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# Critical Magnetic Fields of Superconducting Molybdenum

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Critical magnetic fields of two specimens of molybdenum have been measured down to 0.12°K. Sample *A* with a listed impurity content of less than 27 parts per million was measured as received. Its transition temperature in zero applied magnetic field is 0.958°K and its critical magnetic field at the absolute zero of temperature ($H_0$) is 99.7 G. Sample *B* was formed by the levitation melting of a sample similar to Sample *A*. Its $T_c$ and $H_0$ are 0.930°K amd 98.2 G, respectively. The shapes of the transitions, observed in the presence of an externally applied magnetic field, indicate that these two samples are "soft" or "Meissner-type" superconductors. A calculation which takes into account the fact that the critical field curve is not strictly parabolic leads to values for $\gamma$, the electronic specific heat coefficient, of 1.59 and 1.61 mJ/mole-deg² for Samples *A* and *B*, respectively.

It has recently been reported that several specimens of extremely pure iron-free molybdenum are superconductors with transition temperatures in the range of 0.88 to 0.98°K.[1] The purpose of the present investigation is to determine if Mo is a "Meissner-type" (i.e., soft) superconductor and to measure its critical magnetic field curve.

We have observed the dc differential magnetic susceptibility of two Mo specimens as a function of magnetic field in the temperature range from 0.12 to 4.2°K. Both samples exhibited superconductivity and the data (Fig. 1) show conclusively that the bulk of the samples are, indeed, undergoing the superconducting transition. Figure 2 shows the critical field data which have been obtained down to 0.12°K. The calculated values of the electronic specific heat coefficient ($\gamma$) are approximately 15% lower than the recent calorimetric values.[2]

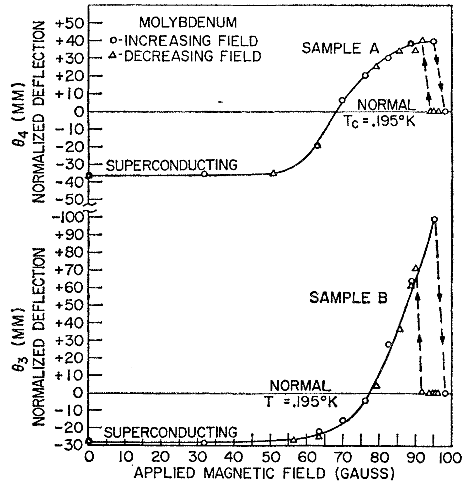

Fig. 1. Galvanometer deflections (∼differential susceptibility) as a function of magnetic field obtained with the temperature approximately constant at 0.19°K.

Sample *A* was a 5.5-mm-long section cut from a 6-mm-diameter bar supplied by Dr. H. G. Sell of the Westinghouse Lamp Division, Bloomfield, New Jersey. Its transition temperature ($T_c$) in zero applied field (residual field 1.5 G) is 0.958°K and ($H_0$) the critical magnetic field at the absolute zero of temperature is 99.7 G. $H_0$ is obtained by an extrapolation of the critical field data when plotted against $T^2$. We define $T_c$ as that value of the temperature at which the susceptibility of the sample first attains a constant value upon warming from the superconducting state. Sample *B* was an irregularly shaped lump cut from a pellet formed by the levitation melting (molten state for 30 min in a vacuum of the order of $10^{-5}$ mm Hg) of a second section cut from the Bloomfield bar. This sample possessed a residual field transition temperature of 0.930°K and an $H_0$ of 98.2 G. The results of a spectrographic analysis of these samples are listed in Table I.

Temperatures below 1°K were produced by the magnetic cooling technique utilizing manganous ammonium sulfate as the cooling agent in the first two runs and potassium chrome alum in the last run. The two samples were cemented to a slotted copper rod which in turn was in contact with the paramagnetic salt. A dc mutual inductance method was employed to measure the susceptibility. A 470-Ω Speer 1/2 W type-1002 carbon resistor, previously calibrated against potassium chrome

Table I. Quantitative spectrographic analysis.

| | Impurities (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Mn | Fe | Mg | Si | Al | Sn | Cr | Ni | Cu |
| Sample *A* | <1 | <1 | 1 | 7 | 1 | <5 | <5 | 5 | 1 |
| Sample *B* | <1 | <1 | <1 | 5 | 1 | <5 | <5 | 5 | 1 |

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[1] T. H. Geballe, B. T. Matthias, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. Letters 8, 313 (1962).

[2] C. A. Bryant and P. H. Keesom, J. Chem. Phys. 35, 1149 (1961).

alum for use as a thermometer below 1°K, was also cemented to the copper rod. After the adiabatic demagnetization, the Dewar was removed from the Bitter magnet and placed in a precision air-core solenoid which supplied the required external magnetic fields for the critical field determinations. The superconducting to normal transitions were observed in two ways, namely field-induced and temperature-induced transitions. The former were obtained by increasing from zero, in a stepwise manner, the applied magnetic field until the superconductivity was destroyed. The results of such a procedure are shown in Fig. 1. The appearance of a reproducible "differential paramagnetic effect" as in Fig. 1, in addition to the observation of a diamagnetic susceptibility of the correct magnitude, is sufficient to allow one to conclude that these samples are "soft" or "Meissner-type" superconductors.[3] Field-induced transitions of this type suffer from the fact that the temperature is slowly increasing during the field sweep. More reliable data are obtained by a temperature-induced transition. Here the applied field is set at some fixed value, less than critical, and the susceptibility is observed as a function of the temperature as the system slowly warms up due to the natural heat leak into it. From a series of such measurements we have constructed the critical field curve depicted in Fig. 2. The temperatures plotted here were derived from the calibrated carbon resistor. The temperatures deduced from the susceptibility of the manganous ammonium sulfate pill, after converting to thermodynamic temperatures, are approximately 0.01°K higher at temperatures below 0.5°K. However, the carbon resistor and the potassium chrome alum were in good accord.

The solid line in Fig. 2 is a plot of

$$H_c = 98.2[1-(T/0.925)^2].$$

This expression is a fair approximation to the observed behavior for Sample $B$ except in the region of $T_c$. A calculation of $\gamma$, the electronic specific-heat coefficient, using the formula $\gamma = (V/2\pi)(H_0/T_c)^2$ yields values of 1.63 and 1.67 mJ/mole-deg$^2$ for Samples $A$ and $B$, respectively. We have taken the atomic volume to be 9.40 cm$^3$ and have used the values of $H_0$ and $T_c$ quoted in the first paragraph. The above formula for $\gamma$ is valid only for parabolic critical field curves. However, if we use the more general expression[4]

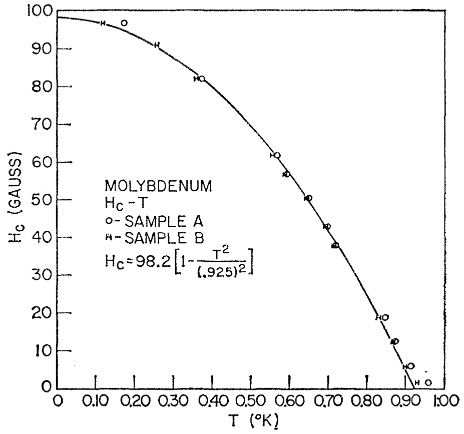

Fig. 2. Critical magnetic fields of Mo as a function of the temperature. The solid line is a plot of the included formula.

$$\gamma = -(VH_0/2\pi)[dH_c/dT^2]_{T^2=0},$$

we obtain, using a value of $-108$ G/deg$^2$ for the limiting value of the slope of the $H_c$ vs $T^2$ plot, a value of 1.59 and 1.61 mJ/mole-deg$^2$. These values of $\gamma$ are 13 to 18% smaller than the lowest calorimetrically determined values.

We wish to express our gratitude to R. L. Falge, Jr. for the use of his solenoid and to acknowledge several interesting conversations with T. H. Geballe concerning the effects of iron on $T_c$. We would also like to thank J. Paterson and A. Wolfe for their excellent spectrographic work.

*Note added in proof.* N. H. Horwitz and H. V. Bohm have recently reported an $H_0$ of 115 G and a $T_c$ of 0.92°K for Mo. Phys. Rev. Letters **9**, 313 (1962).

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[3] R. A. Hein and R. L. Falge, Jr., Phys. Rev. **123**, 407 (1961).

[4] N. M. Wolcott and R. A. Hein, Phil. Mag. **3**, 591 (1958).