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Isotope Effect in Superconducting Osmium

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An experimental study of the relative critical-magnetic-field curves of three isotopically enriched and one natural sample of osmium has been carried out between 0.08 and 0.675°K. Temperatures below 1°K were produced by the magnetic cooling method and superconductivity was detected by means of a dc mutual-inductance method. Data were obtained by first cooling, in the same experiment, three osmium samples to a temperature of approximately 0.08°K and then observing, independently, their differential magnetic susceptibilities, as the samples slowly warmed up in the presence of an externally applied magnetic field. In this manner, one obtains differences in the transition temperatures (ΔT_c) as a function of the critical magnetic field H_c. These data show that the critical-magnetic-field curves of the four samples are indeed distinct. Deviations of the critical-magnetic-field curves from the parabolic law are consistent with the Bardeen, Cooper, Schrieffer (BCS) theory of superconductivity. For the natural sample the quantity

$$H_c/H_0-[1-(T/T_0)^2]$$

attains a maximum value of -0.037 at a value for $(T/T_0)^2$ of 0.52. Here H_c is the measured critical magnetic field, $H_0(=80.4\text{ G})$ is the critical magnetic field at absolute zero, and $T_0(=0.671°\text{K})$ is the transition temperature in zero magnetic field. The other samples exhibited deviations from the appropriate parabolas which range from 0.037 to 0.041. The values of γ, the electronic specific heat coefficient for the four samples, are found to lie in the range of $(4.77\pm0.07)\times10^{-4}$ cal/mole-deg^2. Magnetically induced superconducting to normal-state transitions indicated that all of these samples displayed good "Meissner" properties. In view of this and the fact that the sample with the heavier mean mass $\bar{M}$ possesses the lower critical-magnetic-field curve, we conclude that an isotope effect does exist in Os. The data suggest that the effect be represented by the relationship $T_0\sim\bar{M}^{-0.21}$.

INTRODUCTION

THE empirical discovery that the critical temperature of a superconductor is a function of $1/\bar{M}$, where $\bar{M}$ is the mean atomic mass of the sample has become known as the "isotope effect."[1] This discovery has played an important role in the development of current electron-phonon interaction theories of superconductivity.[2] The BCS theory of superconductivity[3] predicts that the critical temperature is proportional to $\bar{M}^{-1/2}$, in reasonable agreement with the results obtained for superconductors such as Hg, Tl, Sn.[1] In contrast to this, recent work of Geballe and Matthias has shown that the isotopes of Ru and Os certainly do not follow the $\bar{M}^{-1/2}$ law and they viewed their results as an indication that there is no isotope effect in these elements.[4] A complete absence of the isotope effect would indicate that the electron-phonon type of interaction is not the mechanism responsible for superconductivity in the transition metal superconductors.[4a] In keeping with this idea, new types of interactions which lead to superconductivity without an isotope effect have been proposed.[5,6] Due to the importance of the above interpretation of Geballe and Matthias, we felt that additional experimental evidence pertaining to the isotope effect in Os would be of interest. The present work aims to supplement the zero-magnetic-field observations of Geballe and Matthias with critical-magnetic-field data for the same Os samples employed by them in their earlier work.[4]

EXPERIMENTAL DETAILS

The four Os samples employed in this research were supplied by Dr. T. H. Geballe and Dr. B. T. Matthias of the Bell Telephone Laboratories and were studied in the "as-received" condition. These samples were arc melted pellets approximately spherical in shape with a diameter of ~2 mm. The mean atomic masses ($\bar{M}$) were stated to be 187.4, 188.3, 190.2 (natural), and 192.0. The zero-magnetic-field transition temperatures of these Os samples are approximately 0.655°K.[4] Therefore, in order to measure the critical-magnetic-field curves of these samples we resort to the magnetic-cooling method to produce the temperatures of interest.

Our present equipment allows us to observe the magnetic behavior of three Os samples in the same experiment. Thus, this work was undertaken with the following idea in mind. If we cool the samples to a temperature of the order of 0.1°K, then apply a magnetic field and observe the differential magnetic susceptibilities of the three samples as they slowly warm up due to the natural heat leak into the system,

[1] B. Serin, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 15, p. 237.
[2] M. R. Schafroth, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 293.
[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[4] T. H. Geballe and B. T. Matthias, IBM J. Research Develop. **6**, 250 (1962).
[4a] *Note added in proof.* We have been informed by J. W. Garland that this is not the case. In fact, he has used the observed vanishing of the isotope effect in Ru (to be published) as a basis for an argument against the existence of any important attractive interaction between electrons in the transition metals, aside from the interaction arising from the virtual exchange of phonons.
[5] D. S. Falk and R. A. Ferrell, Bull. Am. Phys. Soc. **7**, 325 (1962).
[6] R. F. Soohoo, Bull. Am. Phys. Soc. **7**, 622 (1962).

we should certainly observe three distinct transitions if the critical-magnetic-field curves differ by as much as 0.001°K. We can measure temperature differences with a high degree of accuracy from either the salt itself or from the behavior of a carbon resistor.

Temperatures below 1°K were produced by the magnetic-cooling method using potassium chrome alum as the cooling agent. The differential magnetic susceptibility of the salt, as well as that of the Os samples, was determined by means of a dc mutual-inductance technique.[7] We define the differential magnetic susceptibility as $\chi = [\Delta M/\Delta H]_{H_a=\text{const}}$. In this relationship ΔM is the change in the magnetic moment of the sample which accompanies the application, or removal, of a small incremental magnetic field ΔH. This incremental magnetic field is provided by the primary winding of the mutual-inductance coil system. H_a is a constant externally applied magnetic field which is always longitudinal to the mutual-inductance coils. Thus, ΔH can either add to or subtract from the externally applied magnetic field H_a. $[\Delta M/\Delta H]_{H_a=\text{const}}$ is essentially the slope of the magnetization curve at a point appropriate for the values of H_a and the temperature of the samples. A schematic diagram of the arrangement of the salt pill, samples, and induction coils is presented in Fig. 1.

The "salt pill" was formed by compressing the powdered salt around a system of copper fins. Three Os samples were cemented (GE adhesive number 7031) into small indents provided in the copper bar. This copper bar (1.6 mm×3.2 mm) was placed in thermal contact with the fin assembly by means of a screw fitting and GE adhesive. A carbon resistor, "Old" Speer 1/2 W-470 Ω type 1002, calibrated for use as a thermometer was also cemented to the copper bar. This entire assembly was supported inside a brass vacuum tight "can" by means of a nylon thread. Machined Bakelite spacers were employed to center the samples in the can. Two mutual-inductance coils systems were employed, one for measuring the differential magnetic susceptibility (χ) of the salt and the other for measuring the χ's of the Os samples. The former consists of a primary winding and two equal-turn secondaries wound in series opposition. The latter coil system (i.e., sample system) consists of four equal-turn secondaries and one common primary winding. Any one of the top three secondaries (labeled 2, 3, 4 in Fig. 1) may be placed in series opposition to the fourth secondary or bucking coil.

The secondary circuit of our dc mutual-inductance bridge consists of a pair of secondary coils, one of which contains the specimen whose χ we wish to measure, the other is the bucking coil. As far as the Os samples are concerned, we have a choice (external switch) of three such pairs of secondaries. This allows us to make independent measurements on the χ of the salt or on any one of the three Os samples. In series with the bucking coil is the secondary of a variable mutual inductance and a ballistic galvanometer. The galvanometer deflection θ, which occurs when a current is initiated through the primary coil, is related to the χ of the specimen as follows: $\theta = K\chi + \theta_0$, where K and θ_0 are constants. The experimental procedure was to adjust the variable mutual inductance, when the system was at 4.2°K, to yield a convenient value for θ.

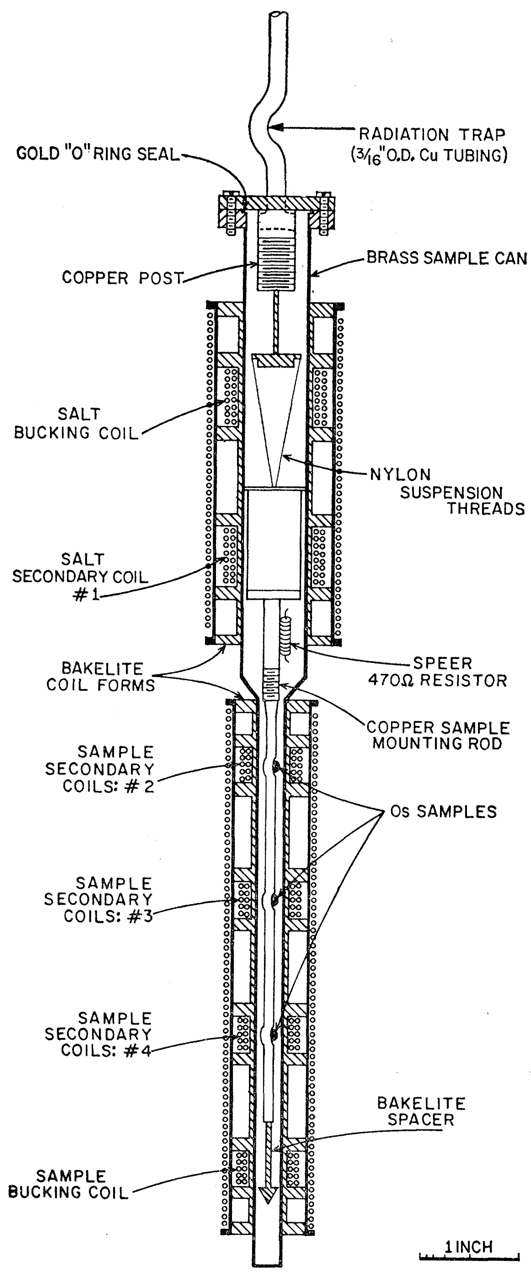

FIG. 1. Schematic diagram of the low-temperature portion of the experiment.

[7] D. de Klerk, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 15, p. 71.

After this adjustment all the circuit parameters were held constant and we observed θ as a function of the temperature as the liquid helium bath temperature was lowered from 4.2 to 1.2°K. After the magnetic cooling had lowered the temperature of the samples from 1.2 to approximately 0.08°K, we observed the χ of the samples as a function of magnetic field and temperature as the system slowly warmed up due to the natural heat leak into it.

RESULTS

Upon the successful cooling of the samples to temperatures of the order of 0.1°K, all three of the Os samples were observed to be superconducting. In order to obtain information concerning the magnetic properties of these samples, we first observed their susceptibilities as a function of magnetic field. A typical result is shown in Fig. 2.

Here we have plotted the magnitude of the observed galvanometer deflections as a function of the applied magnetic field H_a. We obtained data with the incremental field ΔH directed so as to add to or subtract from the external magnetic field H_a. Considering the normal-state susceptibility as zero, we see that there is a range of values of H_a for which $(\Delta M/\Delta H)_{H_a}$ is positive for both directions of ΔH. We refer to this as a reproducible differential paramagnetic effect and consider it as strong evidence that the sample is exhibiting good "Meissner" properties.[8]

The only other feature of this graph that we want to mention here is the supercooling aspects. We see that the normal state persists, for decreasing values of H_a, considerably below the value of H_a required to restore the normal state for increasing values of H_a. This type of behavior is known as supercooling and is indicative of relatively strain-free specimens.[9]

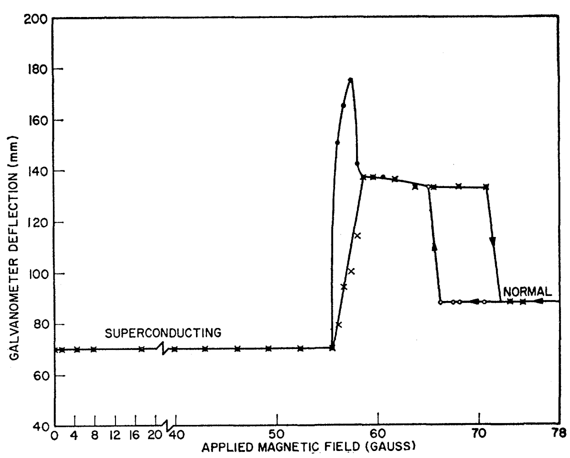

FIG. 2. The magnitude of the galvanometer deflections observed for the $\bar{M}=187.4$ sample. The ●'s denote data obtained with ΔH parallel to H_a while the ×'s denote data obtained with ΔH antiparallel to H_a. The ○'s denote data obtained for decreasing values of H_a with ΔH parallel to H_a.

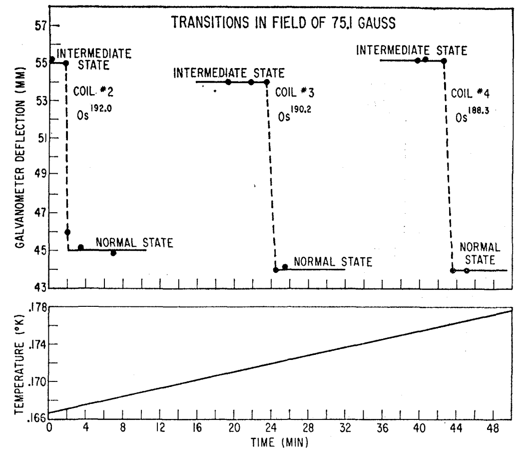

FIG. 3. Galvanometer deflections observed for $Os_{192.0}$, $Os_{190.2}$, and $Os_{188.3}$, and the temperature of the salt as a function of time.

Our most accurate critical-magnetic-field data are obtained by holding H_a constant and observing the χ as a function of the temperature as the system slowly warms up due to the natural heat leak into it. We adjust H_a to a value 2 to 3 G below the critical value determined by the previous field sweeps; this places the samples in the intermediate state and we then make measurements every 20 sec or so until a transition is noted. Because of the supercooling which was observed in Fig. 2, we decided to make all measurements with ΔH directed so as to subtract from H_a. This should, in principle, cause a discontinuous change in the susceptibility when the temperature becomes equal to the transition temperature appropriate for the magnetic field H_a. Figure 3 is a plot of the observed galvanometer deflections as a function of the time for a warm up in a field of 75.1 G. Also included in Fig. 3 is a plot of temperature (°K) versus time deduced from the χ of the salt pill. Note that the transitions are quite distinct and that the heavier isotope possesses the lower transition temperature. This graph and subsequent ones show only that portion of the warmup curves which are germane for the determination of the transition temperatures. Since we have no *a priori* knowledge as to the exact time at which a sample will pass from the intermediate state to the normal state, we take a great many susceptibility measurements with the samples in the intermediate state. The graphs show only the readings in the neighborhood of the abrupt changes in the susceptibilities. By taking measurements as rapidly as possible, we have shown these abrupt changes occur in a temperature interval of less than 0.0003°K. We take for T_c the temperature appropriate for the midpoint of the sudden change depicted in these

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

[9] T. E. Faber and A. B. Pippard, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. I, p. 159.

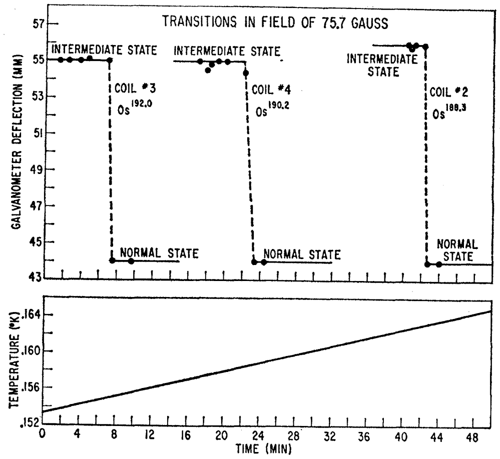

FIG. 4. Galvanometer deflections observed for $Os_{192.0}$, $Os_{190.2}$, and $Os_{188.3}$, and the temperature of the salt as a function of time.

graphs.[10] After observing the three transitions for the particular value of H_a, the magnetic field was reduced until the samples re-entered the intermediate state. The magnetic field was then increased to a value 2 to 3 G below the previous value and the χ's were again observed as a function of the time. During the subsequent warmup (24 h to reach 0.7°K) approximately 15 such transitions were observed. The heavier isotope always passed into the normal state at a lower temperature than did the lighter isotopes.

After this experiment had been completed the samples were taken off the copper rod, and then reglued to the copper rod, in a position different from the previous arrangement and the results of a warmup in a field of 75.7 G are shown in Fig. 4. Figure 5 shows some results

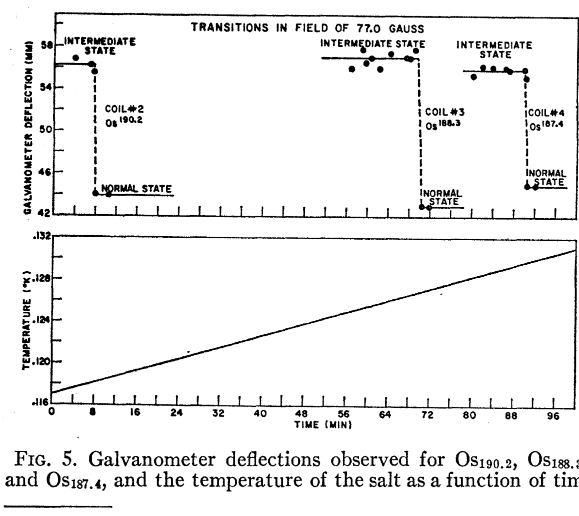

FIG. 5. Galvanometer deflections observed for $Os_{190.2}$, $Os_{188.3}$, and $Os_{187.4}$, and the temperature of the salt as a function of time.

[10] In the course of this paper we will always use the symbol T_c to denote the transition temperature observed in the presence of an externally applied magnetic field. We reserve the symbol T_0 to denote the special case of the transition temperature in zero applied magnetic field.

obtained with a different salt pill, the sample $\bar{M}=192.0$ being replaced with sample $\bar{M}=187.4$.

A summary of the results of a series of five experiments is presented in Figs. 6 and 7, where we have plotted the observed ΔT_c's versus H_c. Figure 6 is normalized to $\bar{M}=190.2$, i.e., $\Delta T_c=T_c(\bar{M})-T_c(190.2)$, while Fig. 7 is normalized to $\bar{M}=188.3$. The experimental ΔT_c's are calculated from the slope of the resistance versus temperature behavior of the carbon resistor. The solid lines in Figs. 6 and 7 depict the behavior we would expect for parabolic critical-field curves for the cases where $T_0\sim\bar{M}^{-1/2}$ (curve a), $\sim\bar{M}^{-1/4}$ (curve b), and $\sim\bar{M}^{-1/8}$ (curve c), respectively. These solid curves all have finite cutoff values. Curves of type a, i.e., those depicting the $\bar{M}^{-1/2}$ dependence, attain maximum values in Fig. 6 at $\Delta T_c=-0.046$ and $+0.020$°K. These maximum values occur at $H_c=80.2$

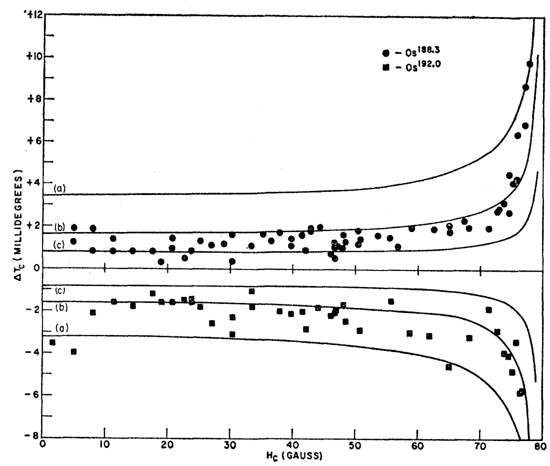

FIG. 6. Differences in the observed transition temperatures of $Os_{192.0}$ and $Os_{188.3}$ with respect to $Os_{190.2}$ as a function of the applied magnetic field. The solid curves depict the behavior expected if H_0 and $T_0\sim\bar{M}^{-1/2}$ (curve a), $\sim\bar{M}^{-1/4}$ (curve b), $\sim\bar{M}^{-1/8}$ (curve c).

G, which is the H_0 value for the sample with $\bar{M}=192.0$. In Fig. 7, these maximum values are -0.047 and $+0.011$°K which occurs at $H_c=80.4$ G, the H_0 value for the sample with $\bar{M}=190.2$.

We can use the above results to construct the critical-magnetic-field curves of these four specimens for temperatures between 0.12 and 0.674°K. The critical-field curves are quite similar. However, small systematic differences between these curves do exist as can be seen from Fig. 8. These critical-field curves are not strictly parabolic. Deviations from parabolicity, expressed by $H_c/H_0-[1-(T/T_0)^2]$, where H_c is the measured critical magnetic field and H_0 and T_0 are the values which determine the fiducial parabola, are in accord with the BCS predictions. Maximum deviations are found to be between 0.037 and 0.041 and occur in the vicinity of a reduced temperature (T/T_0) of 0.5.

DISCUSSION OF RESULTS

All of the results obtained here indicate that the critical-magnetic-field curves of these samples are indeed distinct. The displacements of these curves are such that the samples with the heavier mean mass ($\bar{M}$) possess a consistently lower critical-magnetic-field curve than the ones with a lighter $\bar{M}$.

The following considerations show that this effect is not caused by either a temperature or magnetic-field gradient along the rod. If a temperature gradient exists, the most likely temperature gradient is one where the end of the bar farthest from the pill is the hotter end. Thus, we see that if all samples possess the identical T_c, the sample in coil 4 should go normal sooner in time than the sample in coil 3, and indeed the sample in coil 2 should be the last to go normal. Such an effect is just opposite to the observed behavior shown in Fig. 3. Calculations based on a value for the thermal conductivity of copper $\lambda = \alpha T$, where $\alpha = 1.76$ W/cm-deg^2, show that for our copper bar of 0.051 cm^2 cross section and for a maximum length of 8 cm between the samples a heat input into the "hot" end of 120 ergs/min could support a ΔT of 0.0003°K. At a temperature of 0.1°K our heat leak was of the order of 50 ergs/min. To further show that temperature gradient is not responsible for the observed ΔT_c we reran the experiments after interchanging the samples with respect to position along the rod. Figures 3 and 4 show that the heavier isotopes always go normal at a lower temperature than do the lighter ones, regardless of their positions with respect to the salt pill.

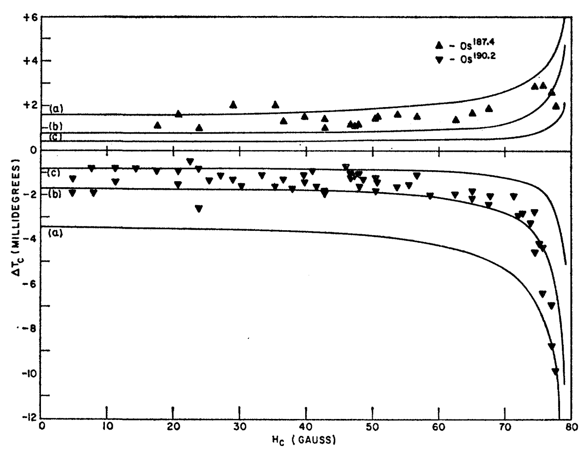

FIG. 7. Differences in the observed transition temperatures of $Os_{190.2}$ and $Os_{187.4}$ with respect to $Os_{188.3}$ as a function of the applied magnetic field. The solid curves depict the behavior expected if H_0 and $T_0 \sim \bar{M}^{-1/2}$ (curve a), $\sim \bar{M}^{-1/4}$ (curve b), and $\sim \bar{M}^{-1/8}$ (curve c).

Figure 8 shows that the slopes of the critical-field curves are of the order of -80 G/deg at about 0.2°K. The solenoid used in the present work is known to be homogeneous, over the volume of interest to better than 0.15%. Thus, we see that at 74 G such an inhomogeneity would give rise to a ΔT_c of 0.0012°K. The observed ΔT_c is 0.006°K. In addition to this, the consistency of the data upon interchanging of sample position also rules out field inhomogeneities as a possible cause of the observed ΔT_c's. In view of these considerations, we are inclined to view the observed ΔT_c's as being indicative of the superconducting properties of the samples.

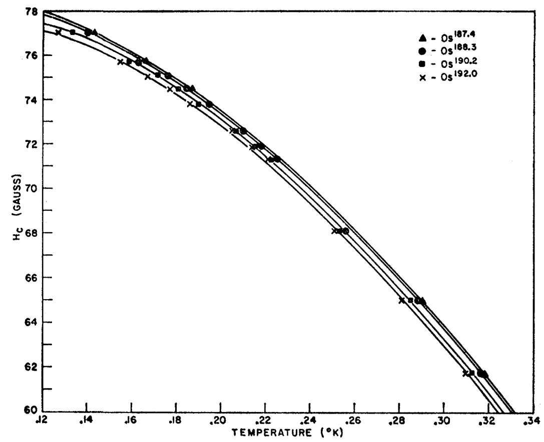

FIG. 8. A portion of the critical-magnetic-field curves of the Os samples as a function of the absolute temperature.

Since the displacements of the critical-field curves correlate with the mean mass ($\bar{M}$) of the samples, we feel that these results are consistent with theoretical ideas which predict that T_0 is a function of $1/\bar{M}$. Extrapolations of the ΔT_c versus H_c curves lead to the values of $\Delta T_0 = \Delta T_c(H_c = 0)$ presented in Table I. In the extrapolation of the ΔT_c versus H_c curves, we have ignored the lowest two data points obtained for the 192.0 sample. If $T_0 \sim \bar{M}^{-1/2}$ the ΔT_0 between the $\bar{M} = 192.0$ and $\bar{M} = 187.4$ samples would be 0.0082°K. Thus, our extrapolated value is only about half of this or $\Delta T_0 = 0.0037$°K.

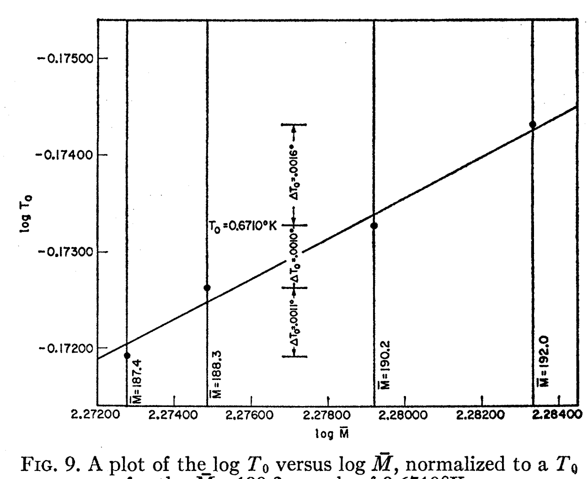

FIG. 9. A plot of the log T_0 versus log $\bar{M}$, normalized to a T_0 for the $\bar{M} = 190.2$ sample of 0.6710°K.

TABLE I. Differences in transition temperature extrapolated to zero field and the electronic specific heat coefficient.

Samples	Experimental Reference sample $\bar{M}=190.2$			Theoretical[a] $H_0, T_0 \sim \bar{M}^{-1/2}$		$H_0, T_0 \sim \bar{M}^{-1/4}$	
$\bar{M}$	H_0[b] (G)	ΔT_0 (°K)	γ[c]	H_0 (G)	ΔT_0 (°K)	H_0 (G)	ΔT_0 (°K)
187.4	80.9	+0.0021	4.81	81.0	+0.0050	80.7	+0.0025
188.3	80.7	+0.0010	4.84	80.8	+0.0034	80.6	+0.0017
190.2	80.4	...	4.70	80.4	...	80.4	...
192.0	80.2	−0.0016	4.71	80.0	−0.0032	80.2	−0.0016

[a] Based on the values of 80.4 G and 0.6710°K for H_0 and T_0, respectively, of the reference sample ($M=190.2$). We have expressed T_0 in four significant figures for calculations of ΔT_0 although we only know it to three significant figures.
[b] These values of H_0 are obtained by linearly extrapolating the H_c versus T^2 curves, utilizing the data obtained below $T^2=0.05$.
[c] γ expressed in units of 10^{-4} cal/mole-deg^2.

These extrapolated values for ΔT_0, allow us to determine T_0 for three of the samples, relative to the fourth one. We can then plot log T_0 versus log $\bar{M}$ to obtain a value for the mass exponent. Such a plot is shown in Fig. 9. This graph (Fig. 9) and the over-all character of the data presented in Figs. 6 and 7 suggest that the data can be represented, to a fair degree of accuracy, by a variation of the form $T_0 \sim \bar{M}^{-0.21}$. While the ΔT_0 values in Table I yield a mass exponent of -0.21, the H_0 values suggest an exponent of magnitude somewhat greater than 0.25. The main point which we wish to make here is that all the data are consistent with the existence of an isotope effect in Os, for which the negative exponent is not less than 0.21.

The critical-magnetic-field curves permit us to evaluate γ, the electronic specific heat coefficient. From the low-temperature portion of our data we calculate γ by the use of the relation

$$\gamma = -\frac{V_0 H_0}{2\pi}\left(\frac{dH_c}{dT^2}\right)_{T=0}.$$

The values of γ so calculated can be represented by a single value, namely, $(4.77\pm0.07)\times10^{-4}$ cal/mol-deg^2. Wolcott[11] has determined γ calorimetrically and reported it to be 5.6×10^{-4} cal/mol-deg^2. Thus, our value for γ is approximately 15% lower than that due to Wolcott. In view of the "ideal" behavior of our samples, we would expect the two methods of determining γ to yield better agreement than that given above. Our value is also about 30% lower than the magnetically determined value of Carruthers and Connelly.[12]

The values of T_0 found in the present work are about 0.015 to 0.020°K higher than these reported by Geballe and Matthias. Ordinarily we would regard such agreement as satisfactory, but in the present work we must be concerned about this small discrepancy. We have to weigh the possibility that these samples may have been strained in the time between their work and the present experiments. Our belief that these samples are strain-free stems from the observation of supercooling which is characteristic of strain-free samples.[9]

CONCLUSIONS

The definite relative displacements of the critical-magnetic-field curves of these samples, and the correlation of these displacements with the mean mass of these samples lead us to conclude that there is an isotope effect in Os. We feel that our data indicate that the mass exponent is not smaller in magnitude than 0.21 and could be higher depending on whether we use the mass dependence of ΔH_0 or ΔT_0. Thus, theories which attribute superconductivity in the transition metal to electron-electron interactions which involve no isotope effect[5,12] are inconsistent with this conclusion. The lack of the full $\bar{M}^{-1/2}$ dependence reported here is in accord with the results[13] reported for Mo, i.e., $T_0 \sim \bar{M}^{-1/3}$. An exponent of -0.21 for an isotope effect in Os is in keeping with the ideas of Swihart[14] and those of Morel and Anderson[15] who predict that Os should possess a negative exponent of magnitude considerable smaller than 0.5. Swihart finds (private communication) that a reasonable estimate for the exponent of Os is -0.35.

Our conclusion that an isotope effect does exist in Os is in conflict with the conclusion of Geballe and Matthias.[4] Due to the small size of the samples employed to date in the study of the isotope effect in Os, as well as the relatively small theoretically predicted shifts in T_0, additional experimental information regarding the isotope effect in Os is clearly desirable. It is also desirable to have data on several samples with the same mean mass in order to check on the reproducibility of the transition temperatures. The recent results which Mapother[16] obtained with several isotopically enriched samples of Ru emphasizes this latter need.

[11] N. M. Wolcott, *Conference de Physique des Basses Temperature, Paris, 1955* (Centre National de la Recherche Scientifique, and UNESCO, Paris, 1956) "Supplement au Bulletin de l'Institut International du Froid, Annexe 1955-3," p. 286.

[12] J. A. Carruthers and A. Connolly, in *Proceedings of the Fifth International Conference on Low Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958), p. 276.

[13] T. H. Geballe and B. T. Matthias, Eighth International Congress on Low Temperature Physics, London, 1962 (unpublished), p. 95.

[14] J. C. Swihart, IBM J. Research Develop. **6**, 14 (1962).

[15] P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

[16] D. K. Finnemore and D. E. Mapother, Phys. Rev. Letters **9**, 288 (1962).