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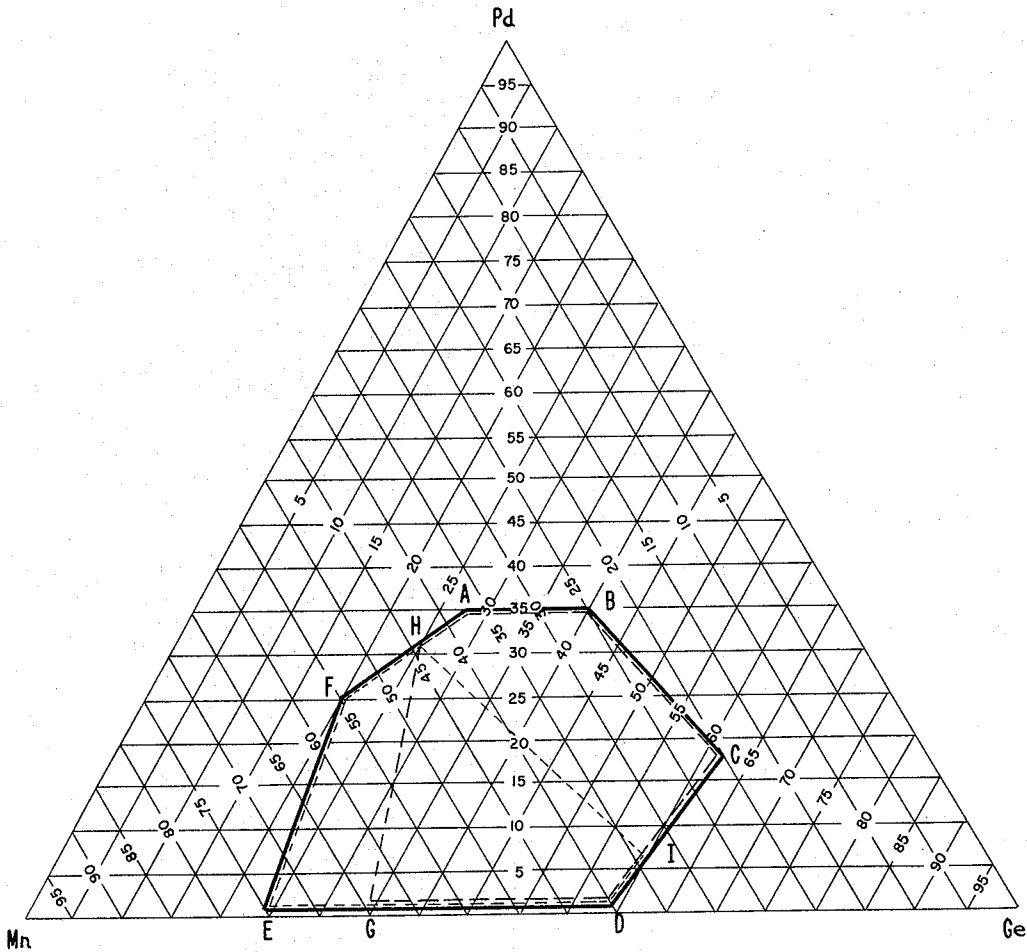
T. A. BITHER, JR
MAGNETIC ALLOYS OF MANGANESE, GERMANIUM AND EITHER
OR BOTH OF PALLADIUM AND RHODIUM

3,279,914

Filed June 8, 1965

2 Sheets-Sheet 1

FIG. 1



--- HEXAGONAL COMPOSITIONS
- - - D88 COMPOSITIONS
— BROAD RANGE

INVENTOR
TOM A. BITHER, JR.

BY *James H. Ryan*

ATTORNEY

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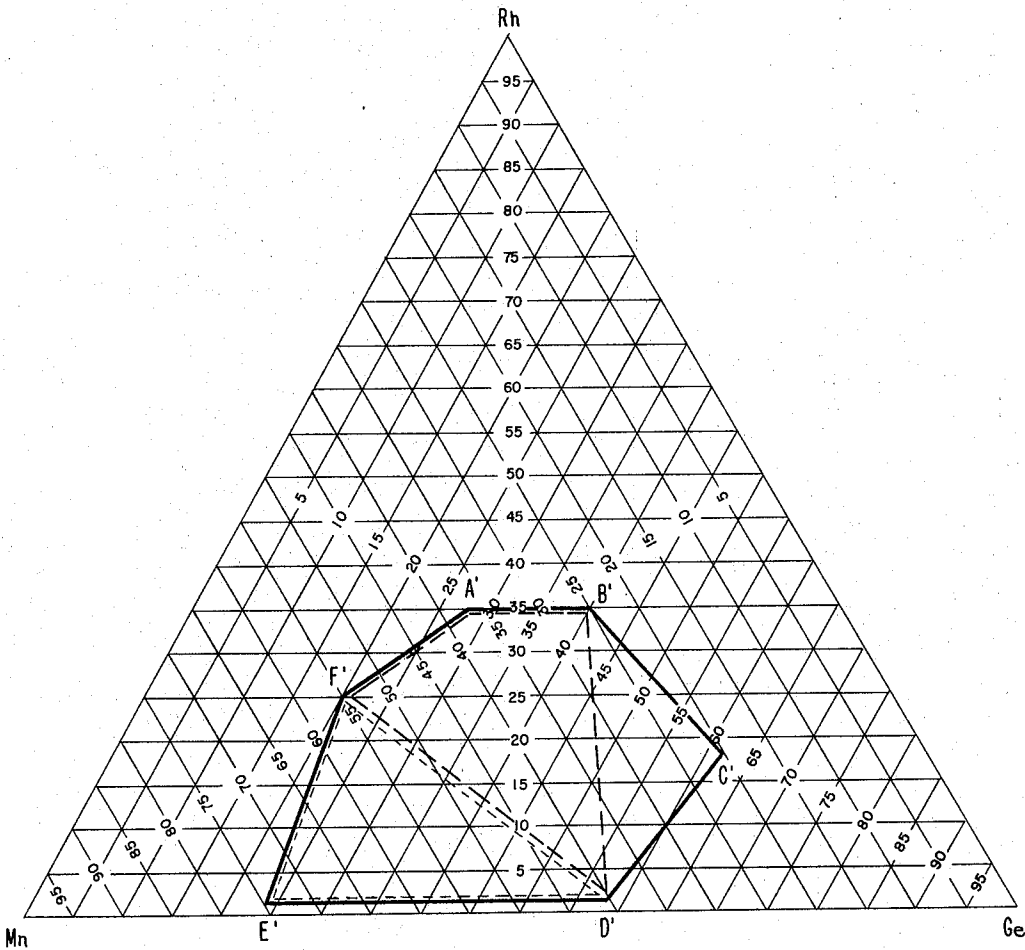
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2 Sheets-Sheet 2

FIG. 2



----- HEXAGONAL COMPOSITIONS
..... D₈ COMPOSITIONS
———— BROAD RANGE

INVENTOR
TOM A. BITHER, JR.

BY

James H. Ryan

ATTORNEY

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MAGNETIC ALLOYS OF MANGANESE, GERMANIUM AND EITHER OR BOTH OF PALLADIUM AND RHODIUM

Tom A. Bither, Jr., Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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12 Claims. (Cl. 75-134)

This application is a continuation-in-part of my co-pending application Serial No. 197,316, filed May 24, 1962, and now abandoned.

This invention relates to, and has as its principal object provision of, certain novel magnetic metallic compositions of matter or alloys.

It may be noted, with regard to nomenclature, that all of the compositions of matter, or products, of this invention are alloys but that an alloy consisting of a single phase may be referred to simply as a "phase."

There are now provided alloys containing as essential components manganese, germanium and palladium and/or rhodium. More particularly, there are provided certain ternary magnetic manganese-rhodium-germanium and manganese-palladium-germanium alloys and certain quaternary manganese-rhodium-palladium-germanium alloys. Expressed in terms of atom percent of each of the components, the preferred compositions are those in which the manganese content is from 20 to 75%, the germanium content is from 20 to 62%, and the palladium and/or rhodium content is from 1 to 35%.

FIG. 1 depicts the ternary system composed of manganese, palladium and germanium and FIG. 2, that of manganese, rhodium, and germanium. Table I defines compositions within specific areas in FIG. 1 and Table II, similar specific compositions within FIG. 2.

TABLE I

Points	Composition, Atom Percent		
	Mn	Pd	Ge
A-----	37	35	28
B-----	25	35	40
C-----	20	18	62
D-----	40	1	59
E-----	75	1	24
F-----	55	25	20
G-----	65	1	34
H-----	44	31	25
I-----	33	7	60

TABLE II

Points	Composition, Atom Percent		
	Mn	Rh	Ge
A'-----	37	35	28
B'-----	25	35	40
C'-----	20	18	62
D'-----	40	1	59
E'-----	75	1	24
F'-----	55	25	20

The principal magnetic phases present within the regions defined in FIGS. 1 and 2 are as follows:

In the ternary manganese-palladium-germanium sys-

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tem, of FIG. 1, the region ABCDEFA includes all the magnetic palladium-containing alloys of this invention. Alloys within the region defined by ABCDGH are magnetic and characterized by the presence of a magnetic phase of hexagonal crystal structure with cell constants within the ranges $a=6.57$ to 6.67 A. and $c=3.54$ to 3.64 A. Magnetic palladium-containing alloys characterized by the presence of a magnetic phase of different hexagonal crystal structure ($D8_3$ type) with cell constants in the ranges $a=7.10$ to 7.25 A. and $c=4.90$ to 5.10 A. are defined by the region HFEDIH.

In the ternary manganese-rhodium-germanium system (FIG. 2) the region A'B'C'D'E'F'A' includes all magnetic rhodium-containing alloys of the invention. Alloys within the region defined by the points A'B'D'F'A' are magnetic and are characterized by the presence of a magnetic phase of hexagonal crystal structure with cell constants in the ranges $a=6.50$ to 6.60 A. and $c=3.50$ to 3.60 A. A second class of magnetic rhodium-containing products characterized by the presence of a magnetic phase of different hexagonal crystal structure is composed of compositions within the region defined by the points F'D'E'F'. This magnetic phase has the $D8_3$ hexagonal type of structure with cell constants in the ranges of $a=7.15$ to 7.25 A. and $c=5.00$ to 5.10 A. Region B'C'D'B' defines alloys characterized by the presence of a magnetic cubic phase having cell constant in the range $a=4.80$ to 4.85 A. An orthorhombic phase with cell constants in the ranges $a=5.64$ to 5.68 A., $b=6.38$ to 6.42 A., and $c=3.29$ to 3.33 A., is also present.

It will be noted that there is overlap in certain composition regions defined above. FIGS. 1 and 2 are not to be construed as phase diagrams defining compositions in isothermal equilibrium, but are indicative of composition ranges with which phases having the hexagonal and/or $D8_3$ crystal structure are produced in melt-cast products cooled to room temperature, or in annealed products subsequently quenched to room temperature under conditions as described in the specific examples included herein.

As will be apparent from the examples below, other components than those described above may be present in certain compositions. These include unconverted starting materials as well as ternary compositions of different crystal structure. It is desirable that the proportion of these additional components be held to a minimum, and, in this respect, alloys or phases in both the manganese-palladium-germanium and the manganese-rhodium-germanium systems of hexagonal crystal structure which contain the constituents in approximately equal atomic proportions are of particular value. For example, compositions containing 32.5-33.3 atom percent of Mn, 33.3-35 atom percent of Rh, and 32.5-33.3 atom percent of Ge exhibit both a high saturation magnetization (77 gauss cm^3/g . at room temperature) and a high Curie temperature (near 380°C . as measured in a field of 1000 oersteds; 420°C . as measured in a field of 15,750 oersteds). The corresponding palladium-containing compositions are exemplified by the composition containing 33.3 atom percent each of manganese, palladium, and germanium. This composition has a saturation magnetization of 70 gauss cm^3/g . at room temperature and a Curie temperature of 304°C . (1000 oersted field).

The phase of hexagonal structure in the manganese-palladium-germanium system occurs over a wider range

of composition than it does in the manganese-rhodium-germanium system. This phase is present along with free germanium and nonmagnetic crystalline material in compositions in the range of 40–25 atom percent of Mn, 25 atom percent of Pd, 35–50 atom percent of Ge, and 35 atom percent of Mn, 30 atom percent of Pd, 35 atom percent of Ge.

In the composition containing 40–50 atom percent of Mn, 20–12.5 atom percent of Pd, and 40–37.5 atom percent of Ge (the phase of hexagonal structure is accompanied by material having a second hexagonal structure of the $D8_8$ type which is also magnetic. This latter structure also is observed in compositions containing 50 atom percent of Mn, 12.5–25 atom percent of Pd, 37.5–25 atom percent of Ge. These compositions have Curie temperatures in the range 11–34° C.

Rhodium-containing alloys with a phase of hexagonal $D8_8$ type crystal structure are also formed and are exemplified by the composition containing 50 atom percent of Mn, 12.5 atom percent of Rh, and 37.5 atom percent of Ge. This composition has a Curie temperature of 30° C.

Especially preferred quaternary manganese-germanium-rhodium-palladium alloys of the invention are those containing approximately one-third each of manganese, germanium, and rhodium-palladium, although all within the broad limits set forth above are magnetic. In these alloys, rhodium and palladium can be used interchangeably although a shift from one to the other may alter the crystal structure. A minimum of about 1 atom percent of each of rhodium or palladium is preferred, the remaining third of the quaternary composition being made up from the other. The alloy consisting of 33.3 atom percent of manganese, 33.3 atom percent of germanium and 16.7 atom percent each of rhodium and palladium exhibits a single phase having a hexagonal crystal structure with cell constants of about $a=6.59$ A. and $c=3.54$ A.

The compositions of this invention can be made either by fusing or by sintering the components. In the fusion method manganese, germanium, rhodium and/or palladium in the desired proportions are thoroughly mixed and placed in a container, e.g., an alumina crucible. The contents are then heated to a temperature which is high enough to melt the mixture completely. This temperature will generally be in the range of 1100° to 1700° C. Heating is carried out in a vacuum under autogeneous pressure, or in an inert atmosphere such as is provided by a helium or argon blanket. After melting is complete, which will generally occur in from 0.10 to 10 hours, the composition is permitted to solidify by cooling to ambient temperature and removed from the container.

In the alternative sintering method the components, in the desired proportions, are intimately mixed, compacted under pressure, and then heated under vacuo or in an inert atmosphere such as helium or argon at a temperature below the melting point of the mixture for from 1 to 350 hours. Thereafter the mixture is allowed to cool to ambient temperature over a period of from 2 to 24 hours.

The temperature employed in the sintering process will generally be in the range of from 800° to 1200° C.

If desired, the composition can be subjected to an annealing treatment and this consists in subjecting it to heat in the range of from 350° to 1200° C. in an inert atmosphere or in vacuo in a closed container for from 1 to 350 hours, and thereafter either allowing it to cool to ambient temperature over a period of from 1 to 24 hours or very rapidly quenching to room temperature.

The alloys of this invention are made from commercially available components. Since these commercially available products contain minor amounts of impurities, it is to be understood that in referring to the alloys as consisting of manganese and germanium and rhodium and/or palladium, it is intended to include such compositions from these metals as may include minor amounts

of other metals not to exceed 3 atom percent and preferably not over 2. Such metals may include other platinum group metals, iron group metals, and the like.

The examples which follow illustrate but do not limit this invention. In these examples the magnetic properties described are the magnetic moment per gram, σ , measured in fields of 1000 to 17,000 oersteds (as indicated in the examples) and the Curie temperature T_c , determined from measurements of the sigma value, σ , as a function of temperature. The composition ratios given under each example number and in the tables are expressed in atom percent.

EXAMPLE 1

33½ Mn–33½ Rh–33½ Ge

An alumina crucible, contained in an outer quartz tube, was charged with a pelleted intimate blend of 0.55 g. of manganese, 1.03 g. of rhodium, and 0.73 g. of germanium and outgassed under vacuo at 250° C. for 16 hours. An atmosphere of argon was then admitted to the tube and the temperature was raised to 1065° C. over a 5½ hour period and held at this temperature for 2½ hours under 1 atm. of argon. The charge was thereafter allowed to cool to room temperature in about six hours. The reaction product was a densely sintered slug, which was strongly magnetic and showed a Curie temperature of 382° C. (1000 oe. field). This product had an hexagonal crystal structure with cell constants $a=6.545$ A. and $c=3.570$ A. as indicated by its X-ray pattern.

A portion of the above material was annealed in vacuo in a quartz tube at 506° C. for 138 hours and was then quenched in ice water. The product remained strongly magnetic with a Curie temperature of 380° C. (1000 oe. field) and an hexagonal crystal structure with cell constants $a=6.539$ A. and $c=3.566$ A.

EXAMPLE 2

33½ Mn–33½ Rh–33½ Ge

An alumina crucible, contained in an outer quartz tube, was charged with a pelleted intimate blend of 1.65 g. of manganese, 3.09 g. of rhodium, and 2.19 g. of germanium, and outgassed under vacuo at 290° C. for 15 hours. Argon was then admitted to the tube and the temperature raised to 1115° C. over an eight-hour period where it was held for one-half hour under 1 atm. of argon. The charge was thereafter allowed to cool to room temperature in approximately six hours. The reaction product was fused to a dense metallic slug which was strongly magnetic at room temperature. Magnetization measurements made at liquid N_2 temperature and room temperature on a powdered sample of this material, compressed into a pellet, showed the following dependence of σ on field strength:

TABLE III.—MAGNETIZATION AT VARIOUS TEMPERATURES OF HEXAGONAL Mn-Rh-Ge PHASE

Field Strength, H (oe.)	Magnetization, σ (gauss cm. ³ /g.)	
	Liquid N_2 Temperature	Room Temperature
2,780	65.5	60.2
5,550	77.6	69.8
8,200	82.1	73.0
10,800	84.5	75.5
13,000	85.6	76.0
14,750	86.0	76.4
16,000	86.2	76.5
16,750	86.6	77.0

The Curie temperature was 383° C. (1000 oe. field), 420° C. (15,750 oe. field). This single-phase alloy had an hexagonal crystal structure with cell constants $a=6.545$ A. and $c=3.570$ A. The X-ray pattern including Miller indices for hexagonal indexing is shown in Table IV.

TABLE IV.—X-RAY DIFFRACTION PATTERN OF HEXAGONAL Mn-Rh-Ge Phase

Intensity ¹	Interplanar Spacing ²	Miller Indices, <i>hkl</i>
M ₃ -----	5.68	100
M ₂ -----	3.57	001
M ₃ -----	3.28	110
S-----	2.415	111
S-----	2.215	201
M ₁ -----	2.140	210
M ₂ -----	1.890	300
M ₁ -----	1.886	211
M ₃ -----	1.783	002
M ₃ -----	1.668	301
M ₂ -----	1.574	310
V-----	1.489	221
M ₂ -----	1.439	311
M ₃ -----	1.418	400
M ₃ -----	1.370	212
F-----	1.317	401
M ₃ -----	1.298	302
F-----	1.237	410
M ₃ -----	1.223	321
V-----	1.179	312
M ₁ -----	1.170	411
V-----	1.119	113
V-----	1.072	420
V-----	1.051	322
M ₃ -----	1.019	510
M ₃ -----	0.979	511

¹ X-ray pattern on film; S indicates the strongest line in the pattern, M₁, M₂, M₃, and M₄ indicate lines of moderate intensity (decreasing in the order M₁ to M₄), F indicates faint lines, and V indicates very faint lines.

² In Angstrom units.

If the rhodium in the above ternary composition is replaced by one of the Group VIII base metals iron, cobalt, or nickel, a magnetic hexagonal phase of the filled B8₂ structure type, and different from that present in the composition MnRhGe, is formed. The magnetic properties of these MnFeGe, MnCoGe, and MnNiGe compositions are markedly different and are inferior to those of the MnRhGe composition. For example, their Curie temperatures are approximately 300° C. lower and within the temperature region where they are magnetic, particularly in the region around room temperature, their saturation magnetization is appreciably lower than that of MnRhGe. These comparisons are summarized in Table V.

TABLE V.—COMPARISON OF VARIOUS Mn-Ge-METAL COMPOSITIONS

Composition	SATURATION MAGNETIZATION, σ , gauss cm. ³ /g.		Curie Temperature, °C., Saturating Field	Crystal Structure
	Liquid N ₂ Temperature	Room Temperature		
MnFeGe*-----	50	3	100	B8 ₂ type: <i>a</i> =4.096 Å. <i>c</i> =6.213 Å.
MnCoGe*-----	<59	4	117	B8 ₂ type: <i>a</i> =4.080 Å. <i>c</i> =5.304 Å.
MnNiGe*-----	<12	Low	87	B8 ₂ type: <i>a</i> =4.058 Å. <i>c</i> =5.381 Å.
MnRhGe-----	87	77	420	Hexagonal: <i>a</i> =6.545 Å. <i>c</i> =3.570 Å.

*These compositions have been reported by L. Castelliz (Mh. Chem. 84, 765 (1953) and Z. Metallkunde 46, 198 (1955)) and data on the MnNiGe composition are taken from his work.

EXAMPLE 3

50Mn-25Rh-25Ge

By the procedure and under the conditions of Example 1, except that the heat treatment was at 1050° C. for one hour instead of at 1065° C. for 2½ hours and the pellet was made from a mixture of 1.10 g. of manganese, 1.03 g. of rhodium, and 0.73 g. of germanium, there was obtained a densely fused metallic slug, which was strongly magnetic at room temperature with a Curie temperature of 102° C. (1000 oe. field). This magnetic alloy differed in crystal structure from the magnetic product of Example 1 and had an X-ray pattern as shown in Table VI.

TABLE VI.—X-RAY PATTERN OF 50Mn-25Rh-25Ge BEFORE ANNEALING

	Intensity ¹	Interplanar Spacing ²	Intensity ¹	Interplanar Spacing ²
5	15	4.672	21	1.994
	10	4.544	16	1.929
	12	3.818	18	1.859
	21	3.485	20	1.768
	12	3.319	7	1.600
10	8	3.173	15	1.495
	12	2.936	7	1.401
	7	2.832	8	1.319
	7	2.824	18	1.298
	9	2.445	9	1.248
	14	2.332	7	1.237
	21	2.271	13	1.230
	90	2.205	12	1.216
15	100	2.141	12	1.206
	100+	2.086	5	1.1636
			6	1.0722

¹ X-ray pattern by diffractometer; intensities in percent referred to the line at 2.141 Å. as 100%.

² In Angstrom units.

A portion of the above material was annealed at 506° C. for 145 hours and then quenched in ice water. This treatment resulted in partial conversion to a phase of hexagonal crystal structure corresponding to that described in Examples 1 and 2 as indicated by the X-ray pattern of the product. The hexagonal material had a Curie temperature of 362° C. and cell constants *a*=6.550 and *c*=3.566.

EXAMPLE 4

50Mn-12.5Rh-37.5Ge

By the procedure and under the conditions of Example 1, except that the pellet was made from 1.10 g. of manganese, 0.52 g. of rhodium, and 1.09 g. of germanium there was obtained a densely fused slug which was magnetic at room temperature with a Curie temperature of 30° C. (1000 oersted field). This magnetic material differed from that described in the previous examples and its structure corresponded in part to a D8₈ type hexagonal phase with cell constants *a*=7.19 Å. and *c*=5.05 Å. The X-ray pattern is shown in Table VII.

The material was essentially unaltered by annealing for 184 hours at 506° C. It showed the following magnetic moments in a field of 16,000 oersteds: $\sigma_{\text{Hq. He temp.}}$ = 35 gauss cm.³/g., $\sigma_{-55^\circ \text{C.}}$ = 24 gauss cm.³/g., $\sigma_{10^\circ \text{C.}}$ = 13 gauss cm.³/g.

TABLE VII.—X-RAY PATTERN OF 50Mn-12.5Rh-37.5Ge COMPOSITION

	Intensity ¹	Interplanar Spacing ²	Intensity ¹	Interplanar Spacing ²
V-----	6.23		M ₃ -----	2.009
M ₃ -----	5.64		M ₂ -----	1.971
F-----	5.04		M ₂ -----	1.932
M ₁ -----	3.59		F-----	1.748
F-----	3.26		F-----	1.729
M ₂ -----	3.025		M ₃ -----	1.697
M ₂ -----	2.919		M ₃ -----	1.665
M ₂ -----	2.820		M ₃ -----	1.633
M ₂ -----	2.795		V-----	1.609
M ₂ -----	2.513		F-----	1.569
M ₂ -----	2.409		F-----	1.527
M ₂ -----	2.360		F-----	1.511
F-----	2.313		F-----	1.455
M ₂ -----	2.279		F-----	1.412
F-----	2.247		F-----	1.369
S-----	2.220		M ₃ -----	1.348
M ₂ -----	2.159		M ₃ -----	1.336
M ₂ -----	2.135		M ₃ -----	1.312
S-----	2.065		M ₃ -----	1.289

¹ X-ray pattern on film; S indicates the strongest line in the pattern; M₂ and M₃ indicate lines of moderate intensity (M₂ stronger than M₃); F indicates faint lines; and V indicates very faint lines.

² In Angstrom units.

EXAMPLE 5

25Mn-25Rh-50Ge

A pellet composed of 0.55 g. of manganese, 1.03 g. of 75 rhodium, and 1.45 g. of germanium was treated accord-

ing to the procedure and under the conditions reported in Example 3. The product was a fused slug which was magnetic when cooled to liquid nitrogen temperature and exhibited a Curie temperature near -100°C . This magnetic material consisted essentially of a magnetic cubic phase having a cell constant $a=4.835\text{ A}$. and an orthorhombic phase having cell constants $a=5.664\text{ A}$., $b=6.409\text{ A}$., and $c=3.317\text{ A}$. The X-ray pattern is shown in the following table:

TABLE VIII.—X-RAY PATTERN OF 25Mn-25Rh-50Ge COMPOSITION

Intensity ¹	Interplanar Spacing ²	Intensity ¹	Interplanar Spacing ²
11	5.697	10	1.399
4	4.247	11	1.383
7	3.204	10	1.339
27	2.945	12	1.308
38	2.832	13	1.306
100	2.789	22	1.296
45	2.614	31	1.277
43	2.414	6	1.251
100+	2.167	6	1.224
100+	2.123	7	1.221
87	2.043	44	1.207
31	2.001	5	1.181
100+	1.971	17	1.171
76	1.813	35	1.147
44	1.797	8	1.138
20	1.707	3	1.130
10	1.656	23	1.108
18	1.609	7	1.079
17	1.543	43	1.054
7	1.527	16	1.071
27	1.456	11	0.9465
5	1.428	29	0.9298
24	1.416		

¹ X-ray pattern by diffractometer; intensities in percent referred to the line at 2.789 A. as 100%.
² In Angstrom units.

EXAMPLE 6

33 $\frac{1}{3}$ Mn-33 $\frac{1}{3}$ Pd-33 $\frac{1}{3}$ Ge

By the procedure and under the conditions of Example 1, except that the heat treatment was for one hour at 1100°C . instead of $2\frac{1}{2}$ hours at 1065°C ., and the pellet was made from 0.55 g. of manganese, 1.06 g. of palladium, and 0.73 g. of germanium, there was obtained a fused, crystalline, metallic slug, which was strongly magnetic at room temperature with a Curie temperature at 304°C . (1000 oe. field). Magnetization measurements made at liquid N_2 temperature and room temperature on a powdered sample of this material, compressed to a pellet, showed a dependence of σ on field strength as indicated in Table IX.

TABLE IX.—MAGNETIZATION AT VARIOUS TEMPERATURES OF HEXAGONAL Mn-Pd-Ge ALLOY

Field Strength, H (oe.)	Magnetization, σ (gauss cm. ³ /g.)	
	Liquid N_2 Temperature	Room Temperature
2,780	50.0	47.5
5,550	61.9	58.5
8,200	68.7	64.2
10,800	72.9	67.2
13,000	74.9	68.4
14,750	76.0	69.0
16,000	76.5	69.4
16,750	77.0	69.9

This alloy consisted essentially of a magnetic phase having a hexagonal crystal structure with cell constants $a=6.643\text{ A}$. and $c=3.569\text{ A}$. This is the same structure observed in the Mn-Rh-Ge ternary alloy described in Examples 1 and 2. The X-ray pattern is given in Table X.

TABLE X.—X-RAY PATTERN OF HEXAGONAL Mn-Pd-Ge ALLOY

Intensity ¹	Interplanar Spacing ²	Miller Indices, ³ hkl
27	5.779	100
8	3.553	001
34	3.319	110
25	2.442	111
18	2.328	-----
80	2.179	-----
100	2.170	210
21	2.048	-----
61	1.920	300
14	1.857	211
8	1.598	310
12	1.440	400
6	1.325	401
9	1.315	320
8	1.255	410
8	1.237	321
6	1.086	420
6	1.082	-----
6	1.033	510
6	0.9954	-----

¹ X-ray pattern by diffractometer; intensities in percent referred to the line at 2.170 A. as 100%.

² In Angstrom units.

³ For hexagonal structure. The remaining lines are unidentified.

After annealing the above material at 506°C . for 138 hours and quenching in ice water, the resultant product was essentially unaltered and had a Curie temperature of 290°C . and a similar X-ray pattern.

EXAMPLE 7

25Mn-25Pd-50Ge

By the procedure and under the conditions of Example 3 except that the pellet made from 0.55 g. of manganese, 1.06 g. of palladium, and 1.45 g. of germanium, there was obtained a fused metallic slug, which was magnetic at room temperature, with a Curie temperature of 280°C . (1000 oe. field). This magnetic product contained as its major component the phase of hexagonal structure described in Example 6, with cell constants $a=6.605\text{ A}$. and $c=3.596\text{ A}$. Minor amounts of an orthorhombic phase with cell constants $a=5.768\text{ A}$., $b=6.306\text{ A}$. and $c=3.444\text{ A}$. and free germanium were also present.

Annealing this alloy at 506°C . for 145 hours followed by quenching in ice water eliminated the magnetic phase. The magnetic phase could be restored by heating at 400°C . The Curie temperature of the thus heated product was 280°C .

EXAMPLE 8

35Mn-25Pd-40Ge

By the procedure and under the conditions of Example 1, except that the heat treatment was for 1.5 hours at 1115°C . instead of $2\frac{1}{2}$ hours at 1065°C . and the pellet was made from 0.961 g. of manganese, 1.330 g. of palladium, and 1.452 g. of germanium, there was obtained a crystalline metallic solid, which was magnetic with a Curie temperature of 279°C . (1000 oe. field). The crystal structure of the alloy was similar to that of Example 7.

EXAMPLE 9

40Mn-25Pd-35Ge

By the procedure and under the conditions of Example 8, except that the pellet was made from 1.099 g. of manganese, 1.330 g. of palladium, and 1.271 g. of germanium, there was obtained a crystalline, metallic slug, which was magnetic, with a Curie temperature of 275°C . (1000 oe. field). The X-ray diffraction pattern indicated that this product contained the same phase of hexagonal crystal structure corresponding to that of Example 6 with cell constants $a=6.613\text{ A}$. and $c=3.604\text{ A}$. Some free germanium and a trace of an orthorhombic phase as in Examples 7 and 8 were also present.

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EXAMPLE 10

35Mn-30Pd-35Ge

By the procedure and under the conditions of Example 8, except that the pellet was made from 0.961 g. of manganese, 1.596 g. of palladium, and 1.271 g. of germanium, there was obtained a crystalline, metallic slug, which was magnetic with a Curie temperature at 297° C. (1000 oe. field). The X-ray diffraction pattern indicated the same magnetic hexagonal phase as in Examples 7, 8 and 9.

EXAMPLE 11

40Mn-20Pd-40Ge

By the procedure and under the conditions of Example 8, except that the pellet was made from 1.099 g. of manganese, 1.064 g. of palladium, and 1.452 g. of germanium, there was obtained a fused solid which was strongly magnetic. This solid exhibited two Curie temperatures, i.e., at 11° C. and 276° C. (1000 oe. field), indicating a mixture of two magnetic phases. The magnetic phase of higher Curie temperature was the same as that of Example 6 (hexagonal structure with $a=6.62$ A. and $c=3.61$ A.), as confirmed by the X-ray diffraction pattern. The second magnetic phase had the $D8_8$ type hexagonal structure with cell constants $a=7.21$ A. and $c=5.07$ A. Some free germanium was also present. The X-ray diffraction pattern of the product, with the lines which correspond to germanium deleted, is given in Table XI.

TABLE XI.—X-RAY PATTERN OF 40Mn-20Pd-40Ge COMPOSITION

Intensity ¹	Interplanar Spacing ²	Miller Indices, hkl^3	
		$D8_8$	Hexagonal
M ₃ -----	5.68	-----	100
M ₃ -----	3.60	110	001
M ₃ -----	2.533	002	-----
S-----	2.434	-----	111
M ₃ -----	2.354	210, 102	-----
S-----	2.241	-----	201
M ₂ -----	2.169	-----	210
M ₂ -----	2.145	211	-----
M ₃ -----	2.079	300, 112	-----
V-----	1.951	202	-----
M ₂ -----	1.909	-----	300
M ₂ -----	1.857	-----	211
M ₄ -----	1.809	220	002
F-----	1.735	310	-----
F-----	1.641	311	-----
V-----	1.584	-----	112
V-----	1.470	222	-----
V-----	1.458	-----	311
F-----	1.435	312, 320	400
M ₃ -----	1.388	321	212
M ₄ -----	1.377	213, 410	-----
F-----	1.328	402	-----
M ₃ -----	1.315	-----	302
F-----	1.267	004	-----
M ₃ -----	1.250	322, 500	410
M ₃ -----	1.237	223	321
F-----	1.181	420	-----
M ₄ -----	1.121	502, 510	-----

¹ X-ray pattern on film; S indicates the strongest line in the pattern; M₂, M₃, and M₄ indicate lines of moderate intensity (decreasing in the order M₂ to M₄); F indicates faint lines; and V indicates very faint lines.

² In Angstrom units.

³ Indices for hexagonal and $D8_8$ structures are shown.

EXAMPLE 12

50Mn-12.5Pd-37.5Ge

By the procedure and under the conditions of Example 6, except that the pellet was made from 1.10 g. of manganese, 0.53 g. of palladium, and 1.09 g. of germanium, there was obtained a fused product which was strongly magnetic and contained the same two magnetic phases described in Example 11 plus a minor amount of germanium.

EXAMPLE 13

50Mn-25Pd-25Ge

By the procedure and under the conditions of Example 7, except that the pellet was made from 1.10 g. of man-

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ganese, 1.06 g. of palladium, and 0.73 g. of germanium, there was obtained a fused product which was magnetic with a Curie temperature at 34° C. This magnetic alloy was shown by its X-ray diffraction pattern to have a $D8_8$ type hexagonal structure like that of the product of Example 11, $a=7.14$ A. and $c=4.92$ A. Minor amounts of other phases were also present.

EXAMPLE 14

33.3Mn-16.7Rh-16.7Pd-33.3Ge

By the procedure and under the conditions described in Example 2, except that the pellet was made from 0.5495 g. of manganese, 0.5150 g. of rhodium, 0.5326 g. of palladium, and 0.7260 g. of germanium, there was obtained a fused, dense, magnetic solid. This solid was heated in an alumina crucible under an atmosphere of argon in a graphite resistance furnace in approximately 30 minutes to 1400° C. The current was shut off and the product cooled rapidly to room temperature. The product was a dense metallic slug, which was strongly magnetic at room temperature. The Curie temperature was 360° C. measured in a 1000 oersted field. In a field of 15,750 oersteds the magnetization was as indicated in the following table:

Table XII

σ Value (gauss cm. ³ /g.):	Temperature, ° C.
78 -----	-195
73 -----	25
58 -----	200
(Curie temperature) -----	415

The essentially single-phase alloy was annealed by heating at 570° C. for 96 hours without substantial change in properties. The crystal structure of the annealed product was hexagonal with cell constants $a=6.585$ A. and $c=3.538$ A. The X-ray pattern is tabulated below in Table XIII.

TABLE XIII.—X-RAY PATTERN FOR HEXAGONAL Mn-Rh-Pd-Ge PHASE

Intensity ¹	Interplanar Spacing ²	Miller Indices, hkl
M ₃ -----	5.712	100
M ₃ -----	3.559	001
M ₃ -----	3.287	110
V-----	2.995	101
V-----	2.736	-----
M ₄ -----	2.650	-----
S-----	2.409	111
S-----	2.220	201
S-----	2.154	210
F-----	2.070	-----
V-----	1.971	-----
M ₂ -----	1.901	300
M ₁ -----	1.840	211
M ₃ -----	1.773	002
M ₄ -----	1.674	301
V-----	1.641	220
M ₄ -----	1.584	310
F-----	1.491	221
M ₄ -----	1.448	311
M ₄ -----	1.424	400
M ₃ -----	1.370	212
F-----	1.325	401
V-----	1.310	320
M ₃ -----	1.296	302
F-----	1.295	410
M ₂ -----	1.229	321

¹ X-ray pattern on film; S indicates the strongest line in the pattern; M₁, M₂, M₃, and M₄ indicate lines of moderate intensity (decreasing in the order M₁ to M₄); F indicates faint lines, and V indicates very faint lines.

² In Angstrom units.

The novel-manganese-germanium-rhodium and/or palladium alloys of this invention exhibit magnetic characteristics which make them especially valuable for use in various specific applications including cores for inductors, solenoids, magnetic recording members, magnetic clutches, microwave attenuators, and the like. Particularly outstanding are the relatively high saturation magnetization values exhibited by certain of these compositions, as well as the high Curie temperature and good values of

saturation magnetization exhibited below the Curie temperature.

Since obvious modifications and equivalents in the invention will be evident to those skilled in the chemical arts, I propose to be bound solely by the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A magnetic alloy consisting essentially, in atom percent, of (1) from 20 to 75% of manganese, (2) from 20 to 62% of germanium, and (3) from 1 to 35% of at least one member of the group consisting of rhodium and palladium.

2. A magnetic ternary manganese-germanium-palladium alloy the composition of which is essentially defined by the region ABCDEFA of FIG. 1.

3. A magnetic ternary manganese-germanium-palladium alloy the composition of which is essentially defined by the region ABCDGH of FIG. 1, said alloy being characterized by the presence of a magnetic phase of hexagonal crystal structure with cell constants within the ranges $a=6.57$ to 6.67 A. and $c=3.54$ to 3.64 A.

4. A magnetic ternary manganese-germanium-palladium alloy the composition of which is essentially defined by the region HFEDIH of FIG. 1, said alloy being characterized by the presence of a magnetic phase of the hexagonal $D8_8$ structure type with cell constants within the ranges $a=7.10$ to 7.25 A. and $c=4.90$ to 5.10 A.

5. A magnetic ternary manganese-germanium-palladium single-phase alloy consisting essentially of about 33.3 atom percent each of manganese, germanium and palladium, said alloy having a hexagonal crystal structure with cell constants a and c of about 6.64 and 3.57 A., respectively.

6. A magnetic ternary manganese-germanium-rhodium alloy the composition of which is essentially defined by the region A'B'C'D'E'F'A' of FIG. 2.

7. A magnetic ternary manganese-germanium-rhodium alloy the composition of which is essentially defined by the region A'B'D'F'A' of FIG. 2, said alloy being characterized by the presence of a magnetic phase of hexagonal crystal structure with cell constants within the ranges $a=6.50$ to 6.60 A. and $c=3.50$ to 3.60 A.

8. A magnetic ternary manganese-germanium-rhodium alloy the composition of which is essentially defined by the region F'D'E'F' of FIG. 2, said alloy being characterized by the presence of a magnetic phase of the hexagonal $D8_8$ structure type with cell constants within the ranges $a=7.15$ to 7.25 A. and $c=5.00$ to 5.10 A.

9. A magnetic ternary manganese-germanium-rhodium alloy the composition of which is essentially defined by the region B'C'D'B' of FIG. 2, said alloy being characterized by the presence of a magnetic phase of cubic crystal structure with a cell constant within the range $a=4.80$ to 4.85 A.

10. A magnetic ternary manganese-germanium-rhodium single-phase alloy consisting essentially of 32.5–33.3 atom percent of manganese, 32.5–33.3 atom percent of germanium and 33.3–35 atom percent of rhodium, said alloy having a hexagonal crystal structure with cell constants a and c of about 6.54 and 3.57 A., respectively.

11. A magnetic quaternary manganese-germanium-rhodium-palladium alloy consisting essentially of about 33.3 atom percent of manganese, 33.3 atom percent of germanium, and a remainder consisting of rhodium and palladium, at least about 1 atom percent of each of rhodium and palladium being present.

12. A magnetic quaternary manganese-germanium-rhodium-palladium single-phase alloy consisting essentially of about 33.3 atom percent of manganese, 33.3 atom percent of germanium, 16.7 atom percent of rhodium and 16.7 atom percent of palladium, said alloy having a hexagonal crystal structure with cell constants a and c of about 6.59 and 3.54 A., respectively.

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DAVID L. RECK, *Primary Examiner.*

R. O. DEAN, *Assistant Examiner.*