

SUPERCONDUCTIVITY IN FILMS OF β TUNGSTEN AND OTHER TRANSITION METALS

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Ever since Hardy and Hulm's discovery of superconductivity in V_3Si the β -W- (or A15-) type crystal structure has been found to be the most favorable structure by far for the occurrence of superconductivity.² The purpose of this Letter is to report the discovery of superconductivity in tungsten films which contain the β -W structure itself. Transition temperatures as high as 3.35°K have been observed in these films which are more than two orders of magnitude higher than that reported for bulk tungsten.³

In 1931 a supposedly new phase of tungsten, the so-called β -W modification, was described.⁴ More than 20 years later it was shown by Hägg and Schönberg⁵ that this was not another modification of tungsten, but was a metallic suboxide possibly of the form W_3O . Subsequent workers have found that tungsten can be prepared in the A15 structure with considerably less than this stoichiometric amount of oxygen.⁶

In the present investigation, films of a series of transition-metal elements have been studied. Thicknesses of about 1000 Å are normally deposited on glass or sapphire substrates by electron-bombardment evaporation. During evaporation a vacuum of 10^{-5} to 10^{-6} mm Hg is maintained by an oil-free turbomolecular pump. The substrate temperature can be controlled and normally reaches a few hundred degrees centigrade. The superconductivity is easily detected by the Schawlow-Devlin⁷ resonant-frequency method using films of about 4-mm² area.

In the cases of tungsten, rhenium, and molybdenum we have usually found transition temperatures considerably higher than those of the bulk metals, namely W films near 3°K, Re films near 7°K, and Mo films near 5°K. In such cases there is x-ray evidence for the presence of a phase other than the normal metal; usually the normal phase of the metal is also present. The formation of the second phase may be due to the presence of small amounts of impurities during the evaporation which are not experimentally controllable.

A large number of tungsten films were prepared under a variety of conditions. The ob-

served transition temperatures ranged from 0.4 to 3.35°K, with the majority of the films having transitions above 1°K. Superconductivity was observed in films while on the substrates, and also when stripped from the substrate and supported by collodion. There was no difference in the x-ray patterns of films when on the substrate or scraped off it. In some cases oxygen, nitrogen, or water vapor was deliberately bled into the vacuum chamber at a rate sufficient to keep the pressure at 2×10^{-5} mm during the evaporation. The temperature of the substrate was varied from 77 to 450°K. Sapphire, glass, and diamond substrates were used. The starting material was either high-purity single-crystal tungsten with a resistance ratio of 25 000 or commercial wire. X-ray fluorescence analysis of the films showed no significant impurities. Films deposited on thin platinum substrates in a vacuum of 7×10^{-6} mm were analyzed for gas content by a vacuum fusion method. They contained 520-540 ppm oxygen and 30-45 ppm nitrogen.

No significant differences were detected as a result of any of the above variations in procedure. The A15 phase was present in all of the films where superconductivity was observed. The x-ray patterns usually showed up to 14 lines of β -W, with one exceptional case where only one diffuse line was present, indicating very small particle size of the film. However, in a few cases it was possible to identify the presence of the β -W phase where superconductivity was not observed down to 0.012°K. A film kindly made by S. Shapiro in a bakeable vacuum-ion system with a pressure of $\leq 2 \times 10^{-7}$ mm during evaporation had only the β -W structure in its x-ray pattern and was superconducting at 1.1°K.

When the films were examined by electron-diffraction techniques, however, only α tungsten was detected. Reproducibly, a film showing both superconductivity and the presence of the β -W phase by x-ray diffraction could be examined by electron diffraction and show only α -W. After the electron diffraction had been carried out, superconductivity was no longer found, even though some β -W could

still be detected by x-ray diffraction. We believe the electron beam, in contrast to x rays, transformed the β -W to α -W locally, and thus produced a diffraction characteristic of α -W only. Islands of β -W left in the film were still detectable by x rays, but were unable to support shielding supercurrents or might have had an unfavorable amount of impurities.

In addition to measuring the transition temperature by the Schawlow-Devlin technique, we checked some of the tungsten films by a ballistic method using a galvanometer with a time constant of 1 sec. The films were able to shield perpendicular fields of the order of 1 G, indicating a supercurrent density of between 10^6 and 10^7 A/cm².

The x-ray pattern of the rhenium film superconducting at 7°K could be completely indexed as fcc with $a = 3.80$ Å. This film was unstable at room temperature, suggesting it to be a subnitride phase. After two months the x-ray pattern showed the presence of hexagonal rhenium plus two diffuse lines presumably remaining from the fcc phase. The superconductivity then showed a smeared-out transition starting at 6.4°K.

Other rhenium films, whose x-ray patterns contained the normal hexagonal rhenium structure and other lines which have not yet been completely indexed, had transition temperatures around 3°K. However, when only hexagonal rhenium was present, the transition temperature was 1.9°K, close to that of the bulk metal.

All the molybdenum films which were superconducting gave x-ray patterns which contained lines in addition to the normal bcc pattern of molybdenum. These extra lines have not been satisfactorily indexed. Spectroscopic trace analysis indicated the presence of only Ca, Na, Si, and Mg in excess of 0.01%. Al, Ba, Cu, Fe, and Sr were present in quantities of less than 0.005%.

We therefore feel that the exceptionally high superconductivity temperatures observed in tungsten, rhenium, and molybdenum films are due to the presence of another phase composed largely of the element in question, but probably stabilized by the presence of an impurity. This assumption is strengthened by the fact that subnitrides of both Mo and Re are super-

conducting near 5°K,⁸ and by the lack of superconductivity found in films of a number of other elements which are not known to form superconducting subnitrides or oxides. Thus Nb and Ta showed much lower transition temperatures than the bulk elements, while Cr, Rh, Ir, and Pt films did not show any superconductivity at all above 0.3°K.

Recently Strongin, Kammerer, and Paskin⁹ reported the superconductivity of tungsten films between 2 and 3°K. Since that temperature was several orders of magnitude higher than that of bulk tungsten as reported by Gibson and Hein³ near 10^{-2} °K, Strongin, Kammerer, and Paskin implied that the enhanced superconductivity might be explained on the basis of Ginzburg's¹⁰ surface-state superconductivity. The present results suggest a simple and entirely different explanation. In order to show the existence of surface-state superconductivity, one must limit the experiment to materials which will never form any superconducting impurity phases.

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