Critical Magnetic Fields of Superconducting Ruthenium Isotopes and Search for an Isotope Effect

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In order to investigate the isotope effect, i.e., the dependence of the superconducting transition temperature on the isotopic mass, the critical-magnetic-field curves of three samples of ruthenium have been measured to temperatures below 0.1°K. The samples had mean isotopic masses of 99.2, 101.1 (natural), and 103.9. Detailed critical-magnetic-field curves were obtained, but no systematic dependence of the transition temperature on the mean isotopic mass was found. The transition temperature in zero external magnetic field characteristic of all three samples is $T_0=0.509\pm0.002$°K and the critical magnetic field at absolute zero is $H_0=70.0\pm0.5$ G. Plots of the critical-field curves are given, as well as plots of H_c versus T^2, which show deviations from parabolicity consistent with the weak-coupling limit of the BCS theory. Values for the electronic specific-heat coefficient γ have been determined from the critical-field curves, and these give $\gamma\simeq2.80$ mJ/mole deg^2. All three samples exhibited "ideal" or "Meissner" properties, that is, the transitions were reversible in a magnetic field.

INTRODUCTION

UNTIL four years ago all pertinent data indicated that the superconducting transition temperature T_0 was a function of the mean mass $\bar{M}$ of the sample. This dependence, which could be expressed as $T_0\propto\bar{M}^{-\alpha}$ with $\alpha=0.5\pm0.05$, became known as the isotope effect. In 1961, Geballe *et al.*[1,2] reported that the transition elements Ru and Os did not agree with the above value for α. Their data for several isotopically enriched samples of Ru indicated a maximum spread of about 0.001° K in the value of the zero-field transition temperature T_0; this spread is only one-tenth of that predicted by the BCS theory, i.e., $\alpha=0.5$. Thus, to within experimental limitations, this work indicated that the most likely value for α was zero. Finnemore and Mapother[3] measured the critical magnetic fields of these same Ru samples between ~0.477°K (their T_0 value) and 0.3°K. These data indicated that the specimens were well-behaved superconductors exhibiting reversible magnetic transitions, and the data were felt to be consistent with the conclusion of Geballe *et al.* concerning the isotope effect.

The over-all situation today seems to be that the nontransition-metal superconductors show the full isotope effect, i.e., $\alpha=0.5\pm0.05$, while the transition metals have values for α less than 0.5, e.g. $\alpha\simeq0$ for Ru[1,2,3] and Zr[4]; $\alpha=0.21$ for Os;[5] $\alpha=0.33$ for Mo.[6] Several theoretical calculations have been presented to explain this behavior, and the present work is in part an outgrowth of one of these, namely, the theoretical calculations of Garland[7] which predict a value for the exponent α of 0 ± 0.20 for the case of ruthenium.

The present work is concerned with a detailed determination of the critical magnetic field curves of two isotopically enriched samples of Ru and one naturally occurring sample. Such data are of interest from two points of view. First, on the isotope effect question, our determination of the relative critical magnetic field curves of these three samples, at temperatures near absolute zero (reduced temperature T/T_0 of 0.1) should shed additional light on the magnitude and sign of α. Second, since these samples are ideally behaved, the determination of the absolute critical magnetic field curves will allow us (1) to check the predictions of the BCS theory regarding their shape, and (2) to calculate a meaningful value for the electronic specific heat coefficient γ, since all earlier magnetic data were either obtained for nonideal samples or did not extend to low enough temperatures.

Table I shows the results of all the pertinent work on the superconducting properties of Ru, and for comparison the results of this work are included.

EXPERIMENTAL DETAILS

The three Ru isotopes used in these experiments were loaned to us by Dr. T. H. Geballe of the Bell Telephone Laboratories, and are the best three of the samples (based on measured resistivity ratios) investigated by Geballe *et al.*[1,2] and by Finnemore and Mapother.[3] The samples are arc-melted pellets of pure Ru of nearly spherical shape with diameters of about 2 or 3 mm. These samples had stated mean isotopic masses $\bar{M}$ of 99.2, 101.1 (natural), and 103.9, and were investigated in their "as received" condition from Bell Laboratories. The method of preparation and isotopic analysis have been described.[1]

The experimental apparatus and procedure, with some minor but significant alterations, which shall be

[1] T. H. Geballe, B. T. Matthias, G. W. Hull, Jr., and E. Corenzwit, Phys. Rev. Letters **6**, 275 (1961).
[2] T. H. Geballe and B. T. Matthias, IBM J. Res. Develop. **6**, 256 (1962).
[3] D. K. Finnemore and D. E. Mapother, Phys. Rev. Letters **9**, 288 (1962).
[4] E. Bucher, J. Muller, J. L. Olsen, and C. Palmy, Phys. Letters **15**, 303 (1965).
[5] R. A. Hein and J. W. Gibson, Phys. Rev. **131**, 1105 (1963).
[6] B. T. Matthias, T. H. Geballe, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. **129**, 1025 (1963).
[7] James W. Garland, Jr., Phys. Rev. Letters **11**, 114 (1963).

TABLE I. Superconducting properties of Ru.

	T_0(°K)	H_0(G)	γ(mJ/mole deg^2)	Remarks
Goodman[a]	0.47	46	···	Superconductivity first observed in Ru
Hulm and Goodman[b]	0.47	46	1.2	Nonideal behavior
Carruthers and Connolly[c]	0.49	66	2.43	
Geballe *et al.*[d]	0.495±0.001	···	···	Ideal behavior, no isotope effect[e]
Fennimore and Mapother[f]	0.474 to 0.479	61.9 to 62.1	···	Ideal behavior, no isotope effect[e]
This work (1965)	0.509±0.002	70.00±0.5	2.80±0.1	Ideal behavior, no isotope effect[e]

[a] B. B. Goodman, Nature **167**, 111 (1951).
[b] J. K. Hulm and B. B. Goodman, Phys. Rev. **106**, 659 (1957).
[c] J. A. Carruthers and A. Connolly, in *Low Temperature Physics and Chemistry*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 276.
[d] See Refs. 1 and 2.
[e] The same samples of Ru were used in these last three investigations of the isotope effect.
[f] See Ref. 3.

described below, have been described in an earlier paper.[5] Low temperatures were achieved by the adiabatic demagnetization of potassium chrome alum which was in thermal contact with the ruthenium samples by means of copper wires. Superconductivity was detected by measuring the susceptibility of the samples by means of a dc mutual-inductance technique. The technique is the same as the one used in measuring the isotope effect in osmium, except for the following: instead of compressing powdered potassium chrome alum around a system of copper fins, the salt was allowed to crystalize from a saturated solution around a bundle of about 750 bare copper wires 0.005 in. in diameter. The resulting pill was machined to a cylinder ~5 cm long and ~2 cm in diameter. Then the three Ru samples were enmeshed in the copper wires using nylon thread and GE 7031 adhesive at distances of 6.5, 10, and 13.5 cm, respectively, from the bottom of the salt pill. In the earlier work with Os, the samples had been glued to a copper bar which was in thermal contact with the salt. We believe that the system of wires provides better thermal contact between the salt and the wires and between the samples and the wires.[8] All other details of this experiment were the same as in the Os experiment.

In any particular experiment all three samples of Ru were run concurrently, and for most of the data the susceptibilities were measured as the samples warmed up in a constant applied external magnetic field. The temperature at which a discontinuous jump in the susceptibility occurred from the intermediate state to the normal state was taken to be the transition temperature. The temperatures were all determined from the susceptibility of the salt. Thermal gradients between the salt and the sample are insignificant in this range[5] and were not corrected for.

By observing the transition temperature for different values of magnetic field, a plot of T_c (the transition temperature in a field) versus H_c is obtained for each sample. Some transitions were measured by increasing the field and measuring the field at which the transition occurs. For such a measurement, the temperature is gradually increasing, but not very much, and can be taken into account.

RESULTS AND DISCUSSION

In order to obtain information concerning the magnetic properties of these samples, we first observed their susceptibilities as a function of magnetic field. The results of one of these magnetically induced transitions are shown in Fig. 1. These data are typical of the magnetically induced transitions for all of the Ru samples. Here we have plotted the observed galvanometer deflections (which are proportional to changes in the susceptibility) against the applied magnetic field. The galvanometer deflections are the result of the application of an incremental magnetic field $\Delta H \simeq 1.5$ G applied in a direction antiparallel to the externally applied magnetic field H_{ext} which is held constant while a measurement is being made. Considering the normal-state susceptibility as zero, we see that there is a range of values of H_{ext} for which the susceptibility is positive.

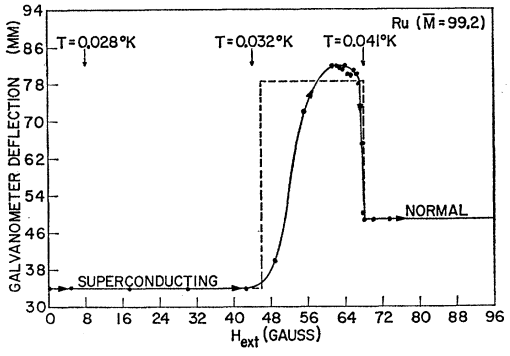
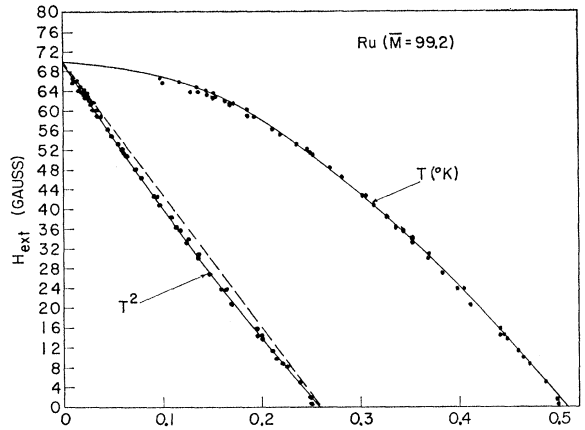
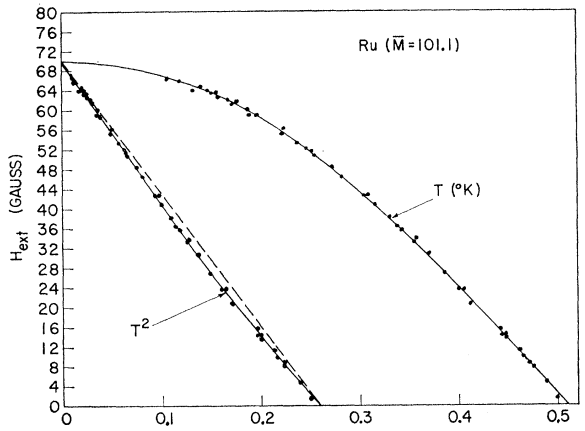


FIG. 1. The reversible differential paramagnetic effect (DPE) for Ru ($\bar{M}$=99.2). The dotted curve shows the DPE that would be expected for a perfectly spherical sample.

[8] J. W. Gibson and R. A. Hein, Phys. Rev. Letters **12**, 688 (1964).



(a)



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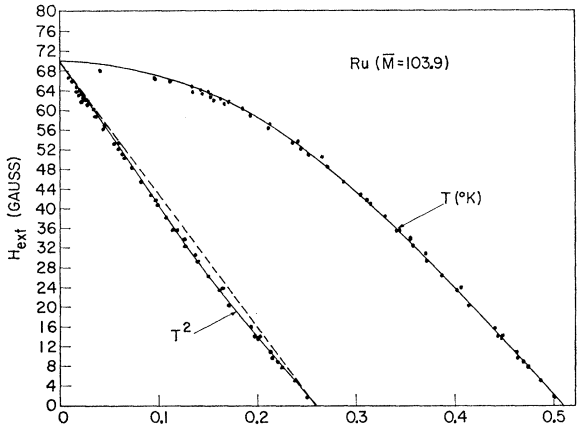

(c)

FIG. 2 (a) Critical magnetic field curve for Ru ($\bar{M}$=99.2). (b) Critical magnetic field curve for Ru ($\bar{M}$=101.1). (c) Critical magnetic field curve for Ru ($\bar{M}$=103.9). The dashed straight line on the H_c-versus-T^2 plot on these figures represents parabolic dependence of H_c on T.

This is referred to as the differential paramagnetic effect (DPE) and confirms in a somewhat different manner the conclusion reached by Finnemore and Mapother[3] that these Ru samples are exhibiting "ideal" or "Meissner" behavior.[9] The DPE is reproducible in the sense that it exists for both increasing and decreasing external magnetic field. The dashed line on the graph of Fig. 1 shows the DPE that would be expected if the samples were ideally behaved perfect spheres. There is evidence that a small amount of supercooling occurs of the order of about 2 G in an externally applied magnetic field of about 65 G. This is much less than we observed with osmium, where supercooling of about 8 G was observed. The reason for applying ΔH opposite to H_{ext} is that if the supercooling field exceeds the ΔH, a sharp discontinuity in the susceptibility will occur at the transition temperature. Indeed, this is what is observed. Further, such supercooling is indicative of relatively strain-free specimens.[10]

Figure 2 shows plots of the critical magnetic fields for the three Ru samples. These data are determined by allowing the samples to warm up in a constant externally applied magnetic field until the transitions to the normal state occur. Three distinct transitions, one for each sample, were always observed in high fields near absolute zero and nearly always at lower fields. That is, the transitions were separated in time, hence, temperature. After the three transitions occurred, the field was decreased slightly until the samples were again in the intermediate states, and transitions were observed for this field value and so on until the transitions in the lowest field values were obtained and the temperature had warmed up past T_0. The extrapolated values of the critical magnetic field at absolute zero and the transition temperature in zero field, respectively, are $H_0=70 \pm 0.5$ G and $T_0=0.509\pm 0.002$°K.

Figure 2 shows three plots for the three separate samples, and each plot has been extrapolated to H_0 and T_0 values which are assumed to be the same for each sample to within experimental errors. The graphs show H_c as a function of both T and T^2. On the T^2 plot the dashed line is a straight line drawn between H_0 and T_0^2 and would represent a parabolic dependence of H_c on T. The deviations from parabolicity shown are consistent with the weak-coupling limit of the BCS theory.[11]

The values of γ, the electronic specific heat coefficient, may be calculated from the critical magnetic field curves. We use the relation

$$\gamma=-(V_0H_0/2\pi)(dH_c/dT^2)_{T=0},$$

where V_0 is the molar volume using a density of 12.2 g/cm^3, and $(dH_c/dT^2)_{T=0}$ is determined from the ex-

[9] R. A. Hein and R. L. Falge, Jr., Phys. Rev. **123**, 407 (1961).
[10] 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.
[11] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

perimental data. The values of γ so obtained are $\gamma=2.88\pm0.05$ mJ/mole deg^2 for $\bar{M}=103.9$; $\gamma=2.72\pm0.05$ mJ/mole deg^2 for $\bar{M}=101.1$; and $\gamma=2.79\pm0.05$ mJ/mole deg^2 for $\bar{M}=99.2$. These values are about 5% higher than the values that would be determined from the BCS relation

$$\gamma\simeq 0.17V_0(H_0^2/T_0^2).$$

The calorimetric value of γ determined by Wolcott[12] is 3.35 mJ/mole deg^2. Thus, our values are between 14 and 19% below Wolcott's value. Better agreement, perhaps, should be expected because of the "ideal" nature of our samples.

ISOTOPE EFFECT

The earlier experimental work concerned with an isotope effect for superconducting ruthenium has already been mentioned. The conclusion has always been that there is no detectable systematic dependence of the transition temperature on the isotopic mass of Ru, at least for the samples tested. Perhaps it is unfortunate that all these data concerned with an isotope effect have been for the same samples of Ru, but one should expect the results to be valid due to the purity of the samples, their "ideal" behavior, etc.

In this work three distinct transitions separated in time (hence temperature) were nearly always observed for the three samples. Consistent results were obtained even when the sample positions were interchanged, i.e., samples removed from the copper wires and enmeshed and reglued in the wires in a different position and in a different order and then rerun. Since the externally applied field is held constant and is known to be homogeneous enough over the volume which the samples occupy, and since temperature gradients between samples have been shown to be negligible, we must conclude that the samples have different transition temperatures for the field value being applied. The transitions were nearly always distinct and the differences in temperature were larger in high fields, say greater than 60 G. At lower fields the transitions were not always distinguishable and the separation in temperatures was much less. Further, the order of the transitions was not correlated with the isotopic mass. In fact, the order of the transitions was different for different values of external field. However, at a particular field value, the order was the same even when the sample positions were interchanged between runs. Figure 3 shows the data of three separate runs. Here we have plotted the difference in transition temperature of the Ru ($\bar{M}=99.2$) and Ru ($\bar{M}=101.1$) as compared with the Ru ($\bar{M}=103.9$) as a function of H_c, i.e., the zero line represents the Ru ($\bar{M}=103.9$) and the data

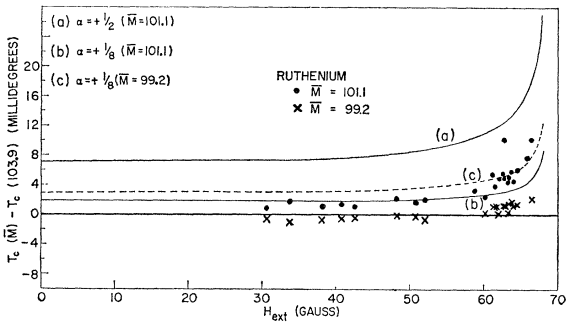

FIG. 3. The "isotope effect." Data points show differences in transition temperatures of Ru ($\bar{M}=99.2$) and Ru ($\bar{M}=101.1$) from Ru ($\bar{M}=103.9$). T_c for Ru ($\bar{M}=103.9$) is represented by the heavy zero line. The solid curves show the expected differences for Ru ($\bar{M}=101.1$), if $T_c\propto\bar{M}^{-1/8}$ and $T_c\propto\bar{M}^{-1/2}$ (BCS predictions) and the dasded curve shows the expected difference for Ru ($\bar{M}=99.2$) if $T_c\propto\bar{M}^{-1/8}$.

points show the differences of the transition temperatures of the other two samples from this one. It is important to note that the relative temperatures of the three samples can be determined with far greater certainty than can the absolute temperatures. It is the relative temperatures which are important here, and we have determined these differences to within about ±0.0002°K. We see that at the higher fields, the order in which the transitions occur, from lower to higher T, is Ru ($\bar{M}=103.9$), Ru ($\bar{M}=99.2$), Ru ($\bar{M}=101.1$), respectively. At lower fields the order has changed, and the separation is less. At fields below about 30 G, the transitions were seldom distinguishable and the data points (not shown on Fig. 3) all lie on the straight line which represents $\bar{M}=103.9$. Also shown on this graph are curves calculated for $T_c\propto\bar{M}^{-\alpha}$ with $\alpha=\frac{1}{8}$ and $\alpha=\frac{1}{2}$. From this graph one can see that if the samples had displayed a consistent $\bar{M}^{-1/8}$ dependence, it would have been readily detectable. As far as the isotope effect is concerned, a consistent result for the three samples would have been meaningful; however, the fact that we do not have an unique answer for all three samples points out the need for a study with a wider selection of samples.

CONCLUSIONS

Due to the fact that these samples are well-behaved ideal "Meissner-type" superconductors, we believe these data represent the most reliable and detailed determination of the critical magnetic-field curves of ruthenium. Therefore, the determination of the electronic specific-heat coefficient γ from the experimental data should give reliable results. As in the case of osmium, these magnetically determined values of γ are about 15% lower than the calorimetric values. Because of the indicated high purity of these strain-free samples, we are inclined to give preference to the magnetic over the calorimetric determination of γ.

Although the shifting of the transition temperature

[12] N. M. Wolcott, *Conference de Physique des Basses Temperature, Paris, 1955* (Centre National de la Recherche Scientifique and UNESCO, Paris, 1956), Bull. Inst. Intern. Froid Suppl. **1**, 286 (1955).

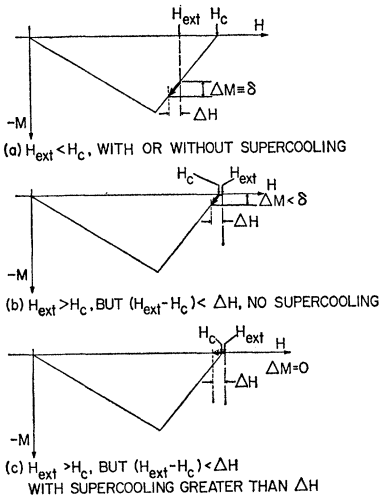

FIG. 4. Plot of magnetic moment versus magnetic field for an "ideal" superconductor showing the effects of supercooling.

with isotopic mass does not seem to be correlated with an isotope effect, we believe the shift to be characteristic of the samples and not due to field inhomogeneities or temperature gradients for the following reasons: We know that field inhomogeneities are insignificant and have been measured exactly at each sample position using electron-paramagnetic-resonance techniques. The temperature gradients between the samples along the copper wires are also negligible with respect to the observed shifts. Further, we know we are justified in making these assumptions because when the sample positions are interchanged the results are not changed.

Perhaps one criticism which might be made of this work concerns the magnitude of the incremental measuring field ΔH. This field ΔH was always applied in a direction such as to oppose the externally applied magnetic field H_{ext}. Then, if the supercooling of the sample exceeded the ΔH, as was the case with our osmium work, the transitions from the intermediate state to the normal state would be sharp discontinuities in the susceptibility occurring at H_c. This is illustrated in Fig. 4. Figure 4(a) shows the situation if $H_{ext}<H_c$ and ΔH is being applied antiparallel to H_{ext}. The slope of the line, $\Delta M/\Delta H$, is what is measured. Here it does not make any difference whether supercooling occurs or not. However, at a higher field (or higher temperature) such that $H_{ext}\gtrsim H_c$, the situation is different. Figure 4(c) shows that if the sample supercools, and the supercooling is greater than ΔH, the slope $\Delta M/\Delta H$ becomes zero at this point and the transition is sharp. This is what is generally observed and is why we assume ΔH is less than the supercooling field. If there were no supercooling, the transition would not be sharp but would have a width ΔH. This is shown in Fig. 4(b). An intermediate case could occur when there is supercooling but ΔH is greater than the extent of it. Sometimes it appeared that there might be a slight initial rounding off of the transition. If this were true and if the supercooling became less at lower fields and was different for the different samples, this might offer some explanation of the results. In conclusion, one can only say that an isotope shift with a mass exponent $\alpha\simeq 0\pm 0.15$ cannot be ruled out, but the small spread in the critical field curves which such an effect would produce could easily be masked by some other factor arising from the lack of "identical" samples.

There is a slight disagreement in the values of T_0 between this work and the earlier work on Ru (see Table I). At present we do not know why this is true. The experimental techniques differ, but one should perhaps expect better agreement. The differences in the H_0 values between this work and others can be attributed to the fact that in the earlier works the H_0 was obtained by extrapolating from higher temperatures. Therefore, the H_0 values reported here should be better since measurements were made to below 0.1°K.

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