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Superconductivity in Binary Alloy Systems of the Rare Earths and of Thorium with Pt-Group Metals

T. H. GEBALLE, B. T. MATTHIAS,* V. B. COMPTON, E. CORENZWIT,
G. W. HULL, JR., AND L. D. LONGINOTTI
Bell Telephone Laboratories, Murray Hill, New Jersey

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Superconductivity has been discovered in many binary systems composed of transition metals having nearly empty and nearly filled *d* shells. With the exception of the Sc-Pt and Ce-Rh systems, all contain at least one superconducting phase and frequently more. By comparing the transition temperatures of analogous compounds, it is inferred that pure Rh should become superconducting above 10 mdeg and pure Pt at a considerably lower temperature.

I. INTRODUCTION

DURING the last few years there has been a substantial increase in the number of elements and compounds that are superconducting above 0.1°K. With this temperature as a lower limit, the majority of the metallic elements are either superconducting or ferromagnetic. Therefore, the question arises why some of the elements have not shown either of the phenomena at this low temperature. It seems possible that the conduction electrons in these elements will also undergo a condensation of one kind or another, if the metal is in a pure state and at low enough temperatures.[1]

The purpose of the present investigation is to search for superconductivity in some of the transition elements which do not as yet have magnetic or superconducting ground states at low temperatures. These include the three elements of the 3rd column, Sc, Y, and Lu; one element of the 9th column, Rh; and two elements of the 10th column, Pd and Pt. The occurrence of ferromagnetism in Sc–In alloys[2] and superconductivity in dilute solutions[3] of Cr in Sc may be considered an indication of the ambivalent nature of Sc. The superconductivity of solid solutions of Y with La and with Th and solid solutions of Lu with La have been studied.[4,5] Since the data are not in the dilute solution range, it is not possible to predict whether Y and Lu will be superconductors. Preliminary results for the Y–Rh and Y–Ir systems have been reported.[6] All the dilute solid solutions in Rh investigated to data are not superconducting. The solutes include Cr, Mo, Ru, and Os.[7]

Since the method of studying superconductivity of dilute solutions as a function of composition was successful in suggesting the occurrence of superconductivity in Mo [8] and in Ir,[9] this technique was again used in the present study. However, since the solid-solution range was not expected to be very large, compounds which are rich with respect to the metal in question, namely Sc, Y, Lu, Rh, Pd, and Pt were also prepared. Since Rh and Ir are in the same column in the periodic table and Ir is a superconductor at 0.14°K,[9] a comparison of the superconducting transition temperatures of Rh-rich phases with the corresponding Ir-rich phases might also suggest a possible T_c for Rh. For this reason solid solutions and compounds containing Ir are also included. The occurrence of superconductivity in Co alloys was briefly investigated to gain some insight into the effect of the ferromagnetic element of the 9th column. In addition, alloys with Ce and Th in place of the group-III elements were prepared to determine the effect of a variation in the number of valence electrons.

II. EXPERIMENTAL TECHNIQUES

The materials used in the preparation of the samples were of high purity; representative analyses are given in Table I. The alloy samples, weighing about 0.3 g, were prepared in an arc furnace in an argon atmosphere. In most cases, the weight loss during melting was not appreciable and the nominal compositions given are considered reliable to ±1%. The samples were examined for superconductivity to 0.32°K using the resonant-frequency shift circuit of Schawlow and Devlin[10] and a measuring frequency of 16 kc/sec. This method which has been described previously[11] is sensitive to traces of superconductivity and is convenient. Volumes as small as 10^{-4} cm^3 that are shielded by superconducting currents can be detected. The frequency shift and loss

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* Present address: University of California, La Jolla, California.

[1] H. B. G. Casimir, Z. Physik **171**, 246 (1963).

[2] B. T. Matthias, A. M. Clogston, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. Letters **7**, 7 (1961).

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[5] K. A. Gschneidner, Jr., and B. T. Matthias, in *Rare Earth Research*, edited by E. V. Kleber (The Macmillan Company, Inc., New York, 1961), p. 158.

[6] B. T. Matthias, T. H. Geballe, V. B. Compton, E. Corenzwit, and G. W. Hull, Jr., Rev. Mod. Phys. **36**, 155 (1964).

[7] B. T. Matthias and T. H. Geballe, (unpublished results).

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

[9] R. A. Hein, J. W. Gibson, B. T. Matthias, T. H. Geballe, and E. Corenzwit, Phys. Rev. Letters **8**, 408 (1962).

[10] A. L. Schawlow and G. E. Devlin, Phys. Rev. **113**, 120 (1959).

[11] T. H. Geballe, B. T. Matthias, G. W. Hull, Jr., and E. Corenzwit, Phys. Rev. Letters **6**, 275 (1961).

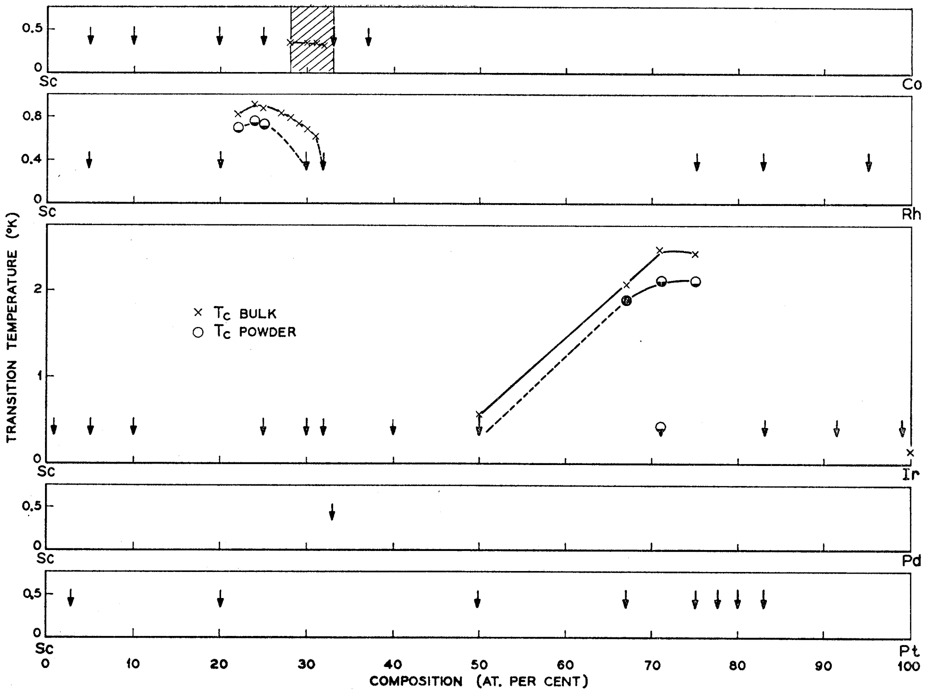

FIG. 1. Superconductivity in Sc alloys of Co, Rh, Ir, Pd, and Pt. Alloys in the shaded portion of the Sc–Co plot contain a small amount of a superconducting phase. In all the figures the amount of shading in the open circles indicates the approximate fraction of the sample which is superconducting. A completely shaded circle means that the entire sample is superconducting. In all the figures the arrows indicate that the alloys are not superconducting above 0.32°K.

characteristic of all transitions were recorded as a function of temperature.

All samples were measured in the bulk form as prepared in the arc furnace. In cases where superconductivity was detected, the sample was powdered and a known volume of loosely-packed particles of about 0.01 cm in size was again measured. This was done in order to determine whether the phase in question is superconducting or whether the phenomenon is caused by filaments or traces of another phase within the immediate composition range. In the crushing process, the connecting paths are usually broken and the remaining signal is expected to be that of the atom fraction which is superconducting. Comparison of the powder results with those of heat capacity measurements verify this correlation.[12] The estimated uncertainty of the powder method in determining the superconducting fraction is about 20%. This uncertainty is due partly to a variable packing factor for the powder and partly to insufficient disruption of the

TABLE I. Source of supply and analysis of raw materials.

Metal	Form	Supplier	Analysis
Sc	Rod	United Mineral & Chemical Corporation	99.98+%.
	Rod	Johnson, Matthey & Company, Ltd.	0.001% Y; 0.1% Ta; 100 ppm Ag; 40 ppm Pb; 30 ppm Fe; 10 ppm Cu; 5 ppm Al; 3 ppm Mn; 3 ppm Si; 1 ppm Mg.
Y	Rod	Research Chemicals, Inc.	Specially purified—none available.
La	Rod	Research Chemicals, Inc.	98–99%.
Lu	Rod	Johnson, Matthey & Company, Ltd.	0.01% rare earth metals; 20 ppm Si; 10 ppm Al; 20 ppm Ag; 5 ppm Cu.
Ce	Rod	Research Chemicals, Inc.	None available.
Th	Crystal bar	Metal Hydrides, Inc.	32 ppm O_2; 20 ppm N_2; 8 ppm H_2; 20 ppm C; 3 ppm Al; 23 ppm Fe; 12 ppm Cu; 2 ppm (Mg, Ca, Si, Mn, Cr, Ni, Ti, and B).
Co	Sponge	Johnson, Matthey & Company, Ltd.	None available.
Rh	Sponge	Engelhard Industries, Inc.	99.95%.
	Sponge	Johnson, Matthey & Company, Ltd.	3 ppm Fe; 2 ppm Si; 1 ppm Ca; 1 ppm Na; <1 ppm Cu, Mg, Ag.
Ir	Sponge	Johnson, Matthey & Company, Ltd.	2 ppm Si; 2 ppm Na; <1 ppm Ca, Cu, Mg, Ag.
Pd	Sponge	Engelhard Industries, Inc.	99.99%.
Pt	Wire	Johnson, Matthey & Company, Ltd.	3 ppm Pd; 2 ppm Si; 2 ppm Fe; 1 ppm Pb; <1 ppm Ca, Cu, Au, Mg, Ag.

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[12] We are indebted to J. P. Maita for the heat capacity measurements.

Table II. Superconducting compounds.

Compound	T_c °K	Structure type[a]	Crystal structure data System	a, Å	b, Å	c, Å
$ScIr_2$	2.07	$C15$	Cubic	7.347		
$ScIr_{2.5}$	2.46	$C15$	Cubic	7.343		
Y_3Rh	0.65					
Y_3Rh_2	1.48					
YRh_3	1.07	$C15$	Cubic	7.424		
YRh_5	0.56					
Y_3Ir_2	1.61					
$Y_{0.35}Ir_{0.65}$	1.38	$C15$	Cubic	7.525		
YIr_2	2.18; 0.88	$C15$	Cubic	7.500–7.520		
	1.09	$C15$	Cubic	7.518		
$Y_{0.31}Ir_{0.69}$	1.98; 1.44[b]	$C15$	Cubic	7.501		
$Y_{0.30}Ir_{0.70}$	2.16[b]	$C15$	Cubic	7.501–7.512		
YIr_3[c]	3.50					
Y_7Pt_3	0.82	$D10_2$	Hexagonal	9.864		6.299
Y_3Pt_2	0.90					
$YPt_{2.2}$	1.70	$C15$	Cubic	7.576		
La_3Co	4.01	$D0_{20}$	Orthorhombic	7.279	10.088	6.578
La_7Rh_3	2.58	$D10_2$	Hexagonal	10.145		6.434
$LaRh_3$	2.60					
$LaRh_5$	1.62					
La_7Ir_3	2.24	$D10_2$	Hexagonal	10.235		6.473
$LaIr_2$	0.48[b]	$C15$	Cubic	7.686		
$LaIr_3$	2.46					
$LaIr_5$	2.13					
$LaPt_2$	0.46	$C15$	Cubic	7.776		
$La_{0.28}Pt_{0.72}$	0.54	$C15$	Cubic	7.722		
$Lu_{0.275}Rh_{0.725}$	1.27	$C15$	Cubic	7.355		
$LuRh_5$	0.49					
$LuIr_2$	2.47	$C15$	Cubic	7.443		
$LuIr_3$	2.89	$C15$	Cubic	7.434		
$CeIr_3$	3.34					
$CeIr_5$	1.82					
ThRh	0.36	B_f	Orthorhombic	3.866	11.24	4.22
$ThRh_5$	1.07					
ThIr	0.37[d]	B_f	Orthorhombic	3.894	11.13	4.266
$ThIr_3$	4.71					
$ThIr_5$	3.93	$D2_d$	Hexagonal	5.315		4.288
Th_2Pd	0.85	$C16$	Tetragonal	7.33		5.93
Th_7Pt_3	0.98	$D10_2$	Hexagonal	10.126		6.346
ThPt	0.44	B_f	Orthorhombic	3.900	11.09	4.454
$ThPt_5$	3.13					

[a] W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals* (Pergamon Press, Inc., New York, 1958), p. 8.
[b] The transition temperature of a powdered sample.
[c] The composition of the superconductor could be YIr_4.
[d] The beginning of the transition of a powdered sample.

connecting paths during the crushing process. Powdering may introduce strains which very often result in a broader and lower transition temperature. In some cases, these are easily removed by annealing the powder and thereby obtaining a transition temperature very similar to that of the bulk sample. The transition temperature of the bulk material is therefore considered more representative of the sample. Since the powdering technique gives a semiquantitative measure of the fraction of the sample which is superconducting, it is of considerable value in determining the appearance and disappearance of a superconducting phase as the composition is varied.

The crystal structures of the phases were determined from x-ray diffraction powder photographs taken with a Norelco camera of 114.6 mm diam and Cu or Cr K radiation.

III. RESULTS AND DISCUSSION

A. Sc Alloys

The occurrence or nonoccurrence of superconductivity in Sc alloys with Co, Rh, Ir, Pd, and Pt is summarized in Fig. 1 and the data are given in Tables II–IV.

(1). Sc–Co: The transition temperature of bulk melts containing 28 to 32 at.% Co begins at 0.35°K. It disappears on powdering the sample and it was not possible to isolate the superconducting phase. The reported $C16$-type ($CuAl_2$) compound[13] Sc_2Co is not superconducting above 0.32°K.

(2). Sc–Rh: Superconductivity occurs in a Sc-rich

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[13] M. V. Nevitt, in *Electronic Structure and Alloy Chemistry of the Transition Elements*, edited by P. A. Beck (Interscience Publishers, Inc., New York, 1963), p. 101.

TABLE III. Nonsuperconducting compounds.

Compound	Structure type[a]	Crystal structure data		
		System	*a*, Å	*c*, Å
Sc_3Co				
Sc_2Co	*C*16	Tetragonal	6.374	5.616
Sc_4Rh				
$Sc_{0.68}Rh_{0.32}$				
$ScRh_3$	$L1_2$	Cubic	3.898	
Sc_3Ir				
$Sc_{0.68}Ir_{0.32}$				
ScIr	*B*2	Cubic	3.205	
$ScIr_3$				
Sc_2Pd	$E9_3$	Cubic	12.442	
Sc_4Pt				
ScPt	*B*2	Cubic	3.268	
$ScPt_3$	$L1_2$	Cubic	3.958	
Y_2Co				
Y_7Rh_3	$D10_2$	Hexagonal	9.793	6.196
Y_2Rh				
YRh	*B*2	Cubic	3.410	
YRh_2	*C*15	Cubic	7.489	
Y_4Ir				
YPd_3	$L1_2$	Cubic	4.076	
YPt				
YPt_3	$L1_2$	Cubic	4.075	
YPt_5				
$LaRh_2$	*C*15	Cubic	7.646	
$LaPd_3$	$L1_2$	Cubic	4.233	
$LaPt_5$	$D2_d$	Hexagonal	5.386	4.376
$LuCo_2$	*C*15	Cubic	7.123	
Lu_3Rh				
Lu_2Rh				
LuRh	*B*2	Cubic	3.334	
$LuRh_2$	*C*15	Cubic	7.404	
Lu_3Ir				
LuIr	*B*2	Cubic	3.330	
$CeIr_{1.8}$	*C*15	Cubic	7.581	
$CePt_2$	*C*15	Cubic	7.730	
$CePt_3$	*C*15	Cubic	7.640	
$CePt_5$	$D2_d$	Hexagonal	5.369	4.385
$ThCo_5$	$D2_d$	Hexagonal	5.005	3.987
$ThRh_2$				
$ThRh_3$	$L1_2$	Cubic		
$ThPd_5$				
$ThPt_2$				
$ThPt_3$				
$ThPt_4$				

[a] See Ref. a, Table II.

melt, Sc_3Rh, at 0.88°K. However, only about $\frac{1}{4}$ of the sample is superconducting as indicated by the small signal obtained for a powder. Attempts to isolate this phase by varying the composition were not successful. The compound $ScRh_3$ which has an $L1_2$-type ($AuCu_3$) structure[13] is not superconducting above 0.32°K.

(3). Sc–Ir: Only one superconducting phase has been identified in this system, namely, the *C*15-type ($MgCu_2$) $ScIr_2$ which has a transition temperature of 2.07°K. This value differs considerably from the previously reported[14] value of 1.03°K and is probably due to the use of a better grade of Sc or to a slightly different stoichiometry for the compound. The maximum transition temperature for the *C*15-type alloy is 2.46°K which occurs in $ScIr_{2.5}$. After being powdered, this sample has two transitions, one at 2.13°K which is that of the *C*15-type phase and one that begins at 0.42°K. The x-ray powder pattern of this melt indicates the presence of two phases, a Laves phase with a somewhat smaller lattice constant and $ScIr_3$. The lower temperature may be that of a nonstoichiometric $ScIr_3$ alloy since the stoichiometric alloy is not superconducting above 0.32°K. The reported *B*2-type (CsCl) structure[13] of ScIr is confirmed and this compound is not superconducting above 0.32°K.

(4). Sc–Pd: Only one compound in this system was investigated for superconductivity. Sc_2Pd which has an $E9_3$-type (Ti_2Ni) structure[13] is not superconducting above 0.32°K.

(5) Sc–Pt: No superconductors were found in this system. The reported phases[13] investigated include ScPt (*B*2-type, CsCl) and $ScPt_3$ ($L1_2$-type, $AuCu_3$).

The Sc systems with Co and Rh show a certain similarity in that superconductivity occurs in alloys in the Sc-rich region. For Sc-Ir alloys superconductivity occurs at the Ir-rich end. The fact that no superconductivity was detected in the Sc–Pt system may be due to the lack of favorable intermediate phases.

B. Y Alloys

The occurrence or nonoccurrence of superconductivity in Y alloys with Co, Rh, Ir, Pd, and Pt is summarized in Fig. 2 and the data are given in Tables II–IV.

(1). Y–Co: A trace of superconductivity beginning at 0.34°K occurs in bulk samples with nominal compositions of $Y_{0.75}Co_{0.25}$ and $Y_{0.72}Co_{0.28}$. The superconducting phase was not isolated.

(2). Y–Rh: Very little solubility of Y in Rh and vice versa is expected based on atomic radius considerations. The fact that very dilute alloys of Rh in Y and of Y in Rh are superconducting in bulk form is probably due to filament formation of the intermediate phase which is nearest in composition to the pure element, that is, Y_3Rh and YRh_5, respectively. The presence of such phases is immediately suggested by the fact that the transition temperature is essentially independent of composition in the regions of 1 to 20

TABLE IV. Alloys containing small amounts of a superconducting phase.

Composition	T_c, °K
$Sc_{0.72}Co_{0.28}$–$Sc_{0.68}Co_{0.32}$	0.35[a]
$Sc_{0.76}Rh_{0.24}$; $Sc_{0.75}Rh_{0.25}$	0.92; 0.88
$ScIr_{2.5}$	0.42[b]
Y_3Co	0.34[a]
$Y_{0.99}Ir_{0.01}$–$Y_{0.9825}Ir_{0.0175}$	0.35; 0.49[a]
$Y_{0.58}Pt_{0.42}$	0.33[a]
$Y_{0.23}Pt_{0.77}$–$Y_{0.20}Pt_{0.80}$	1.80; 1.96
Lu_3Co	0.35[a]
Lu_7Ir_3; Lu_2Ir	0.78; 0.84
$Ce_{0.20}Pt_{0.80}$–$Ce_{0.173}Pt_{0.826}$	1.26–0.70

[a] The beginning of the transition.
[b] The beginning of the transition of a powdered sample.

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[14] B. T. Matthias, T. H. Geballe, and V. B. Compton, Rev. Mod. Phys. 35, 1 (1963).

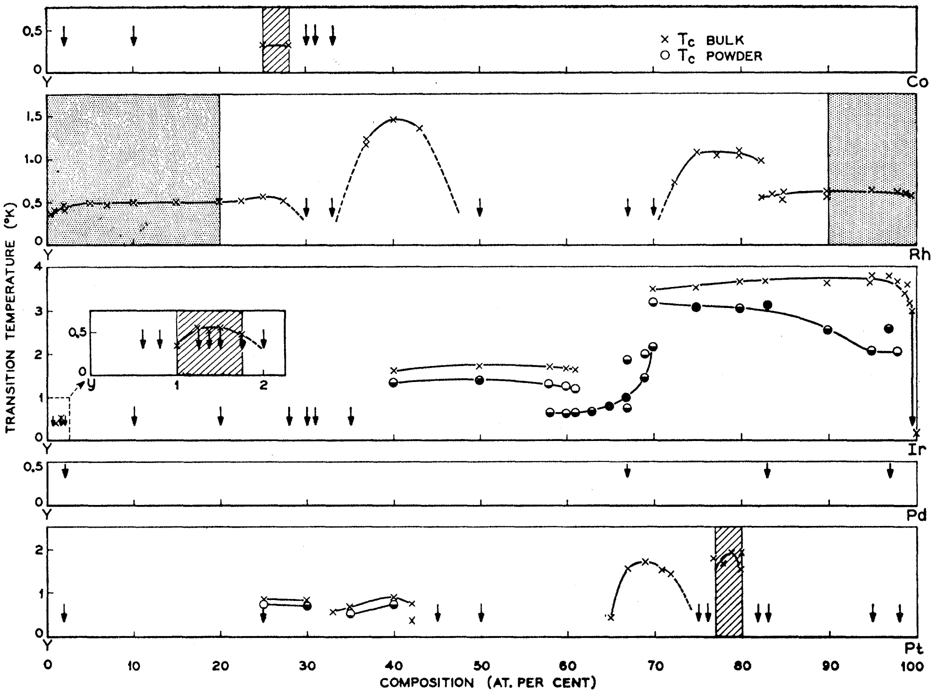

FIG. 2. Superconductivity in Y alloys of Co, Rh, Ir, Pd, and Pt. The shaded portions of the Y–Co, Y–Ir, and Y–Pt plots contain a small amount of a superconducting phase. According to powder data results, no superconductors occur in the shaded portions of the Y–Rh plot.

at.% Rh and 83 to 99.5 at.% Rh, and also by the absence of superconductivity in powdered samples of these melts. The decrease in the transition temperature of an alloy containing 0.5 at.% Rh is similar to the superconducting behavior of very rich Rh alloys in the La–Rh system which is discussed by Arrhenius[15] and coworkers. The superconducting compounds in the Y–Rh system include Y_3Rh ($T_c=0.65$°K), Y_3Rh_2 ($T_c=1.48$°K), and YRh_5 ($T_c=0.56$°K). The crystal structure of these phases has not been determined. A *C*15-type compound YRh_2 is not superconducting at the nominal stoichiometric composition. However, as the Rh content is increased to 72.5 at.%, superconductivity occurs. The maximum transition temperature of the phase is 1.07°K for an YRh_3 alloy. Although an additional phase appears at compositions richer in Rh than 72.5 at.%, the decrease in lattice constant of the *C*15 phase as more Rh is added indicates that the Laves phase has a homogeneity range. The reported *B*2-type compound YRh[13] and Y_7Rh_3 which has a $D10_2$-type (Th_7Fe_3) structure are not superconducting above 0.32°K.

(3). Y–Ir: The superconducting behavior of Y alloys containing 1 to 1.75 at.% Ir can be compared with the behavior of solid solutions of Cr in Sc where superconductivity also occurs in a rather narrow range of low Cr content.[3] The compound Y_3Ir_2 is superconducting at 1.61°K and its crystal structure was not determined. The Laves phase compound YIr_2 is superconducting throughout its homogeneity range. The exact composition of the superconducting phase at the Ir-rich end of the system could not be determined. The superconductivity data for powders with the compositions YIr_3, YIr_4, and YIr_5 indicate that in each case the entire sample is superconducting. However, according to the heat capacity results for YIr_4 and YIr_5 the composition of the superconducting phase is closer to YIr_4.[12] It was not possible to prepare a large melt (about 6 g) of YIr_3, suitable for heat capacity measurements, which was a single phase and had only one transition temperature. Therefore, on the basis of x-ray diffraction patterns and the limited heat capacity data, the superconducting phase is thought to be either YIr_3 or YIr_4. The presence of filaments of YIr_3 (or YIr_4) in the very rich Ir alloys of the system accounts for the observed superconductivity and as their number decreases, the transition temperature becomes broader and also decreases.[15]

(4). Y–Pd: No superconductors were found in the course of cursory investigation of this system. The only compound reported is YPd_3 which has an $L1_2$-type structure.[13]

(5). Y–Pt: This system contains several superconducting phases including a $D10_2$-type compound Y_7Pt_3 ($T_c=0.82$°K) and Y_3Pt_2 ($T_c=0.90$°K). An $Y_{0.58}Pt_{0.42}$ alloy has two transitions, one at 0.76°K which is probably associated with the Y_3Pt_2 compound and the other beginning at 0.33°K. The phase associated with the latter temperature was not isolated. Here again the

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[15] G. Arrhenius, E. Corenzwit, R. Fitzgerald, T. H. Geballe, D. C. Hamilton, B. A. Holm, G. W. Hull, Jr., and B. T. Matthias, J. Appl. Phys. (to be published).

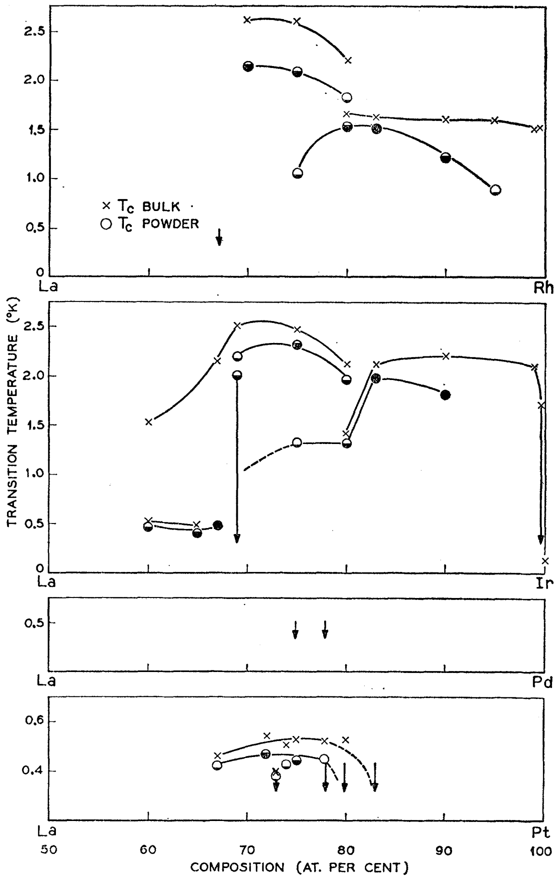

FIG. 3. Superconductivity in La alloys of Rh, Ir, Pd, and Pt.

C15-type Laves phase YPt_2 is superconducting throughout its homogeneity range and a maximum transition temperature of 1.70°K occurs in $YPt_{2.2}$. The superconducting phase which occurs in alloys with nominal compositions close to $Y_{0.23}Pt_{0.77}$ has not been isolated. The transition temperature is 1.80°K and only about $\frac{1}{2}$ of the bulk sample is superconducting. It seems probable that the phase is a nonstoichiometric YPt_3 alloy since the stoichiometric alloy which has the reported $L1_2$-type structure[13] is not superconducting above 0.32°K.

Comparison of the occurrence of superconductivity in Y alloys with those of Sc reveals some similarities which decrease in going from Co to Pt. There is a pronounced similarity between the Co systems in that both metals have a superconducting phase containing about 28 at.% Co. Y and Sc each form a superconductor containing 25 at.% Rh and both their C15-type Ir compounds are superconducting. However, these are the only superconducting phases in the Sc–Rh and Sc–Ir systems (with the exception of $ScIr_{2.5}$), whereas several others occur in the corresponding Y systems. The Pt systems of these metals are completely different —Y forms five superconducting phases and Sc does not form any.

C. La Alloys

The occurrence or nonoccurrence of superconductivity in La alloys containing more than 50 at.% Rh, Ir, Pd, and Pt is summarized in Fig. 3 and the data for all the systems investigated are given in Tables II–IV.

(1). La–Co: The only compound in this system investigated was La_3Co which has the reported $D0_{20}$-type structure[16] ($NiAl_3$) and is superconducting at 4.01°K. Since the data for the powdered sample indicate that the entire sample is superconducting, it does not seem likely that the observed superconductivity is due to the presence of elemental La. However, heat capacity measurements of the compound are planned to check this.[16a]

(2). La–Rh: Three superconducting compounds occur in this system: the $D10_2$-type compound La_7Rh_3 ($T_c=2.58$°K), $LaRh_3$ ($T_c=2.60$°K), and $LaRh_5$ ($T_c=1.62$°K). The crystal structures of $LaRh_3$ and $LaRh_5$ were not determined. Here again the observed superconductivity of La_7Rh_3 does not seem to be due to the presence of unreacted La, since the entire powdered sample of the alloy is superconducting. The occurrence of superconductivity in alloys containing 90 at.% Rh or more is due to traces of $LaRh_5$ and further investigation of this is reported elsewhere.[15] The C15-type compound $LaRh_2$ is not superconducting above 0.32°K; the previously reported temperature was 1.00°K.[14]

(3). La–Ir: The superconductors in the system include the $D10_2$-type compound La_7Ir_3 ($T_c=2.24$°K), the C15-type $LaIr_2$ ($T_c=0.48$°K), $LaIr_3$ ($T_c=2.46$°K), and $LaIr_5$ ($T_c=2.13$°K). The crystal structures of $LaIr_3$ and $LaIr_5$ are unknown. The data for a powdered sample of La_7Ir_3 which indicate that the entire sample is superconducting, seem to rule out the possibility that traces of unreacted La are causing the effect.

(4). La–Pd: $LaPd_3$ which has the $L1_2$-type structure[13] is not superconducting above 0.32°K.

(5). La–Pt: Two compounds occur in the Pt-rich end of this system, the C15-type compound $LaPt_2$ and the $D2_d$($CaCu_5$)-type compound $LaPt_5$.[13] The former is superconducting throughout its homogeneity range and the alloy containing 72 at.% Pt has the maximum transition temperature of 0.54°K. $LaPt_2$ was previously reported nonsuperconducting above 1.00°K.[14] $LaPt_5$ is not superconducting above 0.32°K.

The occurrence of superconductivity in the noble metal-rich end of the La systems bears a striking resemblance to the corresponding Y systems even with respect to its disappearance in the stoichiometric AB_5 phases with Pt. There are superconducting phases at comparable compositions in both systems which, how-

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[16] D. T. Cromer and A. C. Larson, Acta Cryst. **14**, 1226 (1961).

[16a] *Note added in proof.* According to the heat capacity measurements (Ref. 12) of La_3Co, the observed superconductivity is that of the La_3Co compound and is not due to the presence of elemental La.

ever, are not necessarily isostructural. It is interesting to note that the Pt alloys of Y are superconducting at higher Pt concentrations than the corresponding alloys of La.

D. Ce Alloys

The occurrence or nonoccurrence of superconductivity in Ce alloys containing more than 60 at.% Rh, Ir, and Pt is summarized in Fig. 4 and the data are given in Tables II–IV.

(1). Ce–Rh: No superconducting phases were found in this system containing 67 at.% or more Rh.

(2). Ce–Ir: There are two superconducting compounds of unknown crystal structure in the Ir-rich end of this system, $CeIr_3$ and $CeIr_5$. Their transition temperatures are 3.34 and 1.82°K, respectively. The stoichiometric $C15$-type compound $CeIr_2$ is reported nonsuperconducting to 0.37°K[14] and the nonstoichiometric compound $CeIr_{1.8}$ is not superconducting above 0.32°K.

(3). Ce–Pt: Traces of superconductivity, which disappear on powdering, occur in bulk samples containing 80 to 82.6 at.% Pt. The transition temperature has a range from 1.26 to 0.70°K. Although the superconducting phase has not been isolated, it seems probable that it is a nonstoichiometric $D2_d$-type phase. The reported stoichiometric[13] $CePt_5$ is not superconducting above 0.32°K. The $C15$-type compound[13] $CePt_2$ is not superconducting throughout its homogeneity range.

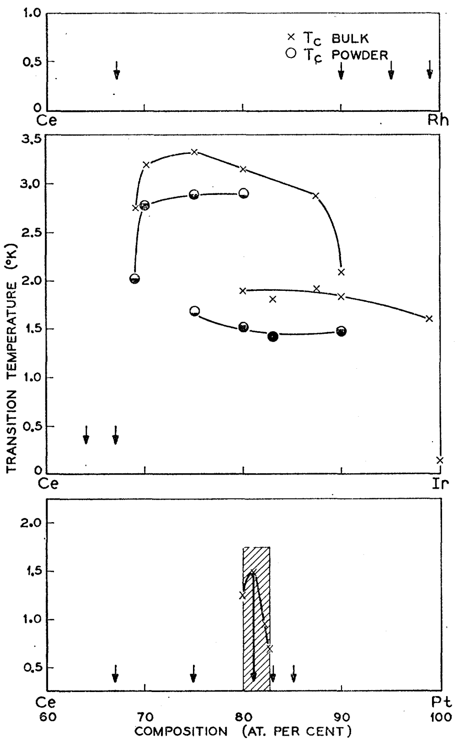

FIG. 4. Superconductivity in Ce alloys of Rh, Ir, and Pt. Alloys in the shaded portion of the Ce–Pt plot contain a small amount of a superconducting phase.

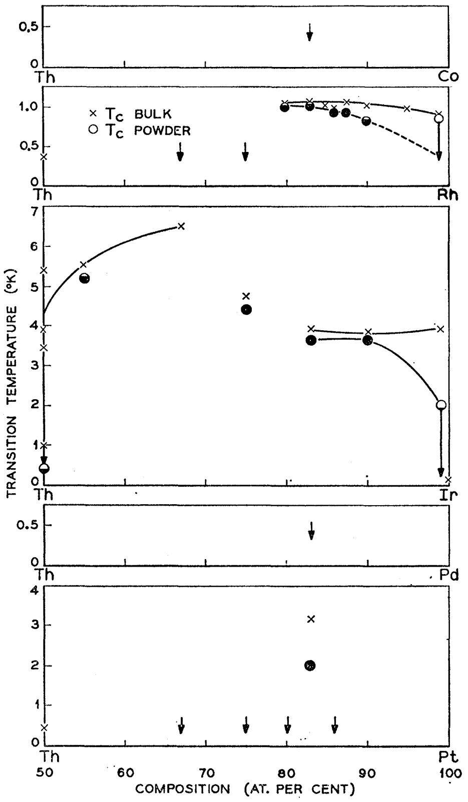

FIG. 5. Superconductivity in Th alloys of Co, Rh, Ir, Pd, and Pt.

Since Ce in its trivalent form has one $4f$ electron which causes magnetic interactions or even ferromagnetism in many of its compounds, the occurrence of superconductivity has been very rare. Previously, only one superconducting compound of Ce, $CeRu_2$, had been reported[14] in which the $4f$ electron was squeezed into the conduction band resulting in the tetravalent state of Ce. The additional superconducting compounds of Ce discovered in the course of this investigation include $CeIr_3$ and $CeIr_5$ in which Ce must also be in its quadrivalent form.

E. Th Alloys

The occurrence or nonoccurrence of superconductivity in Th alloys containing 50 at.% or more Co, Rh, Ir, Pd, and Pt is summarized in Fig. 5 and the data for all compositions investigated are given in Tables II–IV.

(1). Th–Co: The only compound investigated was $ThCo_5$ which has the reported hexagonal $D2_d$-type structure.[13] It is not superconducting above 0.32°K.

(2). Th–Rh: There are two superconductors in this system containing 50 at.% or more Rh. ThRh which has the reported orthorhombic B_f-type (CrB) struc-

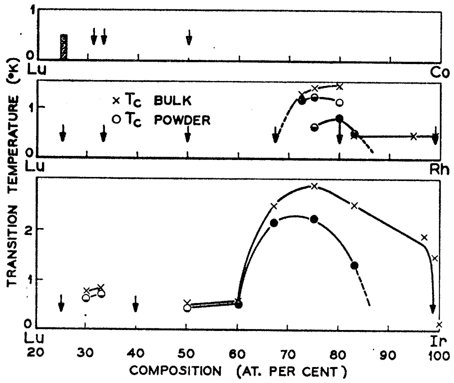

FIG. 6. Superconductivity in Lu alloys of Co, Rh, and Ir. The alloy in the shaded portion of the Lu–Co plot contains a small amount of a superconducting phase.

ture[17] is superconducting at 0.36°K and $ThRh_5$ at 1.07°K. Professor W. H. Zachariasen has suggested that the $ThRh_5$ compound may have a modified and disordered $D2_d$-type structure and that a single crystal analysis is required to determine its exact structure. The nonsuperconductors include $ThRh_2$ of unknown structure and $ThRh_3$ which has the $L1_2$-type structure.[13]

(3). Th–Ir: The three newly discovered superconducting compounds in this system include ThIr, $ThIr_3$, and $ThIr_5$. The transition temperature of a powdered sample of ThIr begins at 0.37°K and its reported orthorhombic B_f-type structure is confirmed.[18] $ThIr_3$ is superconducting at 4.71°K and $ThIr_5$ at 3.93°K.[19] The hexagonal $D2_d$-type structure of $ThIr_5$ reported by Dwight[20] is confirmed. The doubling of some of the lines of the x-ray powder pattern reported by Thomson[21] was not observed.

(4). Th–Pd: Two compounds in this system were investigated. Th_2Pd which has the tetragonal $C16$-type structure[22] ($CuAl_2$) is superconducting[23] at 0.85°K, and $ThPd_5$ is not superconducting above 0.32°K.

(5). Th–Pt: The $D10_2$-type compound Th_7Pt_3 previously reported nonsuperconducting to 1.02°K [14] is superconducting at 0.98°K. The transition temperatures of ThPt which has the B_f-type structure[17] and $ThPt_5$ of unknown crystal structure are 0.44 and 3.13°K, respectively. The nonsuperconductors include $ThPt_2$, $ThPt_3$, and $ThPt_4$.

Since Th definitely has four valence electrons, its alloys were investigated for comparison with the corresponding Ce alloys. The only marked difference in the occurrence of superconductivity is in the Rh-rich systems of these metals. There are no superconducting phases in the Ce–Rh system and one in the Th–Rh system, $ThRh_5$. The Ir systems are identical in that both have superconducting compounds containing 75 and 83 at.% Ir. The Pt systems are similar with both metals forming a superconducting Pt-rich alloy. However, for Ce–Pt superconductivity occurs only in bulk samples indicating that the correct composition of the superconducting phase was not attained. The 3.15°K transition temperature of $ThPt_5$ is unusually high for a compound with a valence-electron concentration of nine. As in the case[24] of $BaAu_5$, this is another example of a marked deviation from the valence-electron rule in the AB_5 compounds.

F. Lu Alloys

The occurrence or nonoccurrence of superconductivity in the Lu alloys investigated is summarized in Fig. 6 and the data are given in Tables II–IV.

(1). Lu–Co: A trace of superconductivity occurs in the bulk sample of Lu_3Co with a transition beginning at 0.35°K. The superconducting phase was not isolated. The $C15$-type compound[13] $LuCo_2$ is not superconducting above 0.32°K.

(2). Lu–Rh: There are two superconducting compounds in the Rh-rich end of this system, a nonstoichiometric Laves phase and $LuRh_5$. The $C15$-type compound[13] $LuRh_2$ is not superconducting at the nominal stoichiometric composition. However, as the Rh content is increased to 72.5 at.%, superconductivity occurs at 1.27°K. The transition temperature of $LuRh_5$ is 0.49°K. The nonsuperconducting compounds include Lu_3Rh, Lu_2Rh, and the $B2$-type LuRh.[13]

(3). Lu–Ir: Superconductivity occurs in the alloys Lu_7Ir_3 and Lu_2Ir at 0.78 and 0.84°K, respectively. After these alloys are powdered, only $\frac{1}{4}$ of the sample is superconducting and this phase has not been isolated. $LuIr_2$ has a $C15$-type structure and is superconducting at 2.47°K. The phase has a homogeneity range and the maximum transition temperature is 2.89°K for an alloy containing 75 at.% Ir. Lu_3Ir and the reported $B2$-type[13] LuIr are not superconducting above 0.32°K.

In order to preserve a continuity in the presentation, the occurrence of superconductivity in Lu alloys was not discussed with the other group-III elements. La, the first element of the rare-earth series, has no permanent $4f$ electrons whereas Lu has a filled shell of 14 $4f$ electrons. The Lu–Co system is very similar to the Sc–Co, Y–Co, and La–Co systems in that all have a superconducting phase containing about 25 at.% Co. With the exception of the La–Co system, the exact composition of the superconductor was not determined. Lu, Y, and La all form superconducting binary alloys containing 75 and 83 at.% Rh. However, the transition temperatures of the La alloys are much higher than those of the corresponding Lu alloys. All metals with

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[18] J. R. Thomson, Nature **194**, 464 (1962).

[19] We are grateful to Dr. J. H. Wernick for his collaboration with the $ThIr_5$ compound.

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the exception of Ce form a superconducting *C*15-type compound with Ir. This is the only Ir-rich superconducting phase for Sc and Lu; Y has one more, YIr_3; and La two more, $LaIr_3$ and $LaIr_5$. The rare earth-rich end of the Lu–Ir and La–Ir systems are similar.

IV. CONCLUSIONS

Except for the Ce–Rh system, superconductivity occurs in all other Rh and Ir systems although not necessarily for identical compositions or crystal structures. Invariably the transition temperature of the 1:5 Ir-rich phases is higher than that of the corresponding Rh phases, generally by a factor of 4 to 7 (for the La alloys this factor is much less). If this relationship is applicable to the transition temperature of the elements, then Rh might be expected to have a T_c near 0.03°K. According to the data for localized moments of Fe in Rh as compared to those of Fe in Ir, a purity of better than 1 ppm of Fe in Rh would be required to detect such a transition.

No superconductivity was observed above 0.32°K in the Pd-rich alloys of Y, La, and Th. This is rather surprising in view of the fact that Raub[25] and co-workers found that Pd formed more superconducting compounds with the nontransition elements than did Rh, Ir, or Pt. No satisfactory explanation for this can be offered at present except that Pd seems to be a zwitter element.

It is interesting to note that superconductivity occurs only in the 1:5 Pt-rich phase with the tetravalent element Th (at a valence electron concentration of nine) and not with any of the trivalent elements. This may be due to the occurrence of a minimum in the variation of T_c with valence-electron concentration just below nine. The "proximity" effect observed in the Rh-rich and Ir-rich alloys, whereby a superconducting phase is apparently able to induce superconductivity, over distances of the order of a correlation length, in adjacent material of another phase which by itself is not superconducting at these temperatures, does not occur in the Th–Pt system. There are two possible explanations: one, that Pt will not become superconducting in a temperature range comparable to that of Rh or Ir; and the other, that there is another more Pt-rich phase which is not superconducting above 0.32°K. There are indications of such a phase in the x-ray powder patterns but its exact composition has not been determined. Since solid solutions of W in Pt are superconducting, it seems reasonable to believe that pure Pt will become superconducting at extremely low temperatures.

All of the group III metals form a superconducting phase with the ferromagnetic element of the 9th column, Co. However, in most systems the superconductor could not be isolated. The fact that superconductivity was observed at all is encouraging since alloys of these metals with Fe usually result in ferro- or ferrimagnetism.

The investigation of binary systems composed of elements having nearly empty and nearly filled *d* shells has shown that the occurrence of superconductivity is not inhibited by charge contrast. These alloys have a large amount of ionic charge at each site and strong screening effects must occur. Very often in such cases the method of predicting the properties of an alloy by averaging over the periodic system is not too successful. For instance, in ferromagnetism marked deviations from the well-known Slater-Pauling curve[26] arise when the charge contrast is large. It is also true for the occurrence of a localized moment of an Fe solute atom dissolved in the 4*d* elements in which the results are predictable only when the alloy is composed of adjacent or nearly adjacent members of the 4*d* row.[27] However, the occurrence of superconductivity has again been successfully predicted by averaging over the periodic system. The results of this investigation confirm the observation that superconductivity is a rather common phenomenon in alloy systems including those of the rare earths and of Th with the Pt-group metals.

ACKNOWLEDGMENTS

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