SUPERCONDUCTIVITY OF SODIUM TUNGSTEN BRONZES*

Ch. J. Raub, A. R. Sweedler, M. A. Jensen, S. Broadston, and B. T. Matthias†
University of California, San Diego, La Jolla, California
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We have discovered the superconductivity of sodium tungsten bronzes. The transition temperatures are in the range below 1°K.

It was Hägg[1] and his collaborators who first explained the nature of these crystals. The formula is

$$Na_xWO_3 \text{ with } 0.1 < x \leq 1.$$

For $x=1$, one has the perfect perovskite lattice with W^{+5} ions. As x decreases there will be sodium vacancies and a corresponding number of W^{+6} ions.

These crystals are either strictly isomorphous to barium titanate or are closely related to the perovskite lattice,[2,3] and it seems probable that they are also ferroelectric in the sense of developing a polar axis, similar again to $BaTiO_3$ and WO_3. The possible connection between ferroelectric transitions and superconductivity has recently been pointed out by Anderson[4] in connection with martensitic transitions observed in the β-W structure.[5]

These bronzes, even though metallic in character, undergo the same cubic-tetragonal transitions as observed in normal ferroelectrics. We chose the sodium tungsten bronzes since there is no danger of observing superconductivity resulting from superconducting impurities or filaments. Tungsten itself does become superconducting but only below 11 millidegrees[6] and no combination of any of the elements in question with each other has as yet been shown to be superconducting.

The large homogeneity range of sodium tungsten bronze with respect to the sodium concentration may permit one to consider these systems as solutions of sodium in WO_3. Even though we have more or less an insulator in the ferroelectric WO_3, once it has been turned into a metal (by as little as 10 at.% sodium) it also becomes a superconductor. Hall effect data indicate that every sodium atom contributes just about one conduction electron.[7] This result suggests that superconducting bronzes will also be obtained when W is replaced by V, Nb, Ta, or Mo, and Na is replaced by any of the alkali metals or alkaline earths.

The crystals were prepared by electrolysis of a fused melt at 850°C with a nominal composition of $Na_2CO_3 + 2WO_3$. The superconducting transition curve of a sample consisting of dark blue crystals is shown in Fig. 1. Crystallographic and optical analysis at room temperature showed the crystals to be tetragonal with $a = 12.1$ Å and $c = 3.75$ Å. According to references 2 and 3 this is bronze I which has a Na concentration between $x = 0.28$ and $x = 0.35$. Samples with sodium concentrations of less than 0.28 and greater than 0.35 were measured to 40 millidegrees and no superconductivity was detected. The concentration of Na in these cases was judged purely by the color which was red for those with more sodium and grey for those with less.[3] Spectrographic analysis showed no impurities above 100 ppm and indicated traces of Cu and Pd below 100 ppm.[8] Superconductivity was measured magnetically in an ac field of approximately 100 milligauss peak to peak at 95 cps. The sample in Fig. 1 was in powdered form and the transition indicated that the total volume of the sample became superconducting.

We have examined thus far other samples with similar sodium concentration, all of which were superconducting with slightly varying transition temperatures. The detailed data covering the entire range of sodium concentration will be published later. The fact that a metallic oxide with 70 at.% O is superconducting indicates how general a phenomenon superconductivity is.

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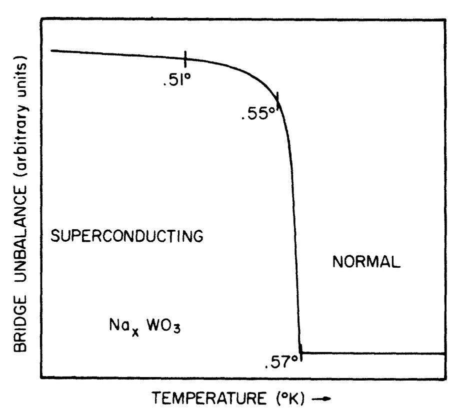

FIG. 1. Superconductivity of sodium tungsten bronze as read directly on an X-Y recorder.

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MOTION OF QUANTIZED FLUX LINES IN SUPERCONDUCTORS*

J. Bardeen
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois
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It has been argued[1] that in a superconductor a flux line moving with velocity $\vec{v}_L$ should be subject to a force $\vec{F}_L = Ne\Phi(\vec{v}_L \times \vec{n})$, where N is the electron concentration, Φ is the total flux, $\vec{n}$ is a unit vector along its direction, and we take units such that $c=1$. This force is presumed to be analogous to the Magnus force acting on a vortex line moving in a liquid. Such a force would give rise to vibrational modes, a large Hall angle for current flow in type-II superconductors, and other effects. There is considerable experimental evidence that no such force exists.[2] The purpose of this note is to point out that the theoretical arguments given for such a force are in error. In the absence of current flow, the only force to be expected is a viscous drag in a direction opposite to the motion of the line. If there is a current density, $\vec{J}=N(-e)\vec{v}_0$, superimposed on that of the flux line, the only driving force is the force $\vec{J}\times\vec{n}$ regardless of the velocity of the line. There are also forces between lines which result from an interaction between the current distributions. When a flux line moves in a neutral fluid at rest there are no currents except those associated with the flux line, and thus no force on the core except the viscous drag.

The only limitation is that the supercurrent flow be large compared with the normal currents generated by the motion, and this will be true except for very high velocities of the line. The motion is essentially adiabatic; the current flow pattern follows the motion. One may calculate the overall force by Ampere's rule, and this leads to $\vec{F}=\Phi\vec{J}\times\vec{n}$. There is, of course, an electric field generated by the vortex motion, but this gives no net force on a neutral system; the force on the electrons is balanced by that on the positive background. The electric field does give rise to a normal current flow (resulting from a nonthermal equilibrium electron distribution), and this in turn gives a frictional drag on the line.

In the bulk of a superconductor, Magnus forces associated with superfluid flow are balanced by the Lorentz force from the magnetic field. How this occurs when the local London theory applies has been described by London.[3] The stresses corresponding to the integrated Lorentz force act at the boundary. The absence of internal stresses follows more generally from the Meissner effect; the supercurrents represent the thermal equilibrium situation in the presence of the magnetic field.

The errors in previous treatments appear to arise from neglect of the forces from the compensating positive background. Suppose that $\vec{v}_s(\vec{r})$ is the velocity field of the flux line at rest. In uniform motion it is approximately $\vec{v}_s(\vec{r}-\vec{v}_Lt)$, giving an inertial force $\partial\vec{v}_s/\partial t = -(\vec{v}_L\cdot\nabla)\vec{v}_s$. Part of this, $-\vec{v}_L\times\nabla\times\vec{v}_s$, contributes to the Magnus force. The magnetic field $H(\vec{r}-\vec{v}_Lt)$ depends in a similar way on time. From the time-varying field, there is an electric field $\vec{E}=-\vec{v}_L\times\vec{H}+\nabla\varphi$, where φ is such that div $\vec{E}=0$. This electric field acts both on the electrons and on the positive back-