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FERROMAGNETIC MATERIALS PREPARED FROM LANTHANONS AND TRANSITION METALS

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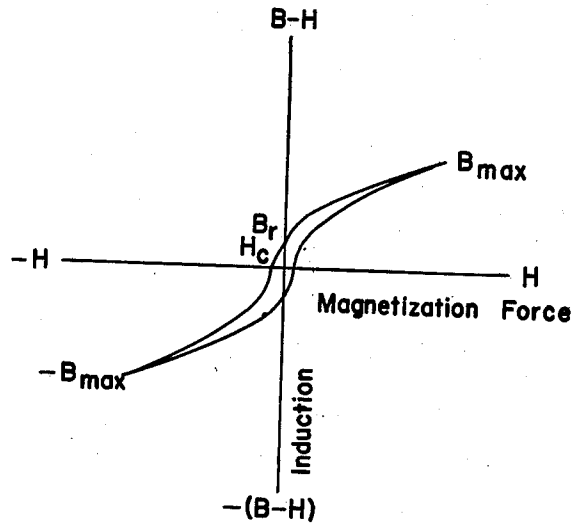

FIGURE 1.

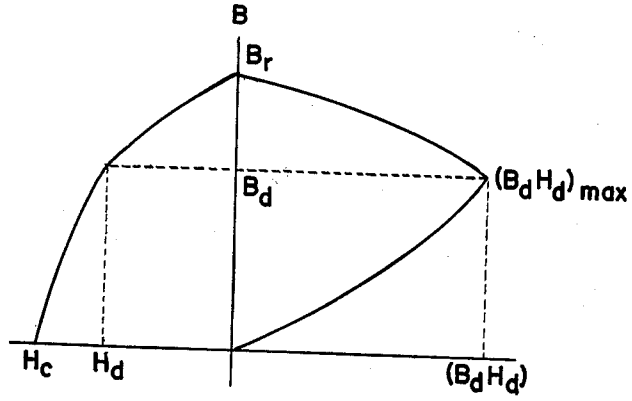

FIGURE 2.

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FERROMAGNETIC MATERIALS PREPARED FROM LANTHANONS AND TRANSITION METALS

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2 Claims. (Cl. 23—204)

This invention relates to a novel group of ferromagnetic materials prepared from certain of the lanthanide elements and the transition metals of the first long period. In one specific embodiment it relates to compounds of the lanthanides and transition metals having compositions corresponding to the formulae AB_5 and AB_2 wherein A is the lanthanide and B is manganese, iron or cobalt.

It is well known that certain metals may be magnetized in a magnetic field or with an electric current. The resulting magnets are classified as either permanent magnets or electromagnets. The electromagnets are materials that become magnetic under the influence of an electric current and lose their magnetic properties as soon as the current is cut off. The permanent magnets vary widely in magnet strength and other properties normally associated with these materials. There are three characteritsics of permanent magnets that are of particular interest; namely, energy product, coercive force and Curie point. The energy product is a measure of the potential energy stored in a material; that is, the power that can be drawn from the magnet. The coercive force is a measure of material's resistance to demagnetization. This is a measure of the force necessary to reduce the magnetism of the material to zero. The Curie point is the temperature above which a magnetic material loses its ferromagnetic properties. Thus, the energy product is a measure of the magnet's strength. The coercive force is a measure of the magnet's permanence and the Curie point is a measure of the magnet's resistance to high temperatures.

The characteristic properties of magnets are indicated by the size and shape of their hysteresis loops. The hysteresis loop for $NdCo_5$, a typical member of this group of compounds, is shown in FIGURE I. When a material to be magnetized is subjected to a gradual increase in magnetization up to H max., the induction in the material increases from zero to B (max.). This change is not permanent, however, so that if the magnetizing force is then gradually reduced to zero the induction decreases from B (max.) to B_r, the point on the vertical axis. This value B_r is a residual induction which is a characteristic property of a particular material. Another important property of the materials is the coercive force. If the magnetization force is reversed in direction and increased in value, the induction of the material is reduced until it finally reaches zero at the point H_c on the horizontal axis. If the negative force is increased further the induction reverses direction and becomes —B (max.) at —H (max.). If the induction force is again reversed from —B (max.) to H (max.), the change in induction does not follow the original curve but follows the curve —B (max.) through $-B_r$ on the vertical axis to B (max.). This section of the curve completes the hysteresis loop.

The characteristic properties of magnets may be determined by inspection from their hysteresis loops. Magnetic materials with high coercive forces have wide, short

loops. If the material has a high energy product it will be characterized by a roughly rectangular loop. A valuable tool for comparing different permanent magnetic materials can be prepared by redrawing sections of the hysteresis loop so that the demagnetization curve of the loop is combined with the energy product curve. Such a curve is shown in FIGURE II. At the right of this curve is a conventional energy product curve which is a product of B and H. This data is taken from the demagnetization curve and plotted against B. The product of B_d and H_d at any point on the demagnetization curve indicates the amount of energy produced per unit of volume. This value is frequently expressed in the C.G.S. system where B_d is in gauss and H_d is in oersteds. The unit

$$\frac{B_d H_d}{8\pi}$$

is equal to the energy product in ergs per cc. The maximum energy product may be roughly determined by visualizing the largest rectangle that can be drawn under the demagnetization curve. The external energy is zero at both B_r and H_c and reaches a peak value at the point $(B_d H_d)_{max}$. This point represents the maximum external energy that can be produced by a unit volume of a given material.

Magnetic materials are classified arbitrarily as hard magnetic and soft magnetic materials. The hard magnets are the magnets with the greatest coercive force, residual magnetism and energy product.

For several years, the magnet steels were the only magnetic materials available. These magnetic steels had energy products in the order of 9 to 10,000 gauss-oersteds but their coercive force in most cases was in the order of 200 oersteds. More recently, other materials have become available which have varied properties and are useful for different applications. These materials are generally divided into four groups. The so-called Alnicos are the materials most widely used in applications where magnets with high energy products and relatively high coercive forces are needed. These magnets are prepared from alloys of aluminum, nickel and cobalt. The energy product of these materials is in the order of 10,000 gauss-oersteds. The coercive force is in the order of 700 oersteds. Other magnetic alloys are known having energy products in the order of 7,000 gauss-oersteds and coercive forces of about 2,000 to 6,000 oersteds. The ferrimagnetic ceramic materials have energy products of about 3,000 gauss-oersteds and coercive forces of about 1,500 oersteds.

The uses of magnetic materials vary widely and certain of the materials are useful in certain areas where other types of materials have no utility. Thus, the Alnicos are used where a strong magnet that is relatively hard to demagnetize is needed. In the electronics industry there are applications where the strength of the magnet is not as important as its permanence. Certain of the so-called soft magnetic materials also find uses in the electronics industry, for example, as magnets surrounding the neck of television tubes. These magnets have a very low energy product and very small coercive force and are effective because they are subjected to electrical currents which change their magnetic properties as needed.

All materials may be classified as ferromagnetic, paramagnetic or diamagnetic. Paramagnetic and diamagnetic

materials are described more conveniently by their magnetic susceptibility than by their magnetic permeabilities.

Magnetic susceptibility is a measure of the increase in magnetic moment caused by the application of a field. Magnetic susceptibility is defined mathematically by the formula

$$K=\frac{I}{H}$$

where I is the intensity of magnetization.

$$\frac{I}{H}=\frac{\mu-1}{4\pi}$$

where μ is the magnetic permeability. The magnetic susceptibility of diamagnetic materials is negative; bismuth, for example, has a magnetic susceptibility of —0.000013. Ferromagnetic materials have positive values which may range as high as 10,000. For substances like iron, the susceptibility may be 1,000 or more.

It is sometimes difficult to draw the line separating weakly ferromagnetic materials from paramagnetic materials. Paramagnetic materials have small positive values of susceptibilities and as a rule the susceptibilities of these substances are independent of field strength and do not show hysteresis. From a practical point of view one may say arbitrarily that the material is ferromagnetic if it has a magnetic permeability greater than 1.1. Ferromagnetic materials are generally designated as "magnetics" whereas paramagnetic materials are not.

We have discovered that certain ferromagnetic materials can be prepared from the lanthanide elements of iron, cobalt and manganese. These materials vary widely in their magnetic properties and thus their possible application would be dependent on the particular material prepared. The applications of these materials, of course, depend on the particular type of properties desired. Thus, certain of these materials find application in the electronics industry where a moderate energy product is required. Others would be useful in the preparation of the magnets that depend in part for their activity on the electrical currents, such as those used in television tubes. Thus, these ferromagnetic materials are useful in a wide variety of applications.

The ferromagnetic materials of our invention fall naturally into certain groups depending on the class of lanthanides from which they are prepared. One of the standard methods of classifying the lanthanides is based on the inorganic chemistry of these compounds such as their solubility, their reactions, etc. This classification is as follows.

A. Cerium group: Lanthanum, cerium, praseodymium, neodymium, promethium and samarium

B. Yttrium group:

(1) Yttrium sub-group—yttrium
(2) Terbium sub-group—europium, gadolinium and terbium
(3) Erbium sub-group—dysprosium, holmium, erbium and thulium
(4) Ytterbium sub-group—ytterbium and lutetium
(5) Scandium sub-group—scandium

The first class of ferromagnetic compounds of our invention are the compounds having the empirical formulae AB_2 or AB_5 prepared from lanthanides in the erbium subgroup. In these compounds the A component is dysprosium, holmium, erbium or thulium, and the B component is manganese, iron or cobalt. The second grouping includes the binary ferromagnetic compounds made from praseodymium, neodymium or samarium which also have the empirical formulae AB_2 and AB_5. The members of this group consist of compounds where praseodymium, neodymium or samarium is the A component and manganese, iron or cobalt is the B component. The third member of this group is made up of the gadolinium and terbium compounds having the formulae AB_2 and AB_5 where A is gadolinium or terbium and B is manganese, cobalt or iron. The fourth grouping includes binary ferromagnetic compounds which have the empirical formulae AB_2 and AB_5 where yttrium is the A component and manganese, iron or cobalt is the B component.

Certain mixed compounds have been prepared also. In these compounds the empirical formulae still fall into the AB_2 or AB_5 classification but the A component may be a mixture of two lanthanide elements or the B component may be mixtures such as a mixture of equal amounts of iron and nickel. Examples of these compounds include: $Gd_{0.83}Y_{0.17}Co_5$; $Gd_{0.61}Y_{0.39}Co_5$; and $DyFe_{2.5}Ni_{2.5}$.

The method of preparing the ferromagnetic compounds of our invention is disclosed and claimed in our copending application S.N. 45,527, filed July 27, 1960. We have found that satisfactory compounds are obtained by melting together weighed amounts of the components under a protective atmosphere of argon. To avoid crucible contamination, the technique of levitation melting may be employed. In preparing our composition, the sample was levitated, melted and stirred by electromagnetic field from a conically shaped induction coil powered by a 10 kilowatt radio frequency generator operated at 450 kilocycles. In operation, the components necessary to prepare the desired compound were placed on a movable quartz pedestal inside the induction coil. Shortly after the power was applied the materials rose from the pedestal and were in contact only with the argon. The materials melted rather rapidly. Even those with the highest melting points and resistivity melted in times on the order of 20 seconds. Our experience showed that thorough mixing of the materials takes place less than 10 seconds after they have been completely melted. The molten samples were kept in that state for a period long enough for mixing to occur and were then dropped into a large copper mold. The copper mold rapidly dissipated the heat and solidification took place very rapidly. This rapid solidification essentially eliminated any tendency of the materials to be contaminated by the copper in the mold.

The compounds were identified using the standard X-ray analysis techniques. The diffraction patterns were obtained using a diffractionometer modified to give a linear response. The AB_2 type compounds were found to exist in the $MgCu_2$ structure. The AB_5 type compounds occurred either in the $CaCu_5$ structure or in an unsolved orthorhombic structure. The samples for X-ray examination were prepared by grinding the compounds to a powder under argon and the diffraction patterns determined over a range from 8° to 40° of 2θ.

The magnetic measurements were made using the standard techniques. The field was provided by a 6-inch electromagnet with Sucksmith type pole pieces which were powered by an electronically stabilized motor-generator. Saturation moments were obtained as usual by determining the specific magnetization, σ, at various field strengths up to 22,800 oersteds and extrapolating to infinite field using the plot of σ against $1/H$. The field strength was measured with a gaussmeter and appropriate corrections for demagnetization effects and image poles were made.

In performing the thermal magnetic analysis the sample was contained in a platinum cup which was placed inside a quartz tube under an atmosphere of argon. This assembly was suspended from one end of an analytical balance with the sample located at the position at which the field gradient was maximum. Data were obtained at a field strength of 1910 oersteds and the temperature range which could be covered extended from about —196° C. to about 1127° C. Temperatures were measured using a platinum, platinum-rhodium thermocouple located in the sample. The Curie point measurements are estimated to be reliable to plus or minus 3° and the magnetic moments to plus or minus 2%.

The invention is further illustrated by the following specific but non-limiting examples.

EXAMPLE I

The preparation of compounds of this nature is particularly difficult because of the contamination problem encountered when a reactive metal is one of the components of the compound. Because of this problem, the levitation melting technique is used.

The essential parts of the levitation melting apparatus are a radio frequency generator, a coupling network and an induction coil. The induction coil is molded above a working table and levitates and melts the sample. After the sample is prepared, it is dropped into a mold which cools the compound rapidly to below 500° C.

In the apparatus used in preparing our novel compounds, the working table was a 12-inch square brass plate. High frequency leads were brought up through polystyrene insulators cemented into place with a special cement. A supporting bar consisting of a 2-inch piece of 8 mm. quartz rod was used to hold the sample until the electromagnetic field lifted it.

The mold consisted of a 2-inch piece of 1½ inch diameter copper bar which had been hollowed out in a suitable fashion. Stainless steel rods, ⅜ inch in diameter, were used for raising and adjusting the position of the supporting bar in the mold. These rods were passed through O-ring seals in the brass plate. The levitation coil was made up of ⅛ inch diameter 0.02 inch wall copper tubing and was soldered directly to high frequency leads by means of small copper elbows. The equipment was covered with a bell jar 9 inches in diameter by 16 inches high, equipped with a brass rim and an O-ring seal. When the system was to be used it was evacuated with a rotary vacuum pump.

Three different techniques were used for making the compounds. If the two pieces of metal were about the same size, they would levitate together and mix when melted. If one of the pieces was larger than the other, the small piece was placed in the mold and the larger piece levitation melted and dropped onto it. In this case, the two pieces would generally adhere and could be levitated as one piece and remelted. The third method involved the use of a small magnetically operated hopper installed underneath the bell jar so that while one piece is floating in the molten state, another piece can be dropped into it. The levitation was followed with an optical pyrometer which indicated that temperatures up to 2000° C. were reached during the levitation process.

The levitation forces produced every efficient mixing. The sample could be observed to be spinning rapidly about a vertical axis but there was probably vortex-type mixing as well.

One of the three methods outlined was used to prepare each of the compounds of our invention.

EXAMPLE II

The magnetic properties of the compounds of the first group were determined. This group includes compounds having the formulae AB_2 or AB_5 where A is dysprosium, erbium or holmium. The B component of the compounds was iron, cobalt or manganese. Magnetic measurements were made using the standard techniques. The field was provided by a Varian 6-inch electromagnet using Sucksmith type pole pieces. The electromagnet was powered by an electronically stabilized motor-generator set. The room temperature saturation moments were obtained as usual by determining the specific magnetization σ at various field strengths up to 22,800 oersteds and extrapolating to infinite field by plotting σ against $1/H$. The field strength was measured with a Dyna-Empire gaussmeter. Appropriate corrections were made for demagnetization effects and image poles.

In determining the Curie points, the samples were placed in a platinum cup which was placed inside a quartz tube under an atmosphere of argon. This assembly was hung from one arm of an analytical balance with the sample located in the portion at which the field gradient was maximum. Data were obtained at a field strength of 1910 oersteds. The temperatures range which could be covered by this equipment extended from room temperature to about 1127° C. The temperature was measured using a platinum, platinum-rhodium thermocouple located in the sample. The data collected for the members of this group are presented in Table I.

Table I

Compound	Density	Magnetic moment in c.g.s. units per gram at 25° C.	Magnetization in gauss		Curie point in ° K.
			Calculated saturation (B_s)	Estimated residual (B_r)	
$DyFe_5$	8.9	52	5,800	2,900	420
$DyCo_5$	9.05	40.2	4,570	2,300	1,125
$DyMn_5$	8.7	37.0	4,100	2,100	485
$DyFe_2$	8.3	48.5	5,100	2,500	625
$DyCo_2$	8.9	9.0	1,000	500	300
$DyMn_2$	8.2	11.8	1,200	600	300
$HoFe_5$	9.0	39	4,400	2,200	325
$HoCo_5$	9.2	48	5,500	2,700	1,025
$HoMn_5$	8.8	28	3,100	1,500	300
$HoFe_2$	8.7	61	6,700	3,400	434
$HoCo_2$	9.0	2.7	300	----------	300
$HoMn_2$	8.5	4.25	450	----------	----------
$ErCo_5$	9.27	----------	----------	----------	1,050

EXAMPLE III

The structures of the members of the first group were determined by X-ray examination. The X-ray diffraction patterns were obtained using an XRD3 General Electric Geiger counter machine equipped with a linear rate meter. A molybdenum tube with a zirconium filter was operated at 50,000 volts and 20 milliamperes to give molybdenum K_α radiation. The source slit was 0.1° and the detector slit 1°. Records were taken at a speed of 0.2° of 2θ per minute with a chart speed of 0.4" per minute and a time constant of 10 seconds.

In obtaining the patterns, the samples were cracked and ground in a diamonite mortar under argon. The powder was sprinkled onto cellophane tape and supported in an aluminum frame in an X-ray beam. The diffraction pattern was usually determined from $2\theta=8°$ to $2\theta=40°$. Adequately sharp lines were obtained in each case without annealing. The lattice parameters for these compounds are set out in Table II.

Table II

Compound	Type of Structure	Lattice parameters—A
$DyFe_5$	$CaCu_5$	4.90 4.10
$DyCo_5$	$CaCu_5$	4.89 4.00
$DyMn_5$	Orthorhombic	a=7.18 b=4.40 c=3.11
$DyFe_2$	$MgCu_2$	7.33
$DyCo_2$	$MgCu_2$	7.20
$DyMn_2$	$MgCu_2$	7.58
$HoFe_5$	$CaCu_5$	4.86 4.10
$HoCo_5$	$CaCu_5$	4.88 3.96
$HoMn_5$	Orthorhombic	a=7.10 b=4.36 c=3.09
$HoFe_2$	$MgCu_2$	7.28
$HoCo_2$	$MgCu_2$	7.17
$HoMn_2$	$MgCu_2$	7.50
$ErCo_5$	$CaCu_5$	4.83 3.97
$ErCo_2$	$MgCu_2$	7.07

EXAMPLE IV

The magnetic properties of the compounds of the second group were determined using the equipment and technique described in detail in Example II. This group consists of compounds having the general formulae AB_2 or

AB_5 in which praseodymium, neodymium or samarium is the A component and iron, cobalt or manganese is the B component. The magnetic properties of the compounds are tabulated below.

Table III

Compound	Density	Magnetic moment in c.g.s. units per gram at 25° C.	Magnetization in gauss		Curie point in ° K.
			Calculated saturation (B_s)	Estimated residual (B_r)	
$SmFe_5$	8.4	94	9,900	5,000	
$SmCo_5$	8.5	91	9,700	4,800	1,015
$SmFe_2$	8.5	60.2	6,400	3,200	
$SmCo_2$	8.6	7	750		510
$NdFe_5$	8.2				325
$NdCo_5$	8.32	102	10,700		925
$NdMn_5$					435
$NdFe_2$	8	43.8	4,300	1,700	325
$PrCo_5$	8.34				875

EXAMPLE V

The structure of the members of the second group were determined by X-ray examination. The X-ray diffraction patterns were obtained using the equipment and technique described in detail in Example III. The lattice parameters for the members of the group are set out in Table IV.

Table IV

Compound	Type of Structure	Lattice parameters—A.
$SmFe_5$	$CaCu_5$	4.96 4.15
$SmCo_5$	$CaCu_5$	4.94 3.96
$SmFe_2$	$MgCu_2$	7.45
$SmCo_2$	$MgCu_2$	7.26
$PrCo_5$	$CaCu_5$	4.93 3.93
$PrCo_2$	$MgCu_2$	7.17

EXAMPLE VI

The magnetic properties of the compounds of the third group were determined using the techniques described in detail in Example II. This group consisted of the compounds of terbium and gadolinium having the formulae AB_2 and AB_5 where A is gadolinium or terbium and B is manganese, cobalt or iron. The data on the magnetic properties of these compounds are set out in Table V below.

Table V

Compound	Density	Magnetic moment in c.g.s. units per gram at 25° C.	Magnetization in gauss		Curie point in ° K.
			Calculated saturation (B_s)	Estimated residual (B_r)	
$GdFe_5$	8.6	41.8	4,500	2,800	455
$GdFe_2$					825
$GdCo_5$	8.8	34.8	3,840	1,900	1,030
$GdMn_5$	8.5	34.2	3,600	1,800	472
$GdCo_2$	8.8	55.3	6,100	3,000	408
$TbCo_5$	8.7				975

EXAMPLE VII

The X-ray diffraction patterns for the compounds of the third group were determined using the techniques and equipment described in Example III. The lattice parameters for these compounds are summarized in Table VI below.

Table VI

Compound	Type of Structure	Lattice parameters—A.
$GdFe_5$	$CaCu_5$	5.00 4.10
$GdCo_5$	$CaCu_5$	4.93 3.97
$GdMn_5$	Orthorhombic	a=7.23 b=4.41 c=3.13
$GdCo_2$	$MgCu_2$	7.23
$GdMn_2$	$MgCu_2$	7.73
$TbCo_5$	$CaCu_5$	4.89 3.95

EXAMPLE VIII

The magnetic properties of the compounds of the fourth group were determined using the techniques described in detail in Example II. This group consists of compounds of yttrium having the general formulae AB_2 and AB_5 where A is yttrium and B is iron, cobalt or manganese. The data on the magnetic properties of these compounds are summarized in the table below.

Table VII

Compound	Density	Magnetic moment in c.g.s. units per gram at 25° C.	Magnetization in gauss		Curie point in ° K.
			Calculated saturation (B_s)	Estimated residual (B_r)	
YCo_5	7.58	109	10,400	5,200	973
YMn_5	7.2				495
YCo_2	7.0	3.03	260		
YFe_2					535

EXAMPLE IX

The X-ray diffraction patterns for the members of the fourth group were determined using the techniques and equipment described in Example III. The lattice parameters for these compounds are summarized in Table VIII below.

Table VIII

Compound	Type of Structure	Lattice parameters—A.
YFe_2	$MgCu_2$	7.29
YCo_2	$MgCu_2$	7.22
YMn2	$MgCu_2$	7.62
YFe_5	$CaCu_5$	4.87 4.06
YCo_5	$CaCu_5$	4.83 4.00
YMn_5	Orthorhombic	a=7.12 b=4.34 c=3.05

EXAMPLE X

Three ternary compounds were prepared. These compounds have the formulae $Gd_{0.83}Y_{0.17}Co_5$; $Gd_{0.61}Y_{0.39}Co_5$ and $DyFe_{2.5}Ni_{2.5}$. The magnetic properties of these compounds were demonstrated using the equipment and techniques described in Example II. The magnetic data collected is summarized in the table below.

Table IX

Compound	Density	Magnetic moment in c.g.s. units per gram at 25° C.	Magnetization in gauss		Curie point in ° K.
			Calculated saturation (B_s)	Estimated residual (B_r)	
$Gd_{0.83}Y_{0.17}Co_5$	8.7	34	3,700	1,900	1,037
$Gd_{0.61}Y_{0.39}Co_5$	8.5	50.8	5,400	2,700	995
$DyFe_{2.5}Ni_{2.5}$	9.0	34.4	3,900	2,590	

EXAMPLE XI

The X-ray diffraction patterns for these compounds were determined using the apparatus and techniques described in Example III. The data of these compounds is presented in the table below.

Table X

Compound	Lattice Parameters—A
$Gd_{0.83}Y_{0.17}Co_5$	$a=4.96$, $c=3.97$
$Gd_{0.61}Y_{0.39}Co_5$	$a=4.92$, $b=3.98$
$DyNi_{2.5}Fe_{2.5}$	$a=4.88$, $b=4.06$

Ferromagnetic compounds are arbitrarily defined in the literature as compounds having 1% of the magnetism of iron. The magnetic moment of iron is 218 C.G.S. units per gram. All of the compounds listed had magnetic moments above 2 C.G.S. units per gram.

It is apparent from an examination of the magnetic properties of the compounds prepared that those listed are ferromagnetic.

The X-ray diffraction patterns conclusively show that the levitation melting of the rare earths with iron, cobalt and manganese produces compounds rather than alloys. Each of the compounds prepared had definite X-ray diffraction patterns. The AB_2 type compounds were found to exist in the $MgCu_2$ structure. The AB_5 type compounds appeared either as the $CaCu_5$ structure or in an unsolved orthorhombic structure.

Obviously many modifications and variations of the invention as hereinabove set forth may be made without departing from the essence and scope thereof and only such limitations should be applied as are indicated in the appended claims.

What is claimed is:

1. As compositions of matter, inorganic compounds with magnetic properties having the general formula AMn_5 wherein A is an element selected from the group consisting of holmium, dysprosium, neodymium, gadolinium and yttrium.

2. As compositions of matter, inorganic compounds with magnetic properties having the general formula AMn_2 wherein A is an element selected from the group consisting of dysprosium, holmium, neodymium, gadolinium and yttrium.

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