PHYSICAL REVIEW VOLUME 106, NUMBER 4 MAY 15, 1957

Superconducting Properties of Rhenium, Ruthenium, and Osmium†

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(Received December 4, 1956)

Magnetic measurements have been made on the superconducting properties of rhenium, ruthenium, and osmium, and the influence of various methods of specimen preparation and treatment has been studied. In particular the transition temperature of rhenium could be raised by about 1°K above the ideal value, 1.699°K, by grinding or preparing the specimen as a powder. Although rhenium belongs to the transition elements, specimens of ideal superconducting behavior could also readily be prepared. This reinforces the conclusion of previous workers that the nonideal superconducting behavior frequently found in transition metal specimens is not a fundamental property of this group of elements, but a consequence of the metallurgical history of the specimens.

I. INTRODUCTION

THE superconducting elements form three separate groups in the Periodic System, comprising the "hard" superconductors in Columns 3*A*, 4*A*, 5*A*, and 6*A*, the "soft" superconductors in Columns 2*B*, 3*B*, and 4*B* and the four elements technetium, rhenium, ruthenium, and osmium of Columns 7 and 8, in which superconductivity was discovered quite recently.[1-3] Since the elements of the last group are all hexagonal in structure and resemble each other chemically, one might expect some similarity in their superconducting properties. However, very little detailed information on these properties has so far been published, and the present work was initiated to remedy this situation for the available elements rhenium, ruthenium, and osmium.

In some of the early work on properties of the superconducting elements, emphasis was placed upon the low temperature rather than upon the metallurgical aspects of the problem, with a consequent neglect of the latter. It is well known that in some cases, e.g., vanadium,[4] the superconducting behavior is very sensitive to the physical and chemical impurity conditions in the specimen. In the present work it was considered important to compare the superconducting properties of specimens prepared by completely different methods. In the case of rhenium, special attention was devoted to the problem of producing strain-free, pure samples, and the metallurgical processes are described fully in the present paper. Full details are also given of the magnetic measurements on which were based the critical field and transition temperature data already briefly described.[2,5]

II. EXPERIMENTAL DETAILS

A. Magnetic Measurements

The magnetic measurements studies involved three different types of measurement, which are summarized as follows:

(1) The change in total induction, B, of the specimen was observed on changing an applied field H. The apparatus for measurements above 1°K has already been described.[6] For measurements below 1°K a ballistic modification of the apparatus described by Goodman and Mendoza[7] was sometimes used.

(2) The intensity of magnetization, M, was measured above 1°K as a function of applied field using the method due to Shoenberg.[8]

(3) Below 1°K the magnetic susceptibility of the specimen in a small alternating measuring field was studied as a function of a superimposed steady magnetic field.[7]

In the first two methods, the critical magnetic field was taken to be the field at the entry to the normal state; for the magnetization curves which showed a tail, a linear extrapolation of the intermediate state part of the curve was made. In the third method, entry to the intermediate state was characterized by a sharp increase in ac susceptibility. This occurred at a field $(1-n)H_c$, where $4\pi n$ is the demagnetizing coefficient of the specimen.

In the experiments above 1°K, temperatures were obtained from measured values of the vapor pressure of liquid helium, using the 1955 (Naval Research Laboratory) international scale.[9] Measurements below 1°K were carried out using a technique already described,[7] in which the superconductor was cooled by thermal contact with the salt pill through a copper rod.

Two possible sources of error in the measurement of the temperature of the superconductor must be considered. In the use of the ac technique below 1°K, the need to minimize eddy current heating in the copper connecting rod has already been discussed.[7] In the induction measurements a superconductor may be heated or cooled when a change in magnetic field causes it to pass from the normal to the superconducting state or vice versa. This effect was unimportant in the experiments carried out above 1°K, since the specimens

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† Part of this work was carried out at the Royal Society Mond Laboratory, Cambridge, England, and at the Institute for the Study of Metals, University of Chicago, Chicago, Illinois.

[1] G. Aschermann and E. Justi, Physik. Z. **43**, 207 (1942).

[2] B. B. Goodman, Nature **167**, 111 (1951).

[3] J. G. Daunt and J. W. Cobble, Phys. Rev. **92**, 507 (1953).

[4] A. Wexler and W. Corak, Phys. Rev. **85**, 85 (1952).

[5] J. K. Hulm, Phys. Rev. **94**, 1390 (1954).

[6] G. F. Hardy and J. K. Hulm, Phys. Rev. **93**, 1004 (1954).

[7] B. B. Goodman and E. Mendoza, Phil. Mag. **42**, 594 (1951).

[8] D. Shoenberg, *Proceedings of the International Conference on Fundamental Particles and Low Temperatures, Cambridge, 1946* (The Physical Society, London, 1947), Vol. 2, p. 85.

[9] Clement, Logan, and Gaffney, Phys. Rev. **100**, 743 (1955).

TABLE I. Characteristics of the rhenium specimens.

Specimen	Method of preparation	Main chemical impurities	ρ_0/ρ_{273}	T_c(°K)	Width of zero-field transition (°K)	Demag. coeff.		Frozen-in moment %
						n_s	n_m	
Re 1	Arc melting of Re powder	~1.5% W	0.0165	1.729	···	0.023	0.04	10–15
Re 2	Arc melting of Re powder	<0.05% W, trace of Cu	0.00068	1.698_7	···	0.021	0.023±0.002	5
Re 3*a*	Arc melting of Re powder	Probably the same as Re 2, since these specimens had identical chemical histories	0.0007	1.699_4	0.004	0.104	0.099±0.004	3
Re 3*b*	Re 3*a* ground to a cylinder	Same note as for Re 3*a*	0.0010	2.7_5	0.3	0.057[a]	···	Very large
Re 4*a*	Ellipsoid ground from an iodide crystal bar of Re[b]	Fe 0.0011%, Si<0.01%[c]	0.00134	2.4	···	0.031	···	Very large
Re 4*b*	Re 4*a*, after annealing at 1700°C for 1½ hr in H_2	Fe 0.0011%, Si<0.01%[c]	0.00132	2.3	···	0.031	···	Very large
Re 4*c*	Arc melting of iodide deposited crystal bar[b]	Fe 0.0011%, Si<0.01%, W 0.03%	0.026	1.81	0.05	0.028	0.07	~50
Re 5*a*[d]	Sintering of pure Re powder, followed by alternate cold swaging and annealing in pure H_2 at ~1600°C.	Not known for these particular specimens, but a typical analysis of specimens prepared by this method is as follows.[e] Cu 0.001% Si 0.02 Fe 0.03 Mg 0.03 Al 0.06 Ca 0.01 Mn 0.001 Mo 0.01 Total 0.16%	Probably the same order of magnitude as Re 6*a*	1.68	0.1	0.071[a]	0.08	20
Re 5*b*	Re 5*a* ground to an ellipsoid	Same note as for Re 5*a*	···	···	···	0.039	···	Very large
Re 5*c*	Re 5*b* annealed *in vacuo* ($p<10^{-6}$ mm Hg) for 4 hours at 1500°C.	Same note as for Re 5*a*	···	1.69	0.1	0.039	0.07	16
Re 5*d*	Re 5*c* annealed *in vacuo* ($p<5\times10^{-6}$ mm Hg) for ½ hour at 2000°C.	Same note as for Re 5*a*	0.223	2.0	0.2	0.039	···	Very large
Re 6*a*[f]	Sintering of pure Re powder followed by alternate cold swaging and annealing in pure H_2 at ~1600°C.	Same note as for Re 5*a*	0.0028	1.701	0.015	0.083[a]	0.14	40
Re 6*b*	Re 6*a* ground to an ellipsoid and then annealed in H_2 for ¾ hour at 1700°C.	Same note as for Re 5*a*	0.009	2.3	···	0.027	···	Very large

[a] Cylindrical specimen; n_s taken to be the same as for an ellipsoid of the same axial ratio.

[b] These iodide-deposited crystal bars were kindly supplied by Mr. Harry Croft of the Kennecott Copper Corporation.

[c] The crystal-bar rhenium was deposited on a tungsten wire, but it is assumed that no diffusion of the tungsten into the rhenium took place in the case of Re 4*a* and 4*b*. However, during the preparation of Re 4*c* by arc-melting, it must be assumed that the tungsten dissolved in the rhenium.

[d] This specimen was kindly supplied by Battelle Memorial Institute—bar No. 27.

[e] See reference 12, p. 125, specimens (*b*) and (*c*).

[f] This specimen was kindly supplied by Battelle Memorial Institute—bar No. 55 B-2.

were immersed in liquid helium and returned to the bath temperature in a time short compared with the period of the ballistic galvanometer. However, below 1°K, where the specimens were cooled by contact with a paramagnetic salt through a copper rod, somewhat longer times were required for the system to reach thermal equilibrium. While this effect could be important near T_c, it is unimportant at very low temperatures where H_c is practically independent of temperature. For this reason the ballistic measurements on ruthenium were confined to one very low temperature, 0.09°K; here the error in H_c due to this effect was estimated to be less than 3%.

B. Specimen Preparation

Samples of ruthenium and osmium and a few samples of rhenium were obtained from other laboratories as will be indicated in the discussion of the results. However, we prepared the rhenium samples which exhibited the most nearly ideal superconducting properties by melting in an arc furnace. Since these specimens were much purer than any described by previous workers, and in view of the very high melting point of rhenium (3180°C), it seems appropriate to discuss the preparation technique in some detail.

Rhenium is commercially available in the form of a very finely divided powder prepared at the University of Tennessee by the reduction of either ammonium or potassium perrhenate. The powder contained a few parts per thousand of silver, and of potassium when prepared from the potassium salt, plus a small amount of oil in some cases. Several five-gram samples prepared from potassium perrhenate compressed into slugs of diameter 6 mm and length 12 mm. These were placed end to end in a shallow groove milled in the flat top of a copper crucible in the electric arc furnace. By using a relatively small diameter electrode (6 mm) and low currents (about 60 amperes), it was possible to melt the rhenium slugs over a small region and to join them together. Surface tension caused the sample to contract somewhat and to thicken at its midpoint. This thickening was removed by cold-rolling down to the required 5-mm diameter, and finally the cracks and strains due cold-work were removed by repeated local melting in the arc furnace. The resulting specimen was a uniform rod of length 5 cm and diameter 5 mm.

A specimen Re 1 produced in this fashion, using a tungsten electrode, was found by spectrographic analysis to be free of silver and potassium but contained about 1.5% of tungsten. Thus, although the volatile impurities were driven off during arc melting, a part of the electrode evidently entered the sample. After superconducting studies had been carried out on Re 1, this sample was itself mounted as the arc furnace electrode[10] and used to prepare several other specimens, including Re 2, Re 3*a*, and Re 4*c*. Only traces of impurity could be detected in Re 2, amounting to less than 0.05% tungsten and faint traces of copper.

Since bulk rhenium metal is extremely tough and cannot readily be filed, drilled, or machined, even with the aid of tungsten carbide tools, the removal of a portion of the specimen rods for analysis was quite difficult. To overcome this problem, the spectrograph arc was struck directly to the end of the sample. It should be remarked that for the very pure sample Re 2, the relative intensities of various tungsten lines indicated that a difference of about a factor two between the tungsten contents at opposite ends of the sample. This may perhaps be due to the fact that movement along the sample of a region of local melting in the arc furnace causes a type of zone purification of the metal. There is, of course, little doubt that in the present work the main purification was due to boiling out of volatile impurities like potassium and silver, but it seems likely that this type of arc furnace preparation could readily be adapted to the zone-refining of high melting elements.

III. RESULTS AND DISCUSSION

A. Rhenium

We investigated the superconducting properties of rhenium samples prepared by three completely different methods, *viz.*, arc-melting, iodide deposition and powder metallurgy. The characteristics of the various samples are listed in Table I. In some cases the superconducting behavior was investigated before and after metallurgical treatment; successive stages in the treatment of these specimens are designated by small letters. We have included in the table values of n_s, the demagnetizing coefficient deduced from the shape of the specimen, and, for the better behaved specimens, n_m, the demagnetizing coefficient estimated from the slope of the B *vs* H or $4\pi M$ *vs* H curves in the intermediate state. Good agreement between these two quantities is evidence of ideal superconducting behavior, providing that the boundaries of the intermediate state are sharply defined and the frozen-in moment is negligible.

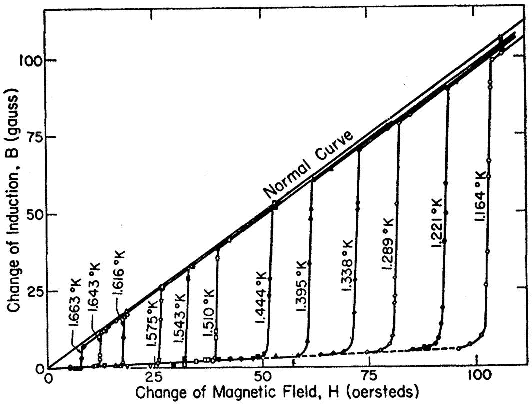

FIG. 1. B *vs* H curves for Re 2.

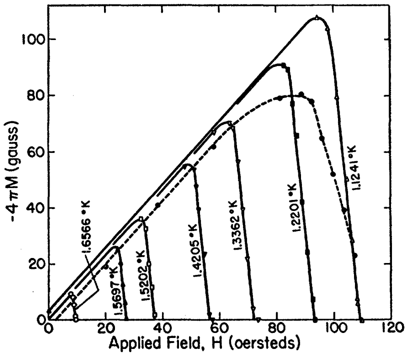

FIG. 2. Magnetization curves for Re 3*a*. Solid curves: increasing field, broken curve: decreasing field.

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[10] Rhenium may be wetted with "*EB*" silver solder.

1. Arc Melted Specimens

Of all the rhenium specimens investigated, Re 2 and Re 3*a* came closest to exhibiting ideal superconducting behavior. Typical *B vs H* curves for Re 2 are shown in Fig. 1, and typical magnetization curves for Re 3*a* are shown in Fig. 2. For both specimens the intermediate state region was quite sharply defined, with good agreement between n_s and n_m, while the frozen-in moments were only a few percent. The transition temperatures of the two specimens were both within a fraction of a millidegree of 1.699°K and the critical field results differed by only a percent or so; those for Re 2 are shown on an H_c *vs* T^2 plot in Fig. 3. It may be noted that the results do not quite lie on a perfect straight line, indicating that there is a departure from a parabolic temperature dependence of H_c.

Despite its 1.5% tungsten content the specimen Re 1 also exhibited fairly sharp transitions from the superconducting to the normal state in a magnetic field, as shown in Fig. 4. In this case, however, the intermediate state region was less well defined, particularly at the normal state end, while n_m was appreciably greater than n_s. There seems little doubt that the tungsten content of this specimen can be held responsible for the departures from ideal superconducting behavior. Furthermore, as may be seen in Fig. 3, the transition temperature of Re 1 was about 0.030°K higher than that of Re 2, and its critical magnetic field curve was raised correspondingly.

2. Iodide Deposited Specimens

Crystalline bars of iodide deposited rhenium were made available to us by Mr. H. Croft of the Kennacott Copper Company. These bars were about 5 mm in diameter and were made up of small dendritic crystals. since this material was not of a suitable shape for accurate magnetic measurements, an ellipsoidal specimen, Re 4*a*, was prepared by centerless grinding using carborundum wheels.

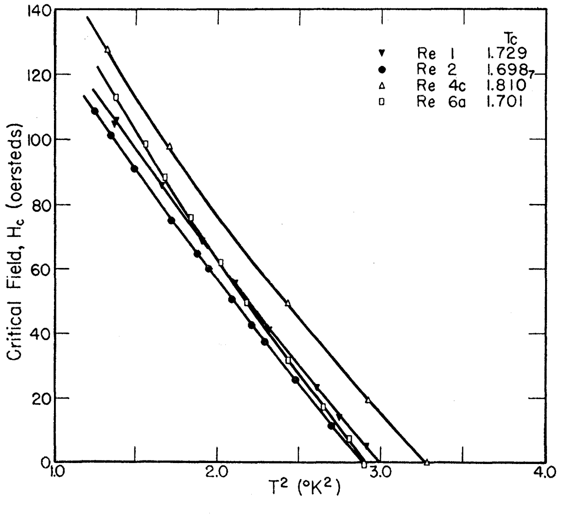

FIG. 3. H_c *vs* T^2 for several rhenium specimens.

The residual resistivity of this specimen was only about twice that of Re 2 and Re 3*a*. It was therefore somewhat surprising to find that the transition temperature of this specimen was 2.4°K, while fields considerably higher than in the case of Re 2 and Re 3*a* were necessary to initiate the destruction of superconductivity. Furthermore, the destruction of superconductivity by the field was extremely gradual, so that, even in fields of five times the initial penetration field, the magnetization had only been reduced to the order of one quarter of the maximum value. The nonideal magnetic behavior of this specimen is reminiscent of the behavior of impure or strained superconductors. Since it seems unlikely that chemical impurities (see footnote 2, Table I) could be held responsible for the poor magnetic properties of Re 4*a*, we are inclined to attribute the behavior to internal strains introduced during the grinding process.

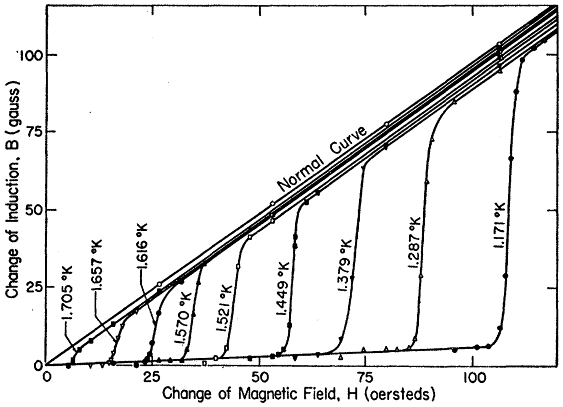

FIG. 4. *B vs H* curves for Re 1.

In order to further investigate this idea, another ground sample Re 3*b* was prepared by grinding the good arc-melted sample Re 3*a* into cylindrical form. As expected, the superconducting properties of the arc-melted sample were also greatly modified by grinding. Thus, the transition temperature was increased from 1.699°K to 2.75°K, the modified transition being spread over a region between 2.6° and 2.9°K. Moreover, at 1.1°K more than 10% of the superconducting magnetic moment still remained in a field of 800 oersteds and nearly 1600 oersteds were required to remove the last traces of superconductivity. The electrical resistivity of the sample in the normal state was increased by about 50%.

It should be pointed out that if the concentration of physical defects introduced into the lattice by grinding is high near the surface of the sample and tapers off in the interior, one might expect the magnetic properties to be much more greatly affected by grinding than the electrical resistivity in the normal state. Thus, if the specimen is regarded as consisting of a strained outer layer, with elevated transition temperature and critical field values, surrounding an unstrained core, it is clear that the outer layer would dominate the magnetic properties by shielding the inner core. On the other hand, the high electrical resistivity of the outer layer due to the high defect concentration would be largely ineffective owing to the presence of the low-resistivity, unstrained core in parallel with it.

The iodide deposited sample, Re 4*a*, was annealed for 1½ hours at 1700°C in pure hydrogen in an attempt to remove the strains introduced by grinding. The resulting specimen, Re 4*b*, had essentially the same properties as Re 4*a*. In contrast, the sample, Re 4*c*, obtained by arc melting another piece of the iodide crystal bar from which Re 4*a* was taken, had greatly improved superconducting properties. Nevertheless, the magnetization curves of this specimen, shown in Fig. 5, indicate that the departure from ideal behavior was more pronounced than for the very pure arc melted specimens Re 2 and Re 3*a*. Furthermore, from Fig. 3 it may be seen that the critical field curve of Re 4*c* was displaced upwards with respect to those of Re 1 and Re 2.

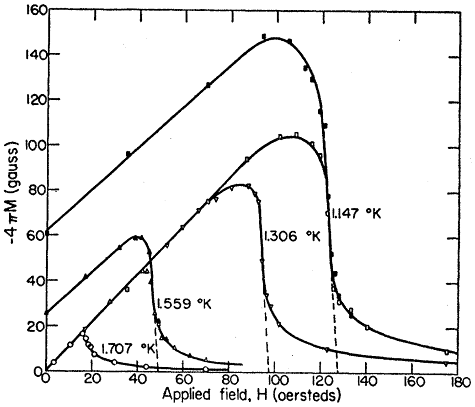

FIG. 5. Magnetization curves for Re 5*c* (field increasing). Open symbols: specimen initially in the virgin state; solid symbols: after several reversals of the field.

The behavior of Re 4*c* should in particular be compared with that of Re 1. Consistent indications of the poorer quality of Re 4*c* are provided by its higher residual resistivity, its broader intermediate state region and its higher frozen-in moment. It may also be noted that its transition temperature is appreciably higher than that of Re 1. It is not possible to attribute the poor behavior of Re 4*c* to its known chemical impurities, since the total chemical impurity content is only a fraction of that of Re 1; furthermore, on considering the individual impurities, the iron and silicon content of Re 4*c* seems to be less than the relatively good specimens Re 5*c* and Re 6*a*. The most reasonable conclusion seems to be that the arc melting did not extend completely through this sample and some regions of strained iodide deposited material were left in the interior.

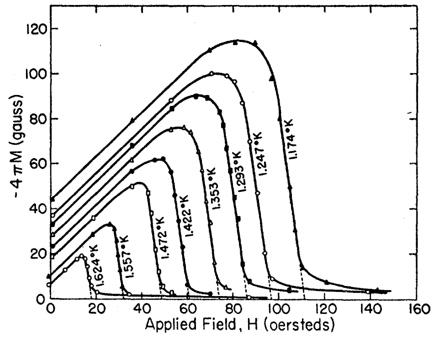

FIG. 6. Magnetization curves for Re 6*a*.

3. *Powder Metallurgy Specimens*

Two powder metallurgy specimens of rhenium, Re 5*a* and Re 6*a*, prepared by sintering compressed rhenium powder at high temperatures, were supplied by Battelle Memorial Institute. These specimens had been formed into cylinders by alternate cold swaging and annealing in pure hydrogen at 1700°C. This method of preparation was known to yield specimens whose density was within about 0.1% of the x-ray value.[11] Both samples became superconducting in the neighborhood of 1.7°K and their magnetization curves, which were quite similar, are typified by these shown in Fig. 6 for Re 6*a*. The observed values of H_c were only a few percent higher than for Re 2 and Re 3*a*, and the results for Re 6*a* are plotted in Fig. 3. While Re 6*a* exhibited the much more sharply defined transition, its frozen-in moment values were about twice those of Re 5*a*.

The specimens Re 5*b* and Re 6*b* were prepared by grinding the two powder metallurgy cylinders into ellipsoidal form. Just as in the case of the two arc melted and iodide deposited samples, this treatment produced very poor materials with anomalously high critical field and transition temperature values. The properties of Re 6*b* were hardly improved by annealing this sample in hydrogen for about ¾ hour at 1700°C. However, the sample Re 5*c* produced by annealing Re 5*b* at 1500°C in vacuum for four hours showed greatly improved magnetic behavior, slightly better than that of Re 5*a*. This treatment restored the transition temperature to the vicinity of 1.7°K.

Since one might expect that annealing rhenium metal at temperatures above its recrystallization temperature (*circa* 1300°C) would remove internal strains due to grinding, it is somewhat puzzling that our hydrogen-annealing treatment did not improve the superconducting properties of Re 4*b* and Re 6*b*, especially since hydrogen annealing has proved successful in producing strain-free samples at the Battelle Memorial

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[11] Wright Air Development Center, Technical Report 54-371, 1954 (unpublished), pp. 30–33.

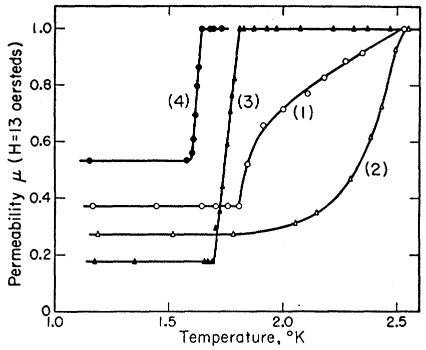

FIG. 7. Permeability of rhenium powder after successive stages of treatment: (1) as received, (2) after compressing under 10 tons per square inch, (3) after annealing *in vacuo* for 12 hours at 1460°C, and (4) after arc melting.

Institute. One possible explanation of this discrepancy is that carbon may have been introduced into samples Re 4*b* and Re 6*b* during the hydrogen anneal. In our furnace the specimens were held between rhenium supports in a graphite crucible, and it is possible that carbon was transferred to the specimens through the formation of gaseous hydrocarbons. In a separate series of experiments involving the preparation of rhenium compounds it was observed that although graphite is only slightly soluble in rhenium, probably less than 0.1%, the small amount which may be dissolved raises T_c to 2.7°K. A minute amount of carbon dissolved in the surface regions of the specimen might account for the poor superconducting properties observed after hydrogen annealing in the present work.

In an effort to further improve the superconducting behavior of Re 5*c*, this sample was subjected to a vacuum anneal for $\frac{1}{2}$ hour at 2000°C. The resulting sample, Re 5*d*, had a high residual resistivity and very poor superconducting properties akin to those of ground samples. The deterioration of the properties is thought to be due to the formation of voids in the sample due to the vaporization of low-boiling-point impurities (e.g., Mg and Ca) at the grain boundaries. Battelle workers[12] have observed such voids in similar powder metallurgical samples tested to 2200°C, and have noted that such samples are usually embrittled after treatment in this temperature region. Although no metallurgical examination of Re 5*d* was performed, in view of the high sensitivity of superconducting properties to internal strain, is reasonable to assume that some embrittlement occurred in the present case.

It is interesting to compare the above results with those of Aschermann and Justi,[1] who first reported superconductivity in rhenium. Working with a sintered bar with residual resistance equal to 0.017 of the ice-point value, these workers found a transition temperature of 0.95°K. Since the present work suggests that when rhenium is cold-worked, the transition temperature is raised above the value 1.7°K for a pure, strain-free sample, it seems an inevitable conclusion that the rather high residual resistance of Aschermann and Justi's sample was due to chemical impurities which also acted to depress the superconducting transition temperature.

4. *Unsintered Powder Specimens*

In measurements on unsintered, finely-divided powder samples of rhenium obtained from the University of Tennessee, Goodman[13] and Daunt and Smith[14] observed superconducting transitions in the vicinity of 2.2° and 2.4°K respectively. Since these samples were of quite high chemical purity, the anomalously high transition temperatures cannot be attributed to dissolved impurities, but are evidently in some way connected with the physical constitution of the powder.

In order to throw further light on the anomalous superconducting behavior of rhenium powder, a single powder sample prepared from ammonium perrhenate was tested for superconductivity under the following successive conditions: (1) as a loose powder, (2) as a compressed slug formed under 10 tons per square inch, (3) annealed *in vacuo* for 12 hours at 1464°C, and (4) melted in the arc furnace. In each case the induction B for a constant applied field of 13 oersteds was measured as a function of temperature. Figure 7 shows the temperature variation of the initial permeability B/H under these conditions. The variations of the limiting permeability μ_0 as T approaches zero, from one condition of the specimen to another, is simply due to variations in the leakage flux through the gap between the specimen and the detector coil windings.

Curve 1 for the loose powder indicates that, in agreement with the work of Goodman and Daunt and Smith, the superconducting transition is smeared out over the range 1.8° to 2.5°K, although from the steepness of the curve at its lower end it appears that the bulk of the powder becomes superconducting close to 1.8°K. However, from curve 2, although the transition of the compressed powder still extends from 1.8° to 2.5°K, the main expulsion of flux occurs at the upper end of the range, near 2.5°K. One possible explanation of this behavior is that in the compressed material the powder grains of high transition temperature shield those of low transition temperatures and prevent flux penetration into the latter. Alternatively, the strains in the compressed material may be such as to elevate the transition, as was believed to be the case for the earlier specimens just after grinding. If the second explanation were correct, one might expect an over-all shift of the transition curve, which does not occur. Thus the magnetic-shielding mechanism seems more likely in this case.

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[12] Wright Air Development Center, Technical Report 54-371, 1954, (unpublished), pp. 118–128.

[13] B. B. Goodman, National Bureau of Standards Circular 519 (U. S. Gov. Printing Office, Washington, D. C. (1952), p. 72.

[14] J. G. Daunt and T. S. Smith, Phys. Rev. 88, 309 (1952).

On annealing the powder sample at 1464°C, the transition curve was shifted down to about 1.76°K and was sharpened considerably (Curve 3). The further step of melting the specimen depressed the curve again by 0.14°K (Curve 4). It should be remarked that owing to the finite measuring field the midpoint of Curve 4 lies about 0.08°K below T_c for pure, bulk rhenium (Re 2 and Re 3*a*).

It is clear that before heat treatment the rhenium powder contains regions of anomalously high transition temperature, but that these regions may be removed by a suitable annealing procedure. In considering the nature of the anomalous regions, it has to be borne in mind that the powder is prepared by the reduction of ammonium perrheate crystals at about 300°C. Since this temperature lies well below the recrystallization temperature of rhenium metal (~1300°C), many of the rhenium crystallites produced in the reduction process may be expected to be small, very imperfect crystals. This raises the possibility that the elevated transition temperatures of such crystallites may be due either to imperfections or to their small size.

Now it was shown in our experiments on bulk rhenium specimens that surface grinding without subsequent annealing may raise the transition temperature to the value shown by the powder. Thus it seems unnecessary to postulate that the transition temperature of the powder crystallites is connected with their small size, and we are inclined, instead, to attribute the effect to imperfections in the crystallites. This conclusion is consistent with Shoenberg's[15] observations on colloidal particles of mercury. These particles were only a few hundred angstroms in diameter and were presumably quite strain-free, since they were cooled slowly through the freezing point of mercury. They became superconducting at a temperature close to the transition temperature of ideal macroscopic specimens of mercury. On the other hand, Buckel and Hilsch[16] have shown that small (~100 A edge) crystals of soft superconductors formed by condensing the metal on to a quartz plate at liquid helium temperatures have transition temperatures higher than those of the bulk metal. These authors also concluded that the elevated transition temperatures were due to imperfections in the crystallites rather than to their small size.

It is interesting to mention that Goodman[13] and Daunt and Smith's[14] measurements on the magnetization curves of rhenium powder both showed that the fields required to quench superconductivity completely were several times the initial penetration fields, as was the case of poorer bulk specimens in the present work. It is probably somewhat coincidental that Daunt and Smith's value for $(dH_c/dT)_{T_c}$, which was obtained by measuring the fields required for the complete quenching of superconductivity in the powder, agrees quite well with the data for pure, bulk rhenium. In the measurements of Goodman at 1.1°K, it was found that even at 500 oersteds the magnetization was still 20% of the maximum value. The magnetic behavior of this powder specimen was in fact similar to that found for Re 3*b*, thus providing further evidence that powder specimens of rhenium are likely to be made up of very imperfect crystals. Since it is clear that the magnetization curves of powder samples may be influenced by such factors as the imperfections in the constituent crystallites, their shape and size and also the distribution of these properties among the crystallites in the samples, the precise interpretation of such measurements is very difficult.

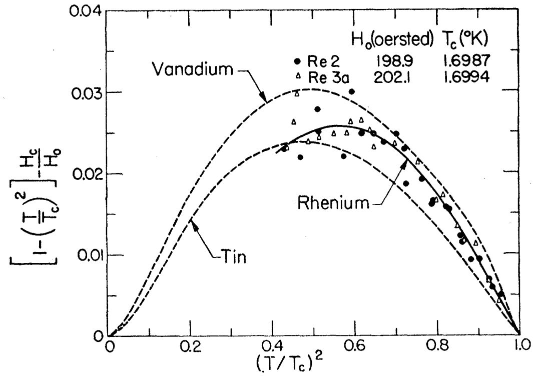

FIG. 8. Reduced deviations from a parabolic H_c *vs* T relationship for rhenium, tin, and vanadium.

5. *The H_c vs T Relationship for Pure Rhenium*

Since the specimens Re 2 and Re 3*a* showed the most nearly ideal superconducting behavior, they afford the most reliable values for the true critical field of rhenium. While these values of T_c may be somewhat high owing to the tungsten impurity content of the specimens, the uncertainty in T_c may be estimated from the effect of this impurity on the transition temperature of Re 1. Thus we find for pure rhenium: $T_c = 1.699 \pm 0.001$°K.

From Fig. 3 it is clear that the temperature dependence of H_c for Re 2 cannot be represented sufficiently accurately by a simple parabolic law of the type $H_c = H_0[1-(T/T_c)^2]$; this is equally true of the results for Re 3*a*. Clear departures from this type of relationship have already been noted for indium,[17] thallium,[17] tin,[17–19] and vanadium.[20] In fact, for these four superconductors the reduced deviations, $1-(T/T_c)^2-(H_c/H_0)$, were very similar.[19] The deviations for Sn and V are reproduced in Fig. 8, while the deviations for In and Tl, which are not shown, lay between these two curves.

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[15] D. Shoenberg, Proc. Roy. Soc. (London) **A175**, 49 (1940).

[16] W. Buckel and R. Hilsch, Z. Physik **131**, 420 (1952).

[17] E. Maxwell, Phys. Rev. **86**, 235 (1952); E. Maxwell and O. S. Lutes, Phys. Rev. **95**, 333 (1954).

[18] Lock, Pippard, and Shoenberg, Proc. Cambridge Phil. Soc. **47**, 811 (1951); Serin, Reynolds, and Lohman, Phys. Rev. **86**, 162 (1952).

[19] W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1956).

[20] Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. **102**, 656 (1956).

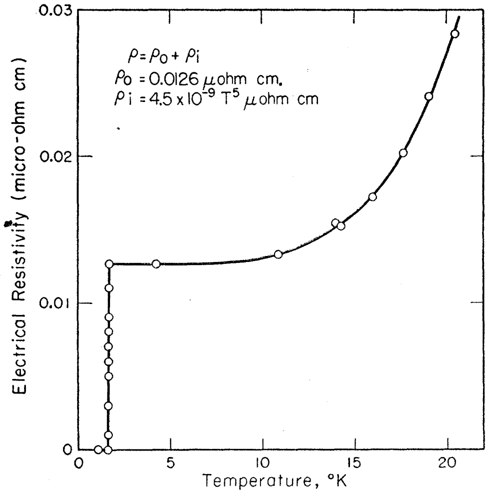

FIG. 9. The low-temperature resistivity of Re 2.

It therefore occurred to us to inquire whether, by means of a suitable choice of H_0, the results for rhenium could be made to result in a similar deviation curve. This proved possible and the resulting deviations are also plotted in Fig. 8; here the nonlinear relation between H_c and T^2 is shown more clearly. It was, however, necessary to choose slightly differing values of H_0 for the two specimens; for Re 2: $H_0 = 199.6$ oersteds, for Re 3*a*: $H_0 = 202.1$ oersteds. Since the transition temperatures of the two specimens agreed to within less than 0.1%, no difference in the values of H_0 was expected. Nor was such a difference expected to arise from the use of two different experimental arrangements for investigating the respective specimens, especially since in each case H_c was the field at the entry to the normal state, and thus no precise knowledge about the shapes of the specimens was necessary. Indeed the difference of 1.2% between the results may not be significant at all in view of the scatter of about 0.5% in the results for each specimen.

It seems, therefore, that the critical field of rhenium above 1°K can best be represented by the deviation curve in Fig. 8 with $T_c = 1.699 \pm 0.001$°K, $H_0 = 201 \pm 2$ oersteds. Furthermore, it is possible that over the whole temperature range down to 0°K the deviations of the critical field from a parabolic temperature dependence may be quite similar to those found for In, Tl, Sn, and V. But in the absence of measurements below 1°K, and in view of the quite different behavior shown by one superconductor, mercury,[19] this is still not certain; thus the above extrapolated value for H_0 may differ from the true value by perhaps 5 oersteds.

TABLE II. Electrical resistivity of Re 2 at various temperatures.

T °K	ρ micro-ohm cm	T °K	ρ micro-ohm cm	T °K	ρ micro-ohm cm
288	19.50	64	1.64	10	0.0130
273	18.58	20	0.0270	4	0.0126
78	2.62	15	0.0161	1.8	0.0126

For a superconductor whose electronic specific heat, C_{es}, is proportional to T^3:

$$VH_0^2/8\pi = \tfrac{1}{4}\gamma T_c^2, \qquad (1)$$

where V is the atomic volume. For the present results, with V = 8.84 cm³ mole⁻¹ at 0°K, this gives $\gamma = 1.97$ millijoule mole^{-1} deg^{-2}, whereas calorimetric measurements on rhenium[21] gave $\gamma = 2.45$ millijoule mole^{-1} deg^{-2}. However, from the deviations of the critical field from a parabolic temperature dependence, it is clear that C_{es} does not follow a T^3 law, and the consequent failure of Eq. (1) for rhenium, together with the uncertainty in H_0, might be sufficient to account for the discrepance between the present estimate of γ and the calorimetric value. Alternatively there may be a genuine difference between the value of γ for our best specimens and the value for the calorimetric specimen, arising from possible differences in the quality of the specimens.

TABLE III. Characteristics of the ruthenium specimens.

Sample No.	Form and method of preparation	Source	Main chemical impurities	ρ_0/ρ_{273}	T_c (°K)	Width of zero-field transition (°K)	n_s
Ru 1	Rod prepared by sintering of Ru powder in H_2 at 1150°C, and then *in vacuo* at 2200°C.	Lent by Prof. E. Justi	0.01% (Ca+Mg) trace of Cu	0.07	0.47	0.01	0.005
Ru 2	Fused button	Hereaus	~0.1%	0.06	0.47	0.01	0.26

6. *Electrical Resistivity of Rhenium*

The electrical resistivity of the purest rhenium sample, Re 2, was determined at various temperatures from room temperature down to the liquid helium range. Figure 9 shows the temperature variation of resistivity below 21°K, while Table II contains the mean values of resistivity at various selected temperatures. Owing to the slightly irregular shape of the specimen the absolute accuracy of these values may be no better than ~3%.

To obtain the electrical resistivity, ρ_i, due to scattering by lattice vibrations, the residual value ρ_0 measured just above the superconducting transition point was subtracted from each of the total resistivity values. The resulting data below 21°K could be well represented by the formula

$$\rho_i = 4.50 \times 10^{-9} T^5\ \mu\text{ohm cm}, \qquad (2)$$

with an uncertainty of about 0.2 in the exponent of

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[21] N. M. Wolcott, *Conférence de Physique des Basses Températures* (Centre National de la Recherche Scientifique and UNESCO, Paris, 1956), pp. 286–289.

T. By comparing Eq. (2) with the Bloch formula[22] and substituting the ice-point resistivity, a Debye temperature of 294°K was obtained. In addition, values of the resistivity at liquid nitrogen temperatures estimated from the Grueneisen-Bloch formula[22] with $\Theta = 294$°K were in agreement with the experimental values of Table II to within 2%. In view of the complex electronic structure of rhenium, it is surprising to find behavior in such good agreement with the free-electron model.

The present result may be compared with Θ values of 283°K and 310°K estimated by Aschermann and Justi[1] and Meissner and Voigt,[23] respectively, from resistance measurements on rather impure samples. Since the purest specimen studied by these workers had a residual resistivity 28 times greater than that of Re 2, the agreement between the various Θ values may be considered quite good.

While a single value $\Theta = 294$°K describes the variation of the electrical resistivity from 11°K to room temperature, specific heat measurements suggest that Θ falls from 450°K at 0°K to 318°K at 20°K,[21] and that at liquid nitrogen temperatures, it has reached 262°K.[24] In view of the well-known failure of the present theory to account for differences between the calorimetric and resistivity values of Θ in the monovalent metals, the present discrepancy is hardly surprising.

B. Ruthenium

In the course of measurements to determine whether various hitherto normal metals became superconducting below 1°K, ruthenium was found to become superconducting at 0.47°K. The characteristics of the two specimens are given in Table III.

The observations on Ru 1 are considered to be the most significant ones because of the low demagnetizing coefficient of this sample. The sample was supplied by Justi, who had already described its preparation and measurements of its electrical properties down to 1°K.[25] Values of the critical field measured by method 3 are shown in Fig. 10, where it is seen that $H_c = H_0[1-(T/T_c)^2]$ describes the results, with $H_0 = 46$ oersteds and $T_c = 0.47$°K. The specimen Ru 2 was investigated in the same manner, but owing to the smaller volume and larger demagnetizing coefficient of this specimen the field at the entry to the intermediate state could not be determined as precisely as for Ru 1. Nevertheless there is quite good agreement between the results for the two specimens.

In order to determine how close the superconducting behavior of Ru 1 was to being ideal, the complete magnetization curve shown in Fig. 11 was obtained at 0.09°K, using a modification of method 1. Measurements were not possible at appreciably higher temperatures owing to the more rapid warming of the salt-superconductor system. Because of the hysteresis shown by the specimen it is not possible to deduce H_c accurately, but a linear extrapolation of the falling part of the magnetization curve suggests a value of 38 oersteds. This figure should be compared with the value 44 oersteds obtained by method 3.

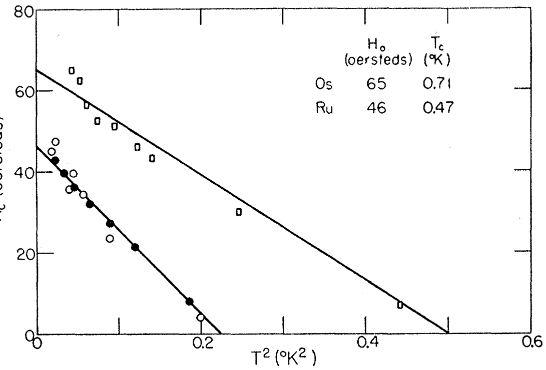

FIG. 10. H_c vs T^2 for ruthenium and osmium. Ru 1: ●; Ru 2: ○; Os 1: □.

At first sight it may seem surprising that the ballistic method yields a lower value for the penetration field than the ac susceptibility method. However, it is believed[26] that in nonideally-behaved superconductors there may exist a network of superconducting filaments with critical fields higher than that of the bulk metal. Thus the specimen will continue to exhibit zero resistance after a static field has begun to penetrate the specimen. So long as the specimen has zero electrical resistance, an alternating field is prevented from penetrating the specimen by currents induced in such a network of superconducting filaments, and it thus exhibits the alternating field susceptibility of a bulk superconductor. At 0.09°K the ac susceptibility of Ru 1 was found by method 3 to depart from the ideal superconducting state value at a field of 44 oersteds, and thus

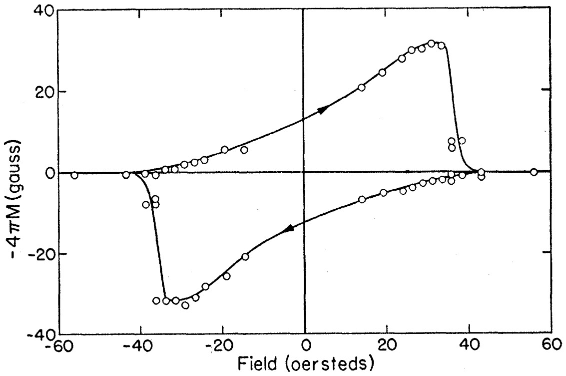

FIG. 11. Magnetization curve for Ru 1 at 0.09°K.

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[22] A. H. Wilson, *Theory of Metals* (Cambridge University Press Cambridge, 1953), second edition, p. 278.

[23] W. Meissner and B. Voigt, Ann. Physik **7**, 761 and 892 (1930).

[24] M. Horowitz and J. G. Daunt, Phys. Rev. **91**, 1099 (1953).

[25] E. Justi, Z. Naturforsch. **4a**, 472 (1949).

[26] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), second edition, pp. 37–47.

TABLE IV. Characteristics of the osmium specimens.

Sample No.	Form and method of preparation	Source	Purity	ρ_0/ρ_{273}	T_c(°K)	Width of zero-field transition (°K)	n_s
Os 1	Fused button	Hereaus	99.9%	0.04	0.71	0.02	0.19
Os 2	Sintered rod	Johnson-Matthey	V. pure	<0.1		see text	0.004
Os 3	Powder	Johnson-Matthey	V. pure	···	0.4	0.2	···

at this field the network of superconducting filaments was sufficiently broken up for the normal resistance to begin to reappear. From Fig. 9 it may be seen that this is also approximately the field at which the penetration by a static field approached completion, in qualitative agreement with previous work[26] on the restoration of the resistance in nonideally-behaved superconductors.

While small alternating fields are unable to penetrate a nonideal superconductor until the superimposed steady field reaches the critical field of the filaments, the static field itself may penetrate the specimen at appreciably lower fields. This can probably be explained as follows.[26] When the steady field is raised above the critical field of the bulk of the specimen, the shielding currents tend to concentrate in the superconducting filaments in such a way that their average field inside the specimen would continue to cancel the applied field. Since the filaments are believed to be extremely thin and to occupy only a small fraction of the volume of the specimen, the local fields at the filament boundaries would then become much greater than the applied field, possibly leading to the destruction of superconductivity in some of them. Thus the shielding field in the specimen produced by these currents can only be a very small fraction of the critical field of the filaments themselves. In the ac method an adequate shielding field was ensured since the alternating field to be excluded from the specimen was very small ($\sim$1 oersted), but the superconducting filaments evidently cannot exclude a steady field which is appreciably greater than the critical field of the bulk of the specimen. Thus there is reason to believe that the critical field values for Ru 1 obtained by method 3 are too high.

It is of interest to compare the behavior of Ru 1 with the rhenium specimens prepared by powder metallurgy, especially since these two elements are chemically similar. Ru 1 may first be compared with a sintered rhenium specimen which we prepared ourselves [curve (3), Fig. 7]. This rhenium specimen was much less well compacted than Ru 1 and it exhibited correspondingly poorer superconducting behavior, with a transition temperature 0.15°K higher than the ideal value for rhenium. On the other hand the specimens Re 5*a*, Re 5*c*, and Re 6*a*, which each exhibited superconducting behavior only slightly better than that of Ru 1, all exhibited transition temperatures which were within 0.01°K of the ideal value for rhenium. It therefore seems unlikely that the transition temperature of Ru 1 differs from the ideal value for this superconductor by more than a few hundredths of a degree. This conclusion is reinforced by the fact that Ru 2, which was prepared by quite a different method, exhibited a fairly sharply defined transition at the same temperature.

With respect to the critical field of pure ruthenium the position is somewhat less satisfactory. The experience gained with the rhenium specimens suggests that the critical fields measured for Ru 1 may be somewhat high, and, as has been pointed out above, the ac susceptibility method for determining H_c is also likely to result in values which are too high. Thus despite the agreement between the results for Ru 1 and Ru 2, the true value of H_0 may be somewhat less than the value determined, 46 oersteds.

On the other hand, according to Eq. (1) (which is unlikely to be in error by more than a few percent), the present results give $\gamma = 1.2$ millijoule mole^{-1} deg^{-2}, which is substantially less than the calorimetric value,[21] 3.35 millijoule mole^{-1} deg^{-2}, thus suggesting that the present critical field values may be too low. Clearly, further experiments are needed to resolve this discrepancy.

C. Osmium

Three specimens of osmium, whose characteristics are given in Table IV, were each found by method 3, to become superconducting below 1°K. Superconductivity had not been observed previously in this element.

The results for Os 1 are shown in Fig. 10 in an H_c *vs* T^2 plot. It can be seen that the results may be described by $H_c = H_0[1-(T/T_c)^2]$ with $H_0 = 65$ oersteds and $T_c = 0.71$°K.

The sintered rod Os 2 was not fully compacted, and was rather fragile. This specimen was found to have a rather broad zero-field transition, beginning fairly sharply at 0.51°K, but extending down to about 0.3°K. At 0.15°K superconductivity was destroyed over the range of longitudinal fields extending from 30 to 40 oersteds. Therefore both H_0 and T_c were appreciably lower for Os 2 than for Os 1.

In order to cool the powder specimen, Os 3, below 1°K it was contained in a sealed-off german silver tube which was in thermal contact with the salt, and which contained enough helium to ensure the powder would be covered with liquid below 1°K. A correction was applied for the magnetic behavior of the empty tube. Detailed observations on Os 3 were difficult to make. However, the zero-field transition appeared to cover the same temperature range, 0.5 to 0.3°K, as for Os 2. The destruction of superconductivity by a magnetic field at 0.15°K, while being half complete at 30 oersteds, (compare 35 oersteds for Os 2) was only 75% complete at 100 oersteds.

In attempting to understand the behavior of the osmium specimens it may be surprising, in view of the present work on rhenium powder and the work of

Buckel and Hilsch,[16] that the transition temperatures of Os 2 and Os 3 are lower than that of Os 1. Although the low transition temperatures of Aschermann and Justi's sintered rhenium specimen may be due to impurities, there is no reason to believe that Os 2 and Os 3 were less pure than Os 1. In fact the reverse may be the case, and in fact the possibility of the 0.1% unknown impurity content of Os 1 being responsible for its higher transition temperature cannot be ignored. For example, the addition of 1% rhodium to zirconium raised its transition temperature by about 2°K.[27] Thus, while the superconductivity of osmium has definitely been established, magnetization measurements on specimens of osmium of more well established purity are necessary for more accurate information on its true critical field curve. The need for further experiments is confirmed by the discrepancy between the value of γ deduced from the present results using Eq. (1), 1.1 millijoule mole^{-1} deg^{-2}, and the calorimetric value,[21] 2.35 millijoule mole^{-1} deg^{-2}.

IV. CONCLUSION

While previous experimenters working with impure samples of rhenium have reported superconducting transitions at 0.95°, 2.2°, and 2.4°K, the present work on pure, strain-free rhenium indicates that the correct superconducting transition temperature of the metal is 1.699°±0.001°K. Measurements on samples of ruthenium and osmium which were not as well characterized metallurgically as the rhenium samples suggest that these metals become superconducting at 0.47°K (Ru) and 0.71°K (Os).

It has been customary[28] to classify the superconducting elements according to certain properties they exhibit and their position in the periodic table. Thus the "soft" superconductors, in groups 2*B*, 3*B*, and 4*B*, were mechanically soft and specimens showing nearly ideal superconducting behavior could readily be prepared; the initial slopes of their critical field curves lay between 100 and 200 oersteds per degree. On the other hand, for the "hard" superconductors, in groups 3*A*, 4*A*, 5*A*, and 6*A*, the specimens were generally mechanically hard and exhibited very nonideal magnetization curves; the initial slopes of their critical field curves were appreciably greater than for the soft superconductors. In addition, there are the four elements technetium, rhenium, ruthenium, and osmium, in groups 7*A* and 8, in which superconductivity was only recently discovered.

TABLE V. $(dH_c/dT)_{T_c}$ for the superconducting elements in the periodic table. The sources of these values are given in the table footnotes. In view of the possible departures from a parabolic H_c *vs* T relationship, the values obtained from $2H_0/T_c$ and $(8\pi\gamma/V)^{\frac{1}{2}}$ may be slightly different from the true values of the initial slope.

3*A*	4*A*	5*A*	6*A*	7*A*	8	2*B*	3*B*	4*B*
							Al 177[a] 190[b]	
	Ti 280[b]	V 436[c] 470[d]				Zn 116[a] 122[b]	Ga 91[a]	
	Zr 170[c] 226[b]	Nb 453[d]		Tc ···	Ru 196[a] 314[b]	Cd 103[a] 116[b]	In 146[c] 154[d]	Sn 151[c] 152[d]
La 274[d]	Hf 217[b]	Ta 320[c] 334[d]		Re 214[c] 260[b]	Os 183[a] 264[b]	Hg 197[c]	Tl 130[c] 139[d]	Pb 200[c]
	Th 191[c] 242[b]		U 470[b]					

[a] $2H_0/T_c$.
[b] $(8\pi\gamma/V)^{\frac{1}{2}}$, where V is the atomic volume.
[c] Direct measurement.
[d] From the specific heat discontinuity at T_c, using Rutger's formula.

As a result of recent measurements, both calorimetric and magnetic, values of $(dH_c/dT)_{T_c}$ are now available for most of the superconducting elements, and it is therefore possible to see whether these values given in Table V are consistent with the classification described above. It is apparent that for many elements there remain significant discrepancies between the values obtained by different methods, possibly arising either from the invalid assumption of a parabolic H_c *vs* T relationship or from genuine differences in the qualities of the different specimens. However, since our interest is focused upon the broad features of the distribution of values of $(dH_c/dT)_{T_c}$ among the elements, a detailed discussion of these discrepancies will be omitted here.

Table V shows that while the values of $(dH_c/dT)_{T_c}$ tend to be higher for the transition metal superconductors than for the nontransition-metal superconductors, it is no longer possible to maintain a clear division of the superconducting elements on the basis of this parameter. In particular, the recently discovered superconductors which form the subject of this paper have intermediate values of $(dH_c/dT)_{T_c}$.

The suggestion that the classification into "hard" and "soft" superconductors might be open to question was in fact made by Shoenberg,[29] who studied the properties of a rather pure specimen of iodide-deposited[4] thorium. Whereas according to the periodic table thorium falls among the "hard" superconductors, Shoenberg's specimen was mechanically soft and exhibited nearly ideal magnetization curves, with a value of $(dH_c/dT)_{T_c}$ of only 191 oersteds per degree. In the present work it has been found that arc-melted specimens of rhenium, which are extremely hard, nevertheless exhibit nearly ideal superconducting behavior, akin to that of the "soft" superconducting elements such as tin and indium. On the other hand, extensive studies of other transition elements such as niobium and vanadium have failed to reveal any metallurgical treatment which produces superconducting properties even approaching ideality. Intermediate behavior is found in tantalum; for

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[27] B. T. Matthias, Phys. Rev. **97**, 74 (1955).
[28] Reference 26, p. 9.
[29] D. Shoenberg, Proc. Cambridge Phil. Soc. **36**, 84 (1940).

the best specimen of this element so far investigated,[30] nearly ideal magnetic behavior was found but the resistance was restored only at appreciably higher fields. Thus, the transition element superconductors exhibit a considerable range in the degree to which their superconducting properties approach ideality.

Among the nontransition-element superconductors, similar differences in behavior are also found. Thus, tin and indium show almost perfect superconducting behavior, but the best specimens of lead so far investigated, while showing ideal magnetic transitions, require appreciably higher fields for the restoration of their normal resistance.[31,32]

Thus, we feel that there are no strong grounds for retaining the classification of superconductors into two fundamentally distinct classes, "hard" and "soft," at least in the previously accepted sense of this classification. Instead, we shall attempt to explain the differences in the degree of approach to ideal superconducting behavior among the elements in terms of their metallurgy and method of preparation. First we note that Wexler and Corak[4] attribute the poor superconducting behavior of their vanadium specimens to small amounts ($\sim$0.05%) of nitrogen and oxygen dissolved in the crystal lattice. These residual impurities are supposed to set up inhomogeneous strains in the lattice, similar to the strains produced by cold work. Whereas the strains due to cold work can be removed by suitable annealing treatment, the relatively high solubility of gases in vanadium makes it practically impossible to remove residual amounts in the neighborhood of a few hundredths of one percent, even by annealing in very high vacuum. This difficulty is, however, not universally present for the transition elements since the solubility of nitrogen and oxygen in these elements decreases rapidly as one moves from left to right along a given row of the periodic table.[33] This is mainly due to a decrease in volume of the holes in the lattice, although other factors such as the strength of the lattice also enter the situation. If the change in solubility which occurs along a row for Group $4A$, $5A$, and $6A$ elements[33] may be extrapolated to Group $7A$, for which no data are available, it is not unreasonable to expect the solubility of oxygen in a Group $7A$ metal such as rhenium to be at least 1000 times lower than in a Group $4A$ metal such as titanium and at least 100 times lower than in a Group $5A$ metal such as vanadium. Thus even when rhenium is melted in the argon arc furnace (where the impurity content is much larger than in a high vacuum furnace) the amounts of oxygen and other gaseous impurities dissolved in the sample are not large enough to produce poor superconducting behavior. This low impurity content is confirmed by the extremely low residual resistance ratio, 0.00068, found for a good arc-melted rhenium sample. In contrast, the best vanadium sample of Wexler and Corak, prepared by iodide decomposition, had a residual resistance ratio of 0.051.

It seems probable that the behavior of the thorium specimens investigated by Shoenberg[29] may also be understood in terms of their dissolved gas content. Since nitrogen and oxygen dissolve readily in this metal, it is not surprising that Shoenberg found poor superconducting behavior in a specimen which had been prepared[4] by calcium reduction of the oxide, followed by powder metallurgy. However, his nearly ideal specimen, referred to above, was prepared by iodide deposition,[4] which it is safe to assume afforded little opportunity for the introduction of gaseous impurities into the lattice. Little is known about the history of the tantalum specimen measured by Preston-Thomas[30] beyond the fact that it was annealed *in vacuo* for 100 hr at 2500°C, i.e., 350°C below its melting point. It is possible that at this very high temperature dissolved gases may be removed from tantalum, but unfortunately the thermodynamic data necessary to test this hypothesis do not seem to be available.

Although our work indicates that dissolved gases are not troublesome as regards the superconducting properties of rhenium, we have shown that cold work has an effect on these properties which is even more dramatic than in the case of other transition metals. Thus surface grinding rises the transition temperature of rhenium by nearly 1°K and raises the field required to quench superconductivity at a given temperature by almost an order of magnitude. However, these changes can be almost completely reversed by annealing the metal at temperatures between 1500° and 2000°C. It is worth noting that Lasarew and Galkin[34] produced even larger changes of the above type in the properties of mechanically soft superconductors such as tin by severely straining the material at low temperatures; here the external forces were maintained during the superconducting measurements. Owing to the comparatively low crystallization temperatures of soft superconductors, it is apparently not possible to introduce enough cold work at room temperature to materially affect their superconducting behavior. However, it would be interesting to try to work harden these metals at low temperatures to see whether their superconducting properties could be substantially altered without the continuous application of external forces.

Finally, we conclude that the anomalous properties of rhenium powder prepared by the reduction of perrhenates is closely connected with the effects of cold work mentioned above. This method of preparation is believed to yield highly strained crystallites containing large numbers of lattice defects, since the transition temperature and critical field values for the powder are

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[30] H. Preston-Thomas, Phys. Rev. **88**, 325 (1952).

[31] D. K. C. MacDonald and K. Mendelssohn, Proc. Roy. Soc. (London) **A200**, 66 (1949).

[32] H. Preston-Thomas, Can. J. Phys. **30**, 626 (1952).

[33] A. U. Seybolt and R. L. Fullman, Trans. Am. Inst. Mining Met. Engrs. **200**, 548 (1954).

[34] B. G. Lasarew and A. A. Galkin, J. Phys. (U.S.S.R.) **8**, 371 (1944).

raised to about the same extent as the corresponding quantities for the ground bulk samples. The assumption that the crystallites are highly strained is certainly plausible in view of the fact that the metal grains are formed at about 300°C, which is much too low a temperature for stress relief to occur in rhenium. The present work re-emphasizes the point that caution must be used in interpreting transition-temperature and critical-field data obtained on samples with a low degree of crystalline perfection, since such results may not reflect the ideal properties of the metal. Of course, such difficulties are likely to arise only for high melting materials such as the transition metals and their compounds and alloys, and it is even possible that the production of highly strained specimens could be turned to advantage as a means of attaining even higher transition temperature than those at present available.

ACKNOWLEDGMENTS

We would like to thank Professor E. Justi, of the Physikalisches Institut der Technischen Hochschule, Braunschweig, Mr. H. Croft, of the Kennecott Copper Company, and Mr. R. I. Jaffe, of Battelle Memorial Institute for supplying us with some of our specimens. We are also grateful to Mr. S. Foldes and Mr. H. Charbnau for helping with the arc melting of rhenium.

PHYSICAL REVIEW VOLUME 106, NUMBER 4 MAY 15, 1957

Photoelectric Emission from Single-Crystal KI

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(Received February 4, 1957)

Photoelectric emission measurements were made on single crystals of KI. Yield curves, obtained after irradiation in the first fundamental absorption band, are similar to those observed on evaporated films and the features are attributed to direct ionization and exciton-induced emission from F centers of density $\sim 10^{18}$ cm^{-3}, only 10 times lower than for films. At 80°K additional structure appears. A small yield for quantum energy below 2.5 ev is attributed to the presence of F' centers. At 5.5 ev, the position of β-band absorption, a small peak is observed. An inversion in the exciton-induced emission yield at 5.8 ev is associated with the sharply peaked surface reflectivity. While the ratio of exciton-induced to direct ionization is slightly higher in crystals than in films, the effective cross section for exciton-induced ionization is still $<10^{-14}$ cm^2; thus, the photoemission provides direct evidence for energy transfer from excitons but not necessarily for migration.

INTRODUCTION

PHOTOELECTRIC emission from evaporated films of KI and RbI have been investigated by Apker and Taft in the energy region below 6 ev.[1] They observed emission from deliberately introduced F centers, of density about 10^{19} cm^{-3}, by the mechanisms of direct ionization and exciton-induced emission. In the latter process excitons are formed by radiation in the region of fundamental absorption and transfer energy to F-center electrons, causing their ejection to the vacuum.

This paper reports photoelectric emission data on cleaved KI single crystals. These are of interest as they are free of the gross disorder inherent in evaporated films.[2] Yield curves are similar to those of evaporated films. F-center concentrations, produced by irradiation in the first fundamental absorption band, are only 10 times lower. At 80°K several additional features are present which substantiate earlier observations on thin films.

EXPERIMENTAL TECHNIQUES

Photoelectric emission measurements were made in cylindrical diodes which have been described before.[3] Crystals,[4] of general size 10×10×1 mm, were firmly held on a platinum disk by means of 4 platinum tabs. For measurements at 80°K larger phototubes incorporating a liquid nitrogen chamber were used. The crystals were clamped to a gold-plated copper extension from the coolant reservoir. Slight modifications in some of the tubes included the presence of a platinum filament evaporator for KI and a side arm containing a pellet of potassium.

Crystals were freshly cleaved prior to mounting. Standard vacuum procedures were employed with bake temperatures limited to 300°C. Several tubes contained crystals which had previously been heated at about 500°C in the presence of either excess potassium or excess iodine in sealed quartz vessels.

Photocurrents were measured by observing the transient response of a galvanometer upon application

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[1] L. Apker and E. Taft, Phys. Rev. 79, 964 (1950); 81, 698 (1951); 82, 814 (1951).

[2] D. L. Dexter and W. R. Heller, Phys. Rev. 84, 377 (1951).

[3] Apker, Taft, and Dickey, J. Opt. Soc. Am. 43, 78 (1952).

[4] The KI was obtained in crystalline form from Harshaw Chemical Company.