimentally.

The novel set of equations is obtained by generalizing the work of Schmid and Schön[2] to include fluctuations about a current-carrying state. We consider a model superconductor with strong spin-independent impurity scattering. Inelastic electron-phonon scattering is introduced phenomenologically only as it is needed to provide a mechanism for the relaxation of the magnitude of the order parameter. The fluctuating order