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54 **Rare earth iron-based permanent magnet.**

57 A rare earth-based permanent magnet is formed of a ternary compound composed of 12-30% by weight of a rare earth element, 1-10% by weight of titanium and the balance of iron or a quaternary compound composed of 12-30% by weight of a rare earth element, 1-10% by weight of titanium, up to 34% by weight of cobalt and the balance of iron. Specifically, the ternary and quaternary compounds have a crystalline structure belonging to the body-centered tetragonal system of the ThMn₁₂ type. Different from conventional neodymium-boron-iron magnets, the inventive magnets are corrosion resistant and free from rusting and have a greatly improved Curie point as compared with rare earth-iron binary magnets. The incorporation of cobalt to the ternary compound has an effect of further increasing the Curie point.

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A RARE EARTH-BASED PERMANENT MAGNET

BACKGROUND OF THE INVENTION

The present invention relates to a rare earth-based permanent magnet alloy or, more particularly, to a
 5 rare earth-based alloy for permanent magnet having excellent magnetic properties and useful as a component of various kinds of electric and electronic instruments.

Various types of rare earth-based alloys are known and now under industrial production as a material of permanent magnets, of which samarium-cobalt alloys give high-performance permanent magnets useful in speakers, electric motors, measuring instruments and the like. One of the problems in these samarium-cobalt alloys is the economical disadvantage thereof as a consequence of the expensiveness of samarium
 10 and cobalt as the constituent metals. Accordingly, it is an important technical problem in the magnet industry to develop a permanent magnet having performance as high as that of the samarium-cobalt magnets by replacing a substantial portion of the expensive cobalt with less expensive iron. Despite the efforts for increasing the proportion of iron substitution for cobalt as far as possible, practically useful rare
 15 earth-based permanent magnets can hardly be obtained by replacing about 20% by moles or more of cobalt with iron in $\text{Sm}_2\text{CO}_{17}$ -type magnets currently under mass production in the magnet industry.

Ternary alloys of neodymium, boron and iron have been proposed in recent years as a material of permanent magnets having magnetic properties even higher than those of samarium-cobalt magnets (see, for example, Japanese Patent Kokai 59-46008) and greatly highlighted in respect of the abundance of the
 20 naturally occurring resources of neodymium and iron as compared with samarium and cobalt. Unfortunately, this ternary magnet alloy has a serious defect of high susceptibility to rusting so that no practically usable permanent magnet can be prepared from the alloy unless the permanent magnet is provided with a protective coating layer against rusting. No industrially applicable coating method for protective coating, however, has yet been developed and this problem is a bottleneck which prevents the permanent magnets
 25 of this type from prevalence.

In addition, permanent magnets of the ternary alloy of neodymium, iron and boron have a relatively low Curie point T_c of 310°C and the residual magnetization thereof has a large temperature dependency of $-0.12\%/^\circ\text{C}$ so that they can hardly be used in the field of applications in which stability of the magnetic properties is essential against variation of the temperature as in electric motors and measuring instruments.
 30 Extensive investigations are of course now under way to develop rare earth-based permanent magnet alloys other than the above mentioned one such as an alloy composed of a rare earth element R and a transition metal M of which the ratio of R:M is 10 or larger and ternary alloys other than $\text{R}_2\text{Fe}_{14}\text{B}$ but no promising magnet alloys have yet been discovered.

On the other hand, binary intermetallic compounds composed of a rare earth element R and iron are
 35 well known as a magnetic material including RFe_2 , RFe_3 and R_2Fe_{17} . They are, however, not satisfactory as a material of permanent magnets because each of them has a disadvantageously low value of either one of the important magnetic properties such as the Curie point T_c , saturation magnetization $4\pi M_s$ and magnetic anisotropy coefficient K_u . Despite these problems, Croat et al. have reported in Appl. Phys. Lett., volume 37, page 1096 (1981) that a permanent magnet of a rare earth-iron binary system can be obtained by
 40 undertaking the method of thin-film quenching method in which a metastable phase is quenched and immobilized. Besides, Cadieu et al. have reported in J. Appl. Phys., volume 55, page 811 (1984) that permanent magnets in the form of a thin film can be prepared from SmFe_5 and $(\text{SmTi})\text{Fe}_5$ by the method of sputtering.

The above described binary intermetallic compounds are each in a metastable phase produced by the
 45 method of sputtering in the form of a thin film of which the crystalline structure is hexagonal according to the report of the authors. It is generally understood that these binary intermetallic compounds cannot provide a permanent magnet in a bulky form. Such a magnet is magnetically isotropic with consequently low magnetic properties and the stability thereof is also questionable as an attribute of the metastable phase forming the basic structure of the magnet. Accordingly, it is eagerly desired to develop a rare earth-
 50 based alloy for permanent magnets having high magnetic properties with stability and rustproofness from inexpensive materials.

As is mentioned above, no R-Fe binary intermetallic compounds were hitherto known which provide a permanent magnet in a bulky form having magnetic properties such as the Curie point sufficiently high as a practically useful permanent magnet. In view of the magnetic properties of the bulky permanent magnets based on the neodymium-iron-boron ternary compound developed by Sagawa et al., the inventors have

continued extensive investigations to develop a ternary or quaternary rare earth-based magnetic compound composed of a rare earth element, iron and one or two elements other than boron and capable of giving a permanent magnet free from the problems in the neodymium-iron-boron ternary magnets to uncover a series of magnetizable ternary or quaternary compounds belonging to the tetragonal crystalline system.

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SUMMARY OF THE INVENTION

10 Thus, the present invention has an object to provide a novel high-performance permanent magnet containing no or a very limited amount of expensive cobalt metal and still capable of exhibiting magnetic properties equivalent to or even higher than those of the samarium-cobalt permanent magnets and freed from the defects in the neodymium-iron-boron ternary magnets.

The permanent magnet of the invention comprises, on one hand, a ternary compound consisting
15 essentially of:

- (a) from 12% to 30% by weight of at least one rare earth element selected from the group consisting of yttrium and the elements having an atomic number of 57 to 71;
- (b) from 1% to 10% by weight of titanium; and
- (c) the balance of iron, the principal phase of the compound having a crystalline structure belonging
20 to the body-centered tetragonal system.

The permanent magnet of the invention comprises, on the other hand, a quaternary compound consisting essentially of:

- (a) from 12% to 30% by weight of at least one rare earth element selected from the group consisting of yttrium and the elements having an atomic number of 57 to 71;
- 25 (b) from 1 % to 10% by weight of titanium;
- (c) up to 34% by weight or, preferably, up to 27% by weight of cobalt; and
- (d) the balance of iron, the principal phase of the compound having a crystalline structure belonging to the body-centered tetragonal system.

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BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a powder X-ray diffraction diagram of a powder of SmTiFe_{11} with crystallographic indices
35 assigned to the peaks.

Figure 2 is a powder X-ray diffraction diagram of a powder of YMn_{12} with crystallographic indices assigned to the peaks.

Figure 3 is a graph showing a relationship between the saturation magnetization and coercive force of a powder of SmTiFe_{11} .

40 Figure 4 is a graph showing the Curie points of RTiFe_{11} and R_2Fe_{17} , R being a rare earth element, as a function of the atomic number of the rare earth element.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

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The inventors have prepared various ternary compounds composed of a rare earth element, titanium and iron and conducted crystallographic studies thereof to find that ternary compounds of the formula RTiFe_{11} have a crystallographic structure of ThMn_{12} belonging to the body-centered tetragonal system. Figure 1 shows a powder X-ray diffraction diagram of a powder of SmTiFe_{11} of $z=1$ with crystallographic
50 indices assigned to the respective peaks and Figure 2 shows a similar powder X-ray diffraction diagram of YMn_{12} compound. Comparison of Figures 1 and 2 clearly indicates that the crystalline structure of the SmTiFe_{11} well coincides with that of the YMn_{12} compound and that the SmFe_{12} compound can be stabilized by the introduction of titanium although the composition of SmTiFe_{11} merely gives an example and stabilization of SmFe_{12} can of course be obtained by the introduction of titanium in different amounts.
55 Further studies have led to a conclusion that the stabilizing effect of titanium is not limited to SmFe_{12} but can be obtained in any of the rare earth-iron compounds of the formula RFe_{12} irrespective of the kind of the rare earth elements including yttrium.

The rare earth element denoted by R in the above and useful as an ingredient of the inventive magnet

include yttrium and the elements having an atomic number of 57 to 71, i.e. lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. Preferably, the rare earth element is yttrium or a so-called light rare earth element having an atomic number of, for example, 57 to 64. Heavy rare earth elements are less preferable because of the possible decrease in the saturation magnetization $4\pi M_s$ of the magnet prepared therefrom. It is of course optional that two kinds or more of the rare earth elements are used in combination, if so desired. Table 1 below gives the lattice constants a_0 and c_0 of the $RTiFe_{11}$ compounds with various rare earth elements as R.

Table 1

Compound	a_0 , nm	c_0 , nm
CeTiFe ₁₁	0.853	0.478
NdTiFe ₁₁	0.859	0.480
SmTiFe ₁₁	0.856	0.479
GdTiFe ₁₁	0.856	0.482
TbTiFe ₁₁	0.852	0.480
DyTiFe ₁₁	0.851	0.479
HoTiFe ₁₁	0.850	0.479
ErTiFe ₁₁	0.846	0.479
LuTiFe ₁₁	0.846	0.478

Ternary compound of a rare earth element, titanium and iron having a crystallographic structure of the body-centered tetragonal system of $ThMn_{12}$ is magnetizable only when the uniaxial crystalline magnetic anisotropy coefficient K_u is sufficiently large. For example, Figure 1 illustrates a powder X-ray diffraction diagram of $SmTiFe_{11}$. The value of the anisotropic magnetic field H_a thereof is about 80 kOe so that it is concluded that the ternary compound has magnetic properties sufficiently high for a practical permanent magnet. Figure 3 also shows the data obtained at a low temperature of 77 K. These results indicate that the ternary compound of $SmTiFe_{11}$ is free from the spin rearrangement unavoidably taking place in the neodymium-iron-boron magnets at 150 K and can be used as a practical magnet even at low temperatures without any problems encountered in the neodymium-iron-boron magnets.

The ternary magnetic compound according to the invention contains from 12% to 30% by weight of the rare earth element or elements in order to have a body-centered tetragonal crystallographic structure of $ThMn_{12}$ with stability. In addition to the instability of the crystalline structure, the permanent magnet would have a greatly decreased coercive force H_c when the content of the rare earth element is smaller than 12% by weight and have a greatly decreased saturation magnetization $4\pi M_s$. The content of titanium in the ternary compound of the invention should be in the range from 1% to 10% by weight. When the content of titanium is too small, the compound hardly has a body-centered tetragonal crystallographic structure of $ThMn_{12}$. When the content of titanium is too large, on the other hand, the body-centered tetragonal structure of $ThMn_{12}$ would be less stable and the volume fraction of this desirable crystalline structure is decreased. It is important that the volume fraction of the body-centered tetragonal structure of $ThMn_{12}$ is at least 50% or, preferably, at least 70%.

The balance of the rare earth element and titanium is iron and an unavoidable amount of impurities including carbon, oxygen and the like.

The permanent magnet of the invention can be prepared by the well known powder metallurgical method. Namely, the rare earth element, titanium and iron each in the metallic form are melted together and cast in a mold and the powder of the compound obtained by pulverizing the ingot is molded in a magnetic field into a powder compact or green body which is sintered and aged according to a schedule of the heat treatment in such a manner that the crystalline grains in the resultant magnet have a particle diameter not exceeding 25 μm or, preferably, in the range from 5 to 15 μm .

The permanent magnet of the invention is composed mainly of the ternary compound of the rare earth element, titanium and iron having a stable crystalline structure of the body-centered tetragonal system of $ThMn_{12}$ as a result of introduction of titanium. As compared with the R_2Fe_{17} -type binary compounds, the ternary compound according to the invention has greatly improved magnetic properties including a higher Curie point and greatly increased saturation magnetization. Figure 4 is a graph showing the Curie points of the $RTiFe_{11}$ -type ternary compounds according to the invention and the R_2Fe_{12} -type binary compounds of

the prior art as a function of the atomic number of the rare earth elements including yttrium and lanthanum through lutetium. The magnet is prepared by the powder metallurgical method and can be imparted with magnetic anisotropy to exhibit magnetic properties equivalent to or even higher than those of the samarium-cobalt magnets. Moreover, such a high-performance permanent magnet is obtained without using expensive cobalt so that a great industrial advantage is obtained.

It is a matter of possibility that the ternary magnetic compound of the invention composed of a rare earth element, titanium and iron is further admixed with a transition element and a light element such as aluminum and silicon with an object to further improve the magnetic properties or, in particular, coercive force H_c although, in most cases, the saturation magnetization $4\pi M_s$ is more or less decreased thereby so that it is important when addition of such elements is intended to consider the balance of the coercive force and the saturation magnetization in the selection of the kind and amount of the additive elements.

As is mentioned before, the most disadvantageous defect in the neodymium-iron-boron magnets is the high susceptibility of the ternary compound to oxidation and a great decrease is caused in the magnetic properties of the magnets prepared by the powder metallurgical method due to the rapid oxidation of the surface of the fine particles thereof in the course of the magnet preparation. A magnet prepared thereby is also susceptible to rusting and cannot be used in a practical application unless a protective surface coating is provided thereon. In contrast thereto, the rare earth-based permanent magnet of the invention is highly corrosion-resistant despite the high content of iron and can be used as such without a protective surface coating although the corrosion resistance can be further enhanced when the magnet is provided with a surface coating by spraying or electrodeposition of a resinous coating composition or by vapor-phase deposition, sputtering or ion plating of a highly corrosion-resistant metallic material.

The quenching thin-film method is also applicable to the inventive permanent magnet to give a thin-film magnet having a high coercive force which is pulverized and processed into an isotropic plastic magnet according to a known procedure. It is of course possible that an anisotropically sintered magnet is pulverized and the powder is processed into a magnetically anisotropic plastic magnet.

As is shown in Figure 4, the above described ternary magnetic compound of a rare earth element, titanium and iron of the formula $RTiFe_{11}$ has an outstandingly high Curie point as compared with the R_2Fe_{17} -type binary magnetic compounds. For example, a magnet of $SmTiFe_{11}$ has a Curie point of about 310°C . However, it is sometimes desired to obtain a permanent magnet having a still higher Curie point. In addition, the improvement obtained by the above described ternary magnetic compound of a rare earth element, titanium and iron is still insufficient in respect of the relatively large temperature dependency of the magnetic properties as in the neodymium-iron-boron magnets. In view of this problem, the inventors have further continued investigations and arrived at a discovery that this problem can be solved when a part of the iron constituent is replaced with cobalt. Namely, the quaternary magnetic compound of the inventive permanent magnet consists essentially of (a) from 12% to 30% by weight of a rare earth element or a combination of two kinds or more of rare earth elements, (b) from 1% to 10% by weight of titanium, (c) up to 34% by weight or, preferably, up to 27% by weight of cobalt and (d) the balance of iron, the principal crystalline phase of the compound belonging to the body-centered tetragonal system of the $ThMn_{12}$ type.

Although no lower limit is given of the content of cobalt to be contained in the quaternary compound, the amount of cobalt should appropriately be selected depending on the desired degree of improvement in the Curie point. It should be noted, however, increase in the content of cobalt over the above mentioned upper limit has no particularly advantageous effect in further increasing the Curie point rather with disadvantageous influences on other magnetic properties if not to mention the increased cost due to the use of a large amount of the expensive cobalt metal. Generally speaking, a cobalt content of 10% by weight has an effect of increasing the Curie point of the magnet by about 90°C or more along with a remarkable effect in decreasing the temperature dependency of the magnetic properties.

In the following, examples are given to illustrate the present invention in more detail.

Example 1.

Metals of samarium, titanium and iron each having a purity of 99.9% were taken by weighing in the proportions shown in Table 2 below and they were melted together in a high-frequency induction furnace. The melt was cast in a steel-made mold to prepare three ingots of different compositions indicated as No. 1, No. 2 and No. 3 in the table. Each of the ingots was crushed and pulverized in a jet mill using nitrogen gas as the jet gas into a fine powder having an average particle diameter of 2 to $10\text{ }\mu\text{m}$. The powder in a mold was magnetically oriented in a magnetic field of 15 kOe and shaped by press-molding in a hydraulic press under a pressure of 1.5 tons/cm^2 into a powder compact which was sintered for 1 hour in an

atmosphere of argon gas at a temperature of 1000 to 1200 °C and subjected to an aging treatment for 1 hour at 400 to 900 °C followed by quenching. Table 2 also shows the coercive force iH_c of the thus prepared permanent magnets. Thus, these magnets were found to have a coercive force high enough for practical purposes.

Table 2

Formulation No.	Composition, % by weight			Coercive force iH_c , kOe
	Samarium	Titanium	Iron	
1	28.9	1.7	69.4	7.0
2	19.7	6.3	74.0	9.9
3	14.2	10.2	75.6	6.7

Example 2.

Three permanent magnets, referred to as No. 4, No. 5 and No. 6 hereinbelow, were prepared each in substantially the same manner as in the preceding example by using metals of cerium, neodymium, samarium, titanium and iron each having a purity of 99.9% in the formulation shown in Table 3 below which also shows the coercive force of the respective magnets.

Example 3.

Four permanent magnets, referred to as No. 7, No. 8, No. 9 and No. 10 hereinbelow, were prepared each in substantially the same manner as in Example 1 by using metals of neodymium, titanium, iron and cobalt each having a purity of 99.9% in the formulation shown in Table 4 below which also shows the Curie point of the respective magnets.

Table 3

Formulation No.	Composition, % by weight					Coercive force iH_c , kOe
	Neodymium	Samarium	Cerium	Titanium	Iron	
4	19.6	0	0	6.8	73.6	9.0
5	12.1	0	7.6	6.6	73.7	6.8
6	7.6	5.0	7.2	6.7	73.5	8.1

Table 4

Formulation No.	Composition, % by weight				Curie point T_C , °C
	Neodymium	Titanium	Iron	Cobalt	
7	18.51	5.92	75.57	0	310
8	18.44	5.88	67.68	8.00	401
9	18.38	5.87	60.03	15.72	482
10	18.33	5.85	52.18	23.64	589

Example 4.

Four permanent magnets, referred to as No. 11, No. 12, No. 13 and No. 14 hereinbelow, were prepared each in substantially the same manner as in Example 1 by using metals of samarium, titanium, iron and cobalt each having a purity of 99.9% in the formulation shown in Table 5 below which also shows the coercive force and Curie point of the respective magnets.

Table 5

Formulation No.	Composition, % by weight				Coercive force iH_c , kOe	Curie point T_C , °C
	Samarium	Titanium	Iron	Cobalt		
11	19.23	6.43	70.32	4.02	10.2	356
12	19.08	6.37	61.45	13.10	9.6	454
13	19.13	6.12	55.30	19.45	8.4	537
14	19.41	6.28	47.94	26.37	6.5	613

Example 5.

Four permanent magnets, referred to as No. 15, No. 16, No. 17 and No. 18 hereinbelow, were prepared each in substantially the same manner as in Example 1 by using metals of neodymium Nd, samarium Sm, dysprosium Dy, yttrium Y, titanium Ti, iron Fe and cobalt Co each having a purity of 99.9% in the formulation shown in Table 6 below which also shows the coercive force iH_c and temperature dependency of saturation magnetization $\Delta M/\Delta T$ of the respective magnets.

Table 6

Formulation No.	Composition, % by weight							μH_c , kOe	$\Delta M/\Delta T$, %/°C
	Sm	Nd	Dy	Y	Ti	Fe	Co		
15	15.98	0	2.93	0	6.03	68.10	6.96	9.9	-0.094
16	0	16.31	0	2.05	6.21	62.06	13.37	5.8	-0.071
17	12.88	5.60	0	0	6.12	63.57	12.03	8.3	-0.077
18	0	18.72	0	0	6.31	55.43	19.54	5.9	-0.061

Claims

1. A permanent magnet which comprises a ternary compound consisting essentially of:

- (a) from 12% to 30% by weight of at least one rare earth element selected from the group consisting of yttrium and the elements having an atomic number of 57 to 71;
- (b) from 1% to 10% by weight of titanium; and
- (c) the balance of iron,

the principal phase of the compound having a crystalline structure belonging to the body-centered tetragonal system.

2. A permanent magnet which comprises a quaternary compound consisting essentially of:

- (a) from 12% to 30% by weight of at least one rare earth element selected from the group consisting of yttrium and the elements having an atomic number of 57 to 71;
- (b) from 1% to 10% by weight of titanium;
- (c) up to 34% by weight of cobalt; and
- (d) the balance of iron,

the principal phase of the compound having a crystalline structure belonging to the body-centered tetragonal system.

3. The permanent magnet as claimed in claim 1 wherein the rare earth element is selected from the group consisting of yttrium and the elements having an atomic number of 57 to 64.

4. The permanent magnet as claimed in claim 2 wherein the rare earth element is selected from the group consisting of yttrium and the elements having an atomic number of 57 to 64.

5. The permanent magnet as claimed in claim 1 wherein the principal phase of the ternary compound has a crystalline structure belonging to the body-centered tetragonal system of the ThMn_{12} type.

6. The permanent magnet as claimed in claim 2 wherein the principal phase of the quaternary compound has a crystalline structure belonging to the body-centered tetragonal system of the ThMn_{12} type.

7. The permanent magnet as claimed in claim 1 wherein the volume fraction of the phase having a crystalline structure belonging to the body-centered tetragonal system in the ternary compound is at least 50%.

8. The permanent magnet as claimed in claim 2 wherein the volume fraction of the phase having a crystalline structure belonging to the body-centered tetragonal system in the quaternary compound is at least 50%.

9. The permanent magnet as claimed in claim 2 wherein the amount of cobalt as the component (c) does not exceed 27% by weight.

Fig. 1

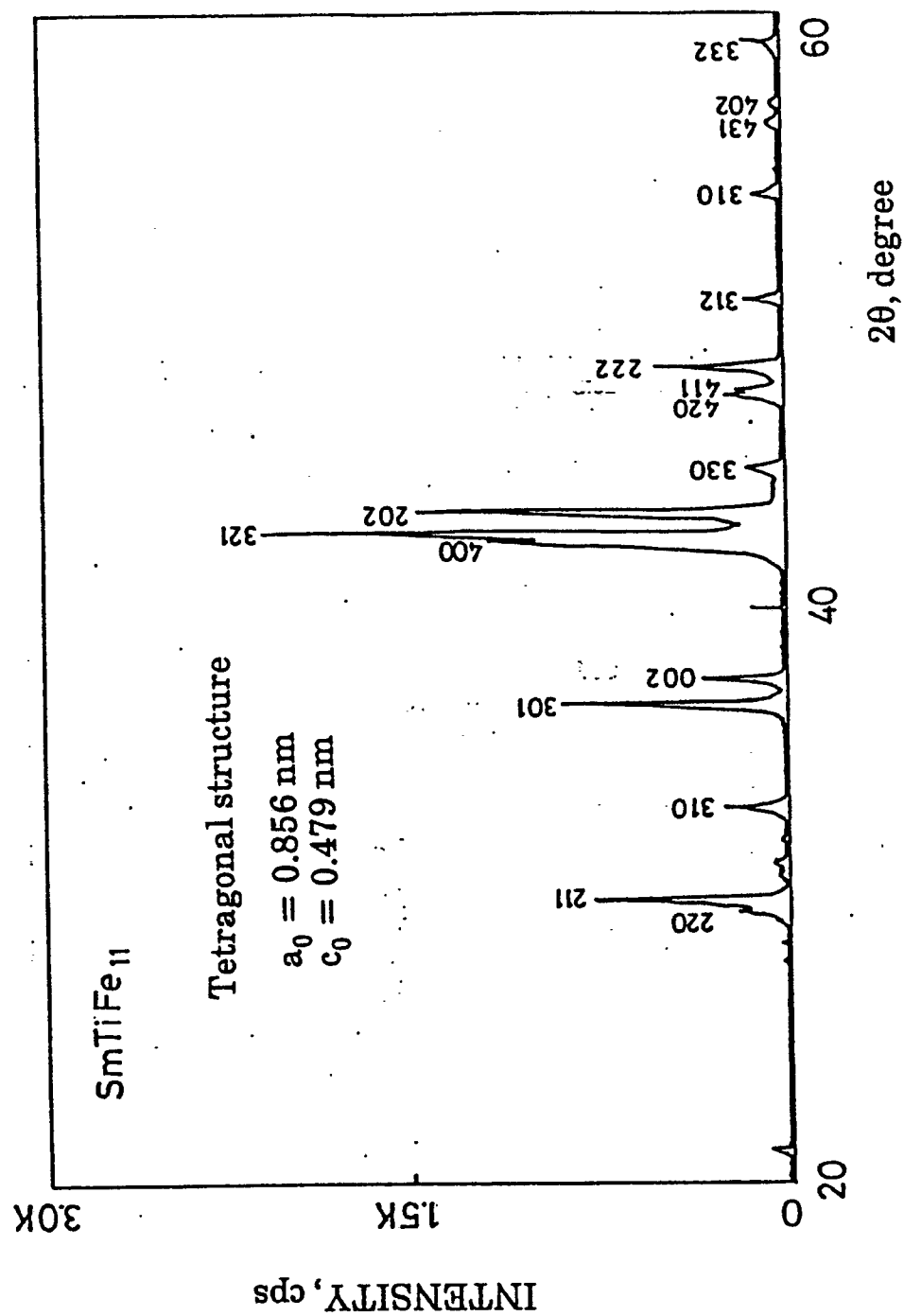


Fig. 2

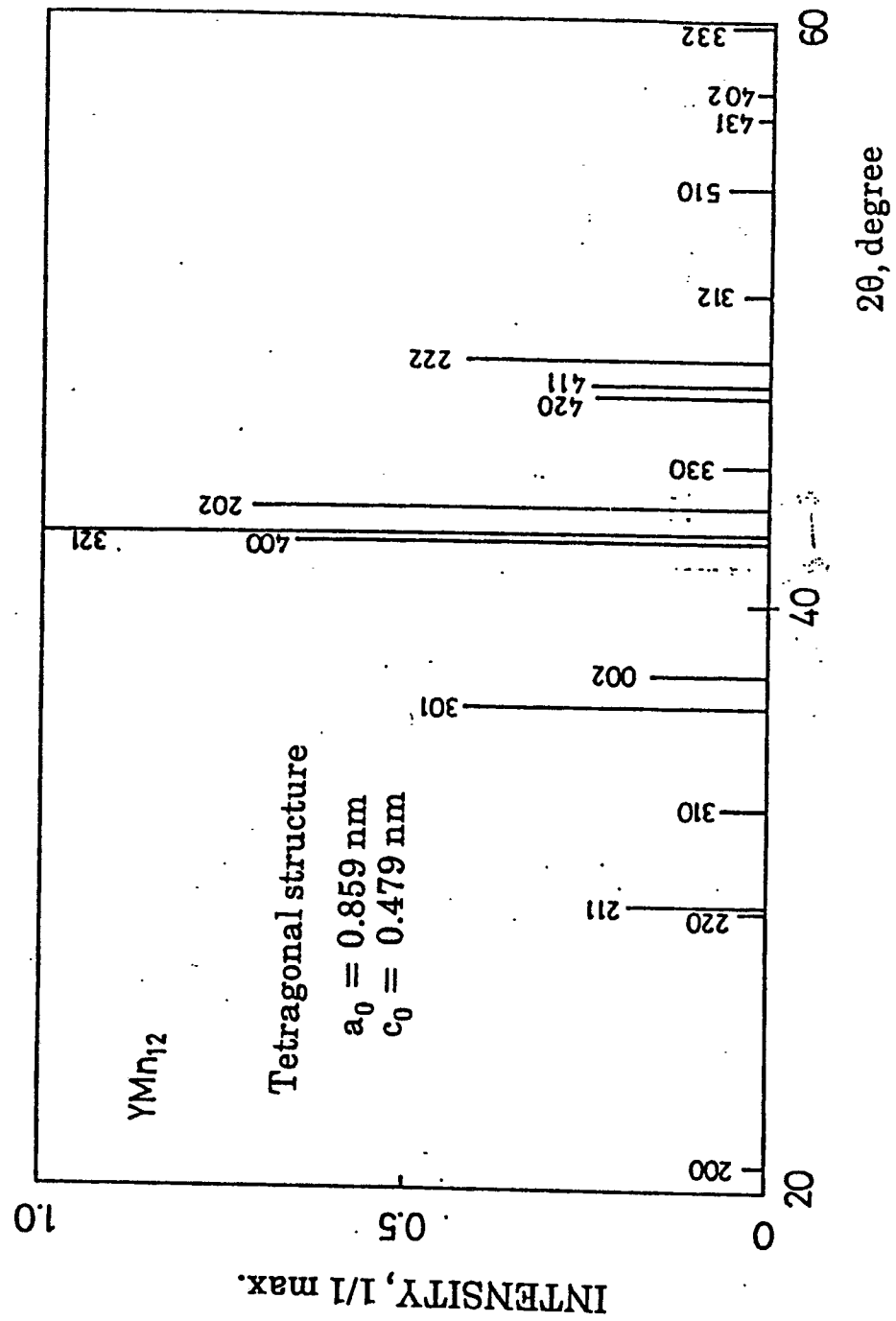


Fig. 3

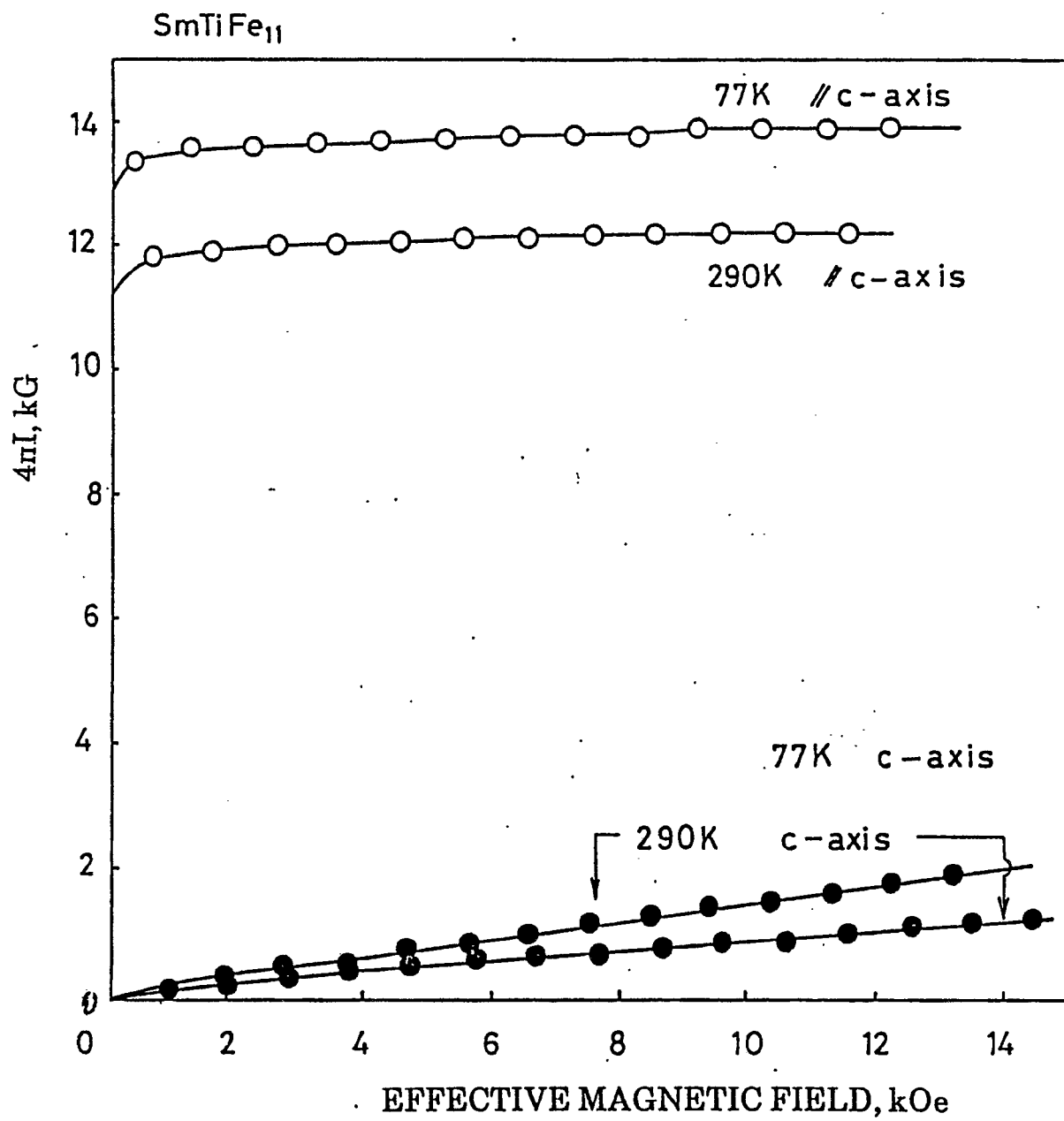
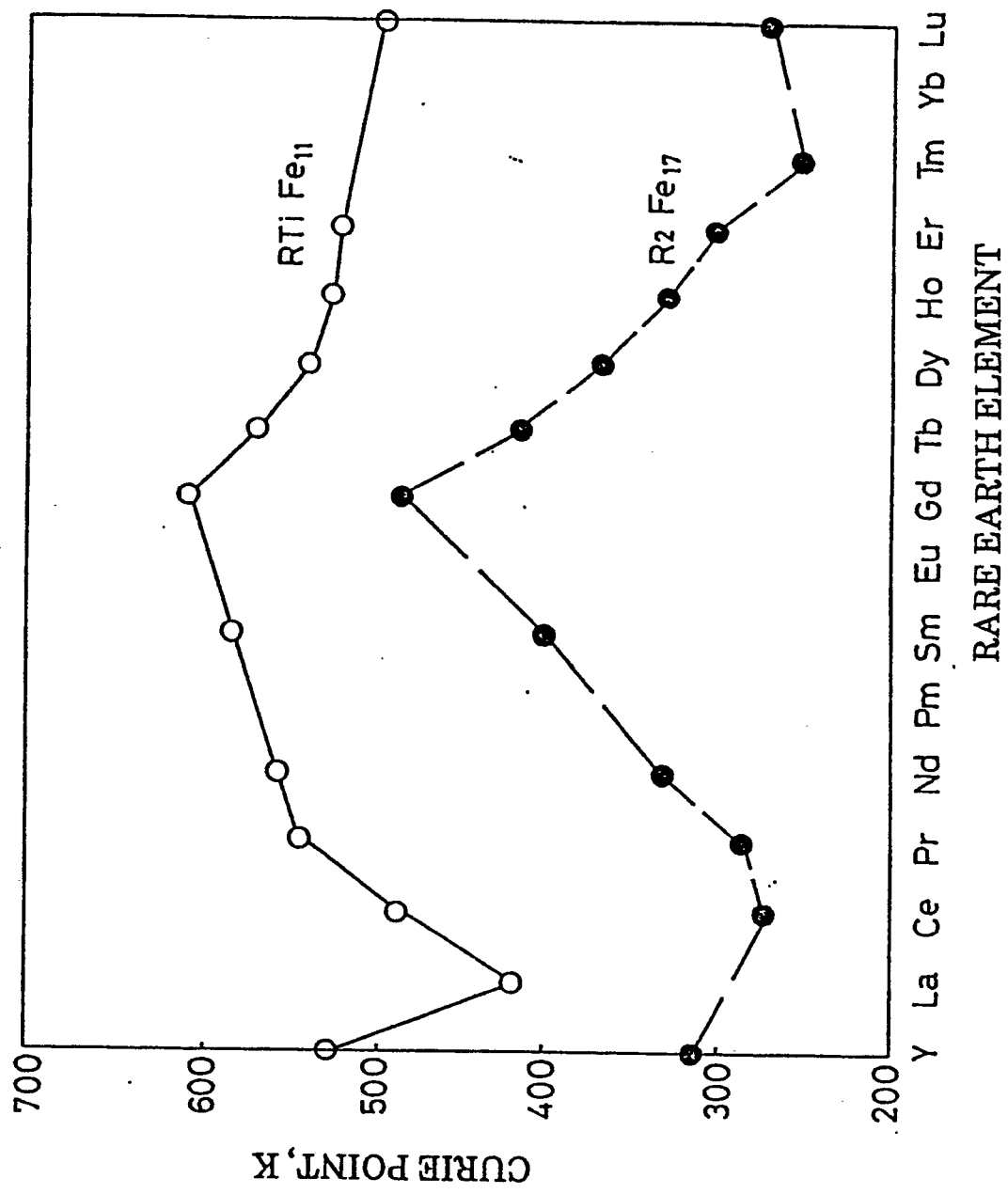


Fig. 4





European Patent
Office

EUROPEAN SEARCH REPORT

Application number

EP 89 10 4002

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	APPLIED PHYSICS LETTERS, vol. 51, no. 24, December 14, 1987, pages 2048-2050, American Institute of Physics, New York, US; G.C. HADJIPANAYIS et al.: "Hard magnetic properties of R-Fe-Ti alloys"		H 01 F 1/053
	* Abstract; page 2048, right-hand column, paragraph 1 *	1,3,5	
Y	--	2,4,6	
X	EP-A-0 242 283 (SHIN-ETSU CHEMICAL CO. LTD.)		
	* Claims 1-3; page 3, lines 16-23*	1,3	
Y	* Claims 1-3; page 3, lines 16-22; page 3, line 60 - page 4, line 2 *	2,4,6	
A	--	9	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
X	EP-A-0 253 428 (N.V. PHILIPS' GLOEILAMPENFABRIEKEN)		
	* Claims 1,2 *	2,4,6	
	--		H 01 F
D,A	JOURNAL OF APPLIED PHYSICS, vol. 55, no. 6, March 15, 1984, pages 2611-2613, American Institute of Physics, New York, US; F.J CADIEU et al.1 "Magnetic properties of a metastable Sm-Fe phase synthesized by selectively thermalized sputtering"		
	--		
A	JOURNAL OF APPLIED PHYSICS, vol. 64, no. 10, November 15, 1988, pages 5714-5716, American Institute of Physics, New York, US	./.	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 19-02-1990	Examiner DECANNIERE
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons a : member of the same patent family, corresponding document			



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
	K. OHASHI et al.: "Magnetic properties of Fe-rich rare-earth inter-metallic compounds with a ThMn ₁₂ structure" -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	