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3,421,889

**MAGNETIC RARE EARTH-COBALT ALLOYS**  
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**ABSTRACT OF THE DISCLOSURE**

Magnetic intermetallic compounds of the general formula  $R_2Co_{17}$  consisting essentially of 85 to 95 atomic percent cobalt and where R is a member selected from the group consisting of cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, yttrium, and lanthanum.

The invention described herein may be manufactured and used by or for the United States Government for governmental purposes without the payment to us of any royalty thereon.

This invention concerns a group of novel ferro- or ferrimagnetic materials, intermetallic (inorganic) compounds of a nominal composition  $R_2Co_{17}$ . In this formula, R represents any of the thirteen rare earth metals having the atomic numbers 58 (cerium) through 71 (lutetium), (with the exception of promethium), and also the elements 39 (yttrium) and 57 (lanthanum).

Both ferro- and ferrimagnetism are properties found in some of the elements and naturally occurring inorganic compounds. Iron, cobalt and nickel, for instance, exhibit ferromagnetism at room temperature, magnetite is ferrimagnetic. The difference between ferro- and ferrimagnetism lies in the way the atomic magnetic moments couple with one another. In their microscopic properties, which are of primary interest to the engineer, materials of these two groups are very similar, often indistinguishable. Therefore, it is justifiable to drop the distinction for the purpose of the following discussion and use the term "ferromagnet" for all these strongly magnetic materials, as is frequently done.

Ferromagnets are of considerable technological importance and, as a consequence, a large variety of synthetic magnetic materials have been invented and developed for special purposes. According to application area, we can distinguish two main groups, magnetically "soft" and "hard" materials, but there are also many specialty materials which do not fit either group very well. The "soft magnetic materials" include the ones used in transformer cores, magnetic amplifiers, chokes, relays, electromagnet cores, also high frequency transformers, antennas, etc. Common to these is that they have high permeabilities, low coercive force, usually high saturation induction and small hysteresis losses. Pure iron, e.g., fits this description; but to optimize selected properties, many solid solution alloys (such as Fe-Si, Fe-Al, Fe-Co, Fe-Ni, etc.) and special rolling procedures and heat treatments have been developed for them. For use at high frequencies where high electrical resistivity is also essential, some of the so-called ferrites, a family of ferrimagnetic oxides, are ideal. All ferrites now in practical use are synthetic compounds which do not occur naturally.

The "hard" magnetic materials, or permanent magnets, are of technological importance because of their ability to maintain a high, constant magnetic flux in the absence of an exciting magnetic field (or electrical current to bring about such a field). The properties which must be optimized in them are primarily the coercive force (resist-

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ance to demagnetization) and the energy product (maximum useful magnetic energy which can be stored in a unit volume of the material). The classical permanent magnet materials were hardened steels, the best permanent magnets now available are two-phase multi-component alloys of the so-called Alnico family. In recent years, it has been found that almost any ferromagnetic material can be given permanent magnet properties by subdividing it into very fine particles [1].

10 The numbers in brackets herein indicate prior publications in the references:

- [1] E. P. Wohlfarth, "Magnetism," vol. 3, p. 351, G. T. Rado and H. Suhl, editors, Academic Press, New York, 1963.
- 15 [2] R. E. Luborsky, J. Appl. Phys. 32, 171 S (1961).
- [3] E. Adams, N. W. Hubbard and E. M. Sykes, J. Appl. Phys. 23, 1207 (1952).
- [4] W. Ostertag and K. Strnat, submitted to Acta Cryst. (1966).
- 20 [5] W. Ostertag, Acta Cryst. 19, 150 (1965).
- [6] K. Strnat, G. I. Hoffer, W. Ostertag and J. C. Olson, 11th Conference on Magnetism and Magnetic Materials (1965).
- 25 [7] G. Conenetz and J. W. Salatka, Journal Electrochemical Society, vol. 105, p. 673, 1958.

Elongated particles of Fe-Co alloys are used in the commercial "Lodex" magnets [2]. It has been shown that some intermetallic compounds such as MnBi can also make good fine powder magnets [3]. The new substances which are the subject of this patent application are most likely to find practical application as permanent magnet materials, too.

Common to all ferromagnetic materials which have found technological uses to date is that they exhibit their beneficial properties: high saturation magnetization, high permeability, coercive force, etc., at room temperature. This requires above all that their "Curie point," the temperature up to which they are ferromagnetic, is above room temperature. For most applications, it must be at least several hundred degrees Celsius, or centigrade, either because the materials are to be used at elevated temperatures, or because the temperature dependence of all magnetic properties near room temperature would be too great if the Curie point were lower.

In order to exhibit strong cooperative magnetism ("ferro"-magnetism), a material must contain a substantial amount of at least one element whose atoms exhibit a strong paramagnetic moment. The metals of the 3d transition series, e.g., iron, cobalt, nickel, and manganese, are such elements. It is well known that manganese, even though not ferromagnetic itself, forms a number of ferromagnetic alloys (e.g. the Heusler alloys) and compounds (e.g. MnBi and some ferrites). There is another important family of elements, the so-called rare earth metals, many of which have high paramagnetic atomic moments, also, some even higher than the traditional magnetic substances of the iron groups. These elements which have only in recent years been available in reasonable purity and technical quantities, are thus very likely to form new useful ferromagnets when combined with other elements. Especially the combinations with metals of the 3d transition series (iron groups) are likely to be strongly magnetic. It has been shown that rare earths and iron-group metals do not form extensive solid solution alloys, but rather a great number of binary intermetallic compounds.

70 Intermetallic compounds are alloy phases of two or more metallic constituents. They are new substances different in crystal structure and physical properties from either of the parent metals. They are single phases in the metallurgical sense, can usually be assigned a "chemical"

formula of simple proportions, but do generally exist over a range of compositions (homogeneity region) which does not even always include the ideal stoichiometry defined in the formula.

Of all the possible binary combinations between the rare earth metals (R) and the iron and cobalt metals (M), the intermetallics of the types  $Rm$ ,  $RM_2$ ,  $RM_3$ ,  $RM_4$  and  $RM_5$  have already been the subjects of magnetic investigations. A number of the  $RM_4$  and  $RM_5$  compounds were shown to have properties promising a possible technological use.

We have prepared an additional family of intermetallic compounds which exhibit strong ferro- and ferrimagnetism, respectively. These are compounds of the nominal composition  $R_2Co_{17}$ , where R is any of the rare earth elements listed in the table below, or yttrium, or a mixture of these, and Co is the element cobalt. The new compounds of this invention also contemplate compositions of matter or intermetallic compounds with useful magnetic properties having nominal compositions of the general formula  $R_2Co_{17}$ , wherein Co is the element cobalt, R is selected from the group of the elements: cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, yttrium, and lanthanum, and inclusive of alloys which deviate slightly from the ideal composition, but exhibit the same basic crystal structure and physical properties very similar to the ones described and lying substantially within the composition range of 85 to 95 atomic percent cobalt.

TABLE I.—CRYSTALLOGRAPHIC AND MAGNETIC DATA

Compound $R_2Co_{17}$	Lattice Parameters, <sup>1</sup> Å.		Space Group	Density, $d$ , g./cm. <sup>3</sup>	Curie Point, $t_c$ , °C.	Saturation Magnetization <sup>2</sup> at Room Temperature (25° C.)			Absolute Saturation <sup>3</sup> at 0° K.	
	$a_0$	$c_0$				$\sigma_\infty$ (RT), emu./g.	$M_\infty$ (RT), emu./cm.	$B_\infty$ (RT), Gauss	$\sigma_\infty$ (0°), emu./g.	$n_0$ Bohr Magnets per Formula Unit
$Ce_2Co_{17}$ -----	8.335	12.153	$R\bar{3}m$ -----	8.73	795	106	925	11,600	108	24.7
(*)-----	8.335	8.102	$P6_3/mmc$ -----	8.73	-----	-----	-----	-----	-----	-----
$Pr_2Co_{17}$ -----	8.415	12.170	$R\bar{3}m$ -----	8.56	887	129	1,110	13,900	143	32.8
$Nd_2Co_{17}$ -----	8.441	12.181	$R\bar{3}m$ -----	8.55	893	154	1,317	16,550	156	36.1
$Sm_2Co_{17}$ -----	8.402	12.172	$R\bar{3}m$ -----	8.72	922	109	950	11,900	101	23.5
$Gd_2Co_{17}$ -----	8.361	12.159	$R\bar{3}m$ -----	8.91	940	66.5	593	7,440	57.5	13.5
$Tb_2Co_{17}$ -----	8.341	12.152	$R\bar{3}m$ -----	8.98	921	58.3	523	6,550	35.9	8.5
$Dy_2Co_{17}$ -----	8.335	12.153	$R\bar{3}m$ -----	9.04	916	61.7	557	6,980	29.9	7.1
(*)-----	8.335	8.102	$P6_3/mmc$ -----	9.04	-----	-----	-----	-----	-----	-----
$Ho_2Co_{17}$ -----	8.325	8.101	$P6_3/mmc$ -----	9.09	910	75.6	686	8,610	24.1	5.7
$Er_2Co_{17}$ -----	8.301	8.100	$P6_3/mmc$ -----	9.18	920	83.7	767	8,600	39.4	9.4
$Tm_2Co_{17}$ -----	8.285	8.095	$P6_3/mmc$ -----	9.24	912	98.6	910	11,400	55.0	13.2
$Lu_2Co_{17}$ -----	8.247	8.093	$P6_3/mmc$ -----	9.41	937	105	989	12,400	114	27.6
$Y_2Co_{17}$ -----	8.331	12.170	$R\bar{3}m$ -----	8.02	940	125	1,000	12,600	129	27.2
(*)-----	8.331	8.114	$P6_3/mmc$ -----	8.02	-----	-----	-----	-----	-----	-----

<sup>1</sup> Based on hexagonal unit cell.

<sup>2</sup> Obtained by extrapolation to infinite field of magnetization curves measured up to 50,000 oersted.

<sup>3</sup> Obtained by extrapolation to infinite field and to 0° Kelvin from measurements at temperatures down to 77° K. in some cases, and to 4.2° K. in others.

The basic crystallographic [4] [5], physical and magnetic properties [6] of these new substances which permit evaluation of their usefulness in magnetic applications are listed in Table I.

The Curie temperatures range from 795 to 940° C. and are thus quite high. (For comparison, the Curie point of iron is 770° C., that of cobalt is 1115° C.) The values of the saturation magnetization at room temperature,  $\sigma_\infty$  (RT), range from approximately 60 electromagnetic units of magnetic moment per gram (emu./g. to 154 emu./g. They lie then between the corresponding saturation values of nickel ( $\sigma_\infty=54.4$  emu./g. and cobalt ( $\sigma_\infty=161$  emu./g.). In both respects, the new materials appear suited for practical use in ferromagnetic devices operating at, below, and even above room temperature. For several of the new substances, the magnetization depends very little upon the temperature in this range which again is favorable for most practical uses. The materials are electrical conductors with metallic behavior (i.e., the resistivity increases with increasing temperature), therefore, they do not appear suited for any high frequency application. Quite high magnetic field strengths of the order of 20 to 50 kilogauss

are required to saturate most substances of this family in their polycrystalline, bulk form. Measurements on samples of  $Sm_2Co_{17}$ ,  $Ho_2Co_{17}$  and  $Tm_2Co_{17}$  which consisted of only a few crystallites with favorable relative orientation indicated that the field necessary for saturation varies strongly with the crystal orientation with respect to the magnetic field. This suggests that these and very probably other members of this group of compounds have a very large magneto-crystalline anisotropy. This would qualify them for application in fine particle permanent magnets.

For any commercial use, one must try to minimize the raw material costs. The individual rare earth metals are still very expensive, but certain mixtures of them can be bought at reasonable prices. The compositions of these mixtures correspond either to the ratio in which the rare earths occur naturally in the various ores, or they are those of byproducts remaining after a marketable metal has been extracted from the natural mixture. Because, apparently, all of the rare earth metals form the  $R_2Co_{17}$  compound, and because the crystal structures of the various  $R_2Co_{17}$  are either identical or very closely related, it is possible to form mixed compounds in which the 10.5 atomic percent R are made up of two or more of the rare earths. R may, for instance, be one of the above-mentioned multiple-rare earth mixtures. Following are trade names and typical compositions for the most readily available alloys of this type (percentages are by weight):

(a) Didymium, neodymium-praseodymium, etc: 70-

<sup>4</sup> The compounds  $Ce_2Co_{17}$ ,  $Dy_2Co_{17}$  and  $Y_2Co_{17}$  exhibit the two closely related structures which are listed. Their simultaneous occurrence is the result of an inconsistent stacking arrangement of the basic  $R_2M_{17}$  layers.

80% Nd, 15–30% Pr, 1–8% other rare earths, <1% other elements.

(b) Cerium-rich Mischmetal, Ceralloy 100x, "Cerium Metal," etc.: 47–55% Ce, 18–26% La, 14–20% Nd, 5–10% other rare earths (mostly Pr). <5% other elements (often 2–3% Fe).

(c) Cerium-free Mischmetal, etc.: 50–55% La, 32–36% Nd, 8–12% Pr, 2–3% other rare earths, 0.5–2% other elements.

(d) LanCerAmp, etc.: 25–35% La, 45–50% Ce, 20–25% Nd+Pr+Y, 1–2% Fe.

Either of these substituted for R will yield a ferrimagnetic alloy. With Didymium, a single phase alloy may be obtained with magnetic properties similar to and intermediate between those of  $Nd_2Co_{17}$  and  $Pr_2Co_{17}$ . The properties must resemble those of  $Ce_2Co_{17}$  if R is one of the rare earth mixtures (b) or (d) above, and those of  $Nd_2Co_{17}$  and  $La_2Co_{17}$  if mixture (c) is used for R.

The  $R_2Co_{17}$  compounds are brittle and hard. They show metallic luster and are quite resistant to atmospheric corrosion at room temperature, much more so than the rare earth metals used in their preparation. However, surface

oxidation occurs quite rapidly at temperatures of 500° C. or higher.

The compounds have been prepared by melting together the metallic constituents by one of three different techniques: (1) Non-consumable arc melting in a water-cooled hearth under a thoriated tungsten electrode. A protective atmosphere of argon or a mixture of argon and helium gases was employed. The ingots were turned over and remelted several times. (2) Conventional induction melting in a high purity recrystallized aluminum oxide crucible, with or without a carbon or tantalum susceptor. This may also be done in a noble gas atmosphere or under vacuum. A number of other crucible materials, such as impure, porous alumina, tantalum and quartz have been tried but were attacked by the melt. (3) Levitation melting in argon at or somewhat below atmospheric pressure. In this technique, the sample is not only heated and melted by induction in a high frequency magnetic field, but also freely suspended in space by the same field without making contact with a container. The melt can be cast into a mold of metal, graphite or ceramic from this levitation [7]. In each of the three cases, the samples were subjected to a homogenization anneal of several days in a vacuum of less than 10<sup>-2</sup> torr at 800 to 1100° C. The samples were heated to this temperature slowly in the course of at least 5 hours to avoid partial melting and segregation.

Having thus described the new ferromagnetic substances, and their properties and preparation, we claim as new and desire to secure by Letters Patent:

5 1. Magnetic intermetallic compounds of the general formula R<sub>2</sub>Co<sub>17</sub>, consisting essentially of 85 to 95 atomic percent cobalt and where R is a member selected from the group consisting of cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, yttrium, and lanthanum.

10 2. A composition of matter selected from the group consisting of Ce<sub>2</sub>Co<sub>17</sub>, Eu<sub>2</sub>Co<sub>17</sub>, Yb<sub>2</sub>Co<sub>17</sub>, Pr<sub>2</sub>Co<sub>17</sub>, Nd<sub>2</sub>Co<sub>17</sub>, Sm<sub>2</sub>Co<sub>17</sub>, Gd<sub>2</sub>Co<sub>17</sub>, Tb<sub>2</sub>Co<sub>17</sub>, Dy<sub>2</sub>Co<sub>17</sub>, Ho<sub>2</sub>Co<sub>17</sub>, Er<sub>2</sub>Co<sub>17</sub>, Tm<sub>2</sub>Co<sub>17</sub>, Lu<sub>2</sub>Co<sub>17</sub>, Y<sub>2</sub>Co<sub>17</sub>, and La<sub>2</sub>Co<sub>17</sub>.

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