INVESTIGATION OF SUPERCONDUCTING PROPERTIES OF MOLYBDENUM

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The superconducting properties of very pure molybdenum [>99.9999%, $R(4.2^\circ K)/R(293^\circ K) = 6 \times 10^{-5}$] were investigated. The temperature of the transition to the superconducting state was found to be 0.916°K, and the width of the transition 0.002 deg. The temperature dependence of the longitudinal critical magnetic field was determined. It was found to be linear in the coordinates $H(T^2)$. Extrapolation to zero temperature gave $H_0 = 86$ Oe. It is shown that the value of T_c may increase as the molybdenum purity decreases.

THE first report that molybdenum is a superconductor was published in 1962.[1] The superconducting transition temperature of samples of the metal, prepared in different ways, was found to range over a very wide interval (0.88–0.98°K), and the width of the transition region amounted to 0.01–0.1 deg. This first paper [1] gave no data on the purity of the investigated molybdenum samples but its authors assumed that the value of the transition temperature rose on increase of the purity.

Later, the same authors investigated the influence of the isotopic composition on the temperature of the superconducting transition of molbdenum[2] and found that the presence of very small amounts of impurities, particularly of iron, could lead to a considerable lowering of the transition temperature and could even destroy the superconductivity completely. Thus, the presence of ≈ 0.01 at.% iron lowered T_c to 0.6°K. For molybdenum with the natural isotopic composition and an atomic weight of 95.95, it was found that $T_c = 0.915^\circ K$ and the width of the transition region was 0.003 deg. Again, the authors did not state the purity of the samples but it could be assumed that it was high.

Investigations using the ultrasonic method [3] gave the value $T_c = 0.92 \pm 0.01^\circ K$ for molybdenum and the critical magnetic field at absolute zero was found to be $H_0 = 114 \pm 5$ Oe. In this case, the investigated molybdenum had the relative electrical resistance $\delta = \rho(4.2^\circ K)/\rho(293^\circ K) = 2.5 \times 10^{-3}$. The fact that the new value of the critical temperature differed from 0.98°K was explained by the authors as being due to the lower purity of their samples compared with those used in the earlier investigation.[1]

The results of an investigation of the critical magnetic fields of superconducting molybdenum by measuring the magnetic susceptibility were reported in [4]. One of the investigated samples, of ≈ 99.998% purity, had $T_c = 0.958^\circ K$ and $H_0 = 99.7$ G. A second sample, somewhat less pure (according to chemical analysis), had $T_c = 0.930^\circ K$ and $H_0 = 98.2$ G. Using these data, the authors of that paper assigned molybdenum to the group of "soft" superconductors (of the Meissner type).

Thus, the data on the superconducting properties of molybdenum cannot be regarded as final and further investigation of these properties is of considerable interest.

In the present work, we investigated molybdenum of very high purity, prepared by zone melting.[5] 1) A sample, 1 mm in diameter, was cut from a 6 mm single crystal by the electromachining method. Current and potential leads made of platinum were soldered by the electrical spark method.

The following point is worth noting. Although the initial single crystal (d = 6 mm) had the relative residual resistance $\delta = 6 \times 10^{-5}$, the sample cut from it (d = 1 mm) had $\delta = 3 \times 10^{-4}$ due to the considerable mean free path of conduction electrons. Consequently, using Nordheim's formula,[7,8] $\rho_d = \rho_\infty(1 + \alpha\lambda/d)$, or, which is equivalent, $\delta_d = \delta_\infty(1 + \alpha\lambda/d)$, and assuming that $\delta_d = 3 \times 10^{-4}$, $\delta_\infty = 6 \times 10^{-5}$, and $\alpha = 1$ (diffuse reflection of electrons from the surface),

1)Volkenshtein et al.[6] showed that molybdenum of ≈ 99.994% purity had the value $\delta = 2.5 \times 10^{-2}$. Comparing this value with $\delta = 6 \times 10^{-5}$, we deduced that the molybdenum used in the present investigation was not less than 99.9999% pure.

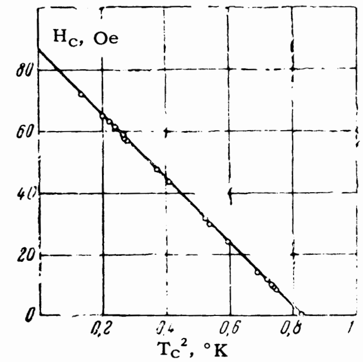
we could estimate in this case the mean free path of conduction electrons to be $\lambda \approx 4$ mm. This also indicated the high purity of the metal.

The measurements of the electrical resistance were carried out by a null method using a circuit whose voltage sensitivity was $\approx 1 \times 10^{-7}$ V. To obtain temperatures below 1°K, we used a device in which the vapor above the liquid He^4 was pumped by a carbon adsorption pump.[9,10] The temperature was measured by means of a condensation thermometer with liquid He^3, placed along the investigated sample. The vapor pressure of He^3 was measured by a truncated U-shaped mercury manometer and a type KM-6 cathetometer, to within 0.01 mm, which made it possible to determine the temperature with an error not greater than 0.001 deg.

We found that the critical temperature was $T_c = 0.916$°K.2) The width of the transition region ΔT_c was 0.002 deg. These data were in very good agreement with the values $T_c = 0.915$°K and $\Delta T_c = 0.003$ deg, given in [2], and with the data of Horwitz and Bohm,[3] although, as previously mentioned, the critical temperature in the latter investigation was measured with an accuracy of only ± 0.01 deg.

The same sample was used to measure the temperature dependence of the critical magnetic field in an external longitudinal field. In this case, the low temperatures were obtained by a device containing liquid He^3 and a carbon adsorption pump.[11] The temperature was determined from the He^3 vapor pressure, measured with a McLeod gauge, a correction being made for the thermomolecular ratio of the pressures. The error in the temperature determination in these experiments was not greater than ± 0.005 deg.

The results of the measurements are shown in the figure in the form of a dependence of the critical magnetic field on the square of the temperature. The experimental points fit a straight line quite well over the whole temperature range. Extrapolation of the data to zero temperature gave $H_0 = 86$ Oe, which was somewhat lower than the value of H_0 given in [4] for the less pure metal. The error in the measurement of H_0 did not exceed ± 1.5 Oe. It seemed interesting to investigate also the behavior of less pure samples of molybdenum. We had three other samples, prepared from the same initial metal by zone melting under similar conditions, but using fewer zone passes. The values of the relative residual resistance δ for the bulk samples, from which the test samples were cut, were 8.5×10^{-5}, 5.7×10^{-4}, and 3×10^{-3}. For the first of these samples, T_c was the same as for the purest sample; for the other two, the values of T_c were found to be 0.937°K and 0.945°K, respectively, and the width of the transition region for the least pure sample was 0.02 deg K. Unfortunately, we were unable to carry out a sufficiently accurate analysis of the impurities in these samples in order to find the reason for the increase in the superconducting transition temperature.



Dependence of the critical magnetic field of molybdenum on the square of the temperature.

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2)The value of the critical temperature was obtained from measurements made using different values of the current through the sample. The data obtained were extrapolated to zero current.

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