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⑤④ **Rare-earth based magnetic materials, production process and use.**

⑤⑦ A new magnetic material of the general formula :



is derived from an intermetallic compound of rhombohedral, hexagonal or tetragonal crystal structure wherein R is one or more rare earth elements, X' is an element of groups IIIA, IIIB, IVA or IVB of the periodic table, Z is one or more elements of group VA of the periodic table, x is a value from 0.5 to 2, y is a value from 9 to 19, a is a value from 0 to 3, b is a value from 0.3 to 3 and wherein when the magnetic material of said general formula is derived from an intermetallic compound of rhombohedral or hexagonal crystal structure Fe is unsubstituted or partially substituted by another element and when the magnetic material of said general formula is derived from an intermetallic compound of tetragonal crystal structure Fe is partially substituted by any element of group IIIA or IVA of the periodic table or a transition metal from another group with the further proviso that in the case of materials derived from said rhombohedral or hexagonal crystal structures the element X' is not boron when the component Z is antimony or bismuth.

In these new materials the element Z is an interstitial addition to the existing structures and is introduced by a gas-solid reaction. The materials exhibit increased Curie temperatures, magnetic strength and easy uniaxial anisotropy and are therefore suitable for fabricating into permanent magnets.

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The invention relates to new magnetic materials having improved magnetic properties, to processes for their production and to the use of the new materials to make permanent magnets.

Magnets have many applications in engineering and science as components of apparatus such as electric motors, electric generators, focussing elements, lifting mechanisms, locks, levitation devices, anti-friction mounts and so on. In order for a magnetic material to be useful for making a permanent magnet three intrinsic properties are of critical importance. These are the Curie temperature (T_c) i.e. the temperature at which a permanent magnet loses its magnetism, the spontaneous magnetic moment per unit volume (M_s) and the easy uniaxial anisotropy conventionally represented by an anisotropy field B_a . The Curie temperature is of particular significance because it dictates the temperature below which apparatus containing the magnet must be operated.

During this century much research has been directed to developing magnetic materials which combine high Curie temperatures and improved magnetic moments with strong uniaxial anisotropy. For many years magnetic materials of the AlNiCo type were used in permanent magnets for practical applications. In the late 1960's it was discovered that alloys of the rare earth elements, particularly samarium when alloyed with cobalt, had magnetic properties which made them superior as permanent magnets to the AlNiCo type. Compounds of samarium and cobalt provided magnets which were particularly successful in many demanding practical applications requiring a magnet with a high energy product. However the high cost of cobalt as a raw material led investigators in the early 1980's to consider the possibility of combining the cheaper and more abundant iron with the magnetically superior rare earth elements to produce permanent magnets with improved magnetic properties. A major breakthrough came in 1983 when the Sumitomo Special Metals Company and General Motors of America independently developed a magnetic material which combined a rare earth element and iron and incorporated a third element, boron, into the crystal lattice to give an intermetallic compound, $Nd_2Fe_{14}B$ which can be used to produce magnets with an excellent energy product, but a lower Curie temperature than the Sm-Co materials. These Nd-Fe-B magnetic materials can have a Curie temperature of up to 320°C and are particularly described in three European applications, EP-A-0101552, EP-A-0106948 and EP-A-0108474. Derivatives of these boride materials represent the state of the art to date in magnet technology. However they are somewhat unstable in air and change chemically, gradually losing their magnetic properties so that despite Curie temperatures in excess of 300°C in practice they are not suitable for operating at temperatures greater than 150°C.

The fact that the incorporation of boron into the crystal lattice of intermetallic materials containing a rare earth element and iron serves to improve magnetic properties has encouraged investigators to search for new compounds of elements other than boron in combination with rare earth elements and iron.

In 1987 Higano et al (IEEE Transactions on Magnetics, vol. Mag-23, No. 5 Sept 1987) reported an attempt to carry out a nitriding reaction by exposure of powders of Sm_2Fe_{17} alloy to gaseous nitrogen at temperatures of 500 and 1100°C. The experiment was intended to produce a compound of the formula $Sm_2Fe_{17}N$ which it was hoped would have improved magnetic properties. However Higano et al found no evidence that such a material was produced by this process but instead found that the nitriding process simply decomposed the rare-earth iron alloy starting material to produce iron and nitrides of the rare earth elements.

The present inventors have now produced a new magnetic material of improved properties which includes at least a rare earth element, iron and a group VA element with optionally one or more other elements. The successful production of these materials is unexpected having regard to the teaching of Higano et al.

In accordance with one aspect of the invention there is provided a magnetic material of the general formula:



which is derived from an intermetallic compound of rhombohedral, hexagonal or tetragonal crystal structure wherein R is one or more rare earth elements, X' is an element of groups IIIA, IIIB, IVA or IVB of the periodic table, Z is one or more elements of group VA of the periodic table, x is a value from 0.5 to 2, y is a value from 9 to 19, a is a value from 0 to 3, b is a value from 0.3 to 3 and wherein when the magnetic material of said general formula is derived from an intermetallic compound of rhombohedral or hexagonal crystal structure Fe is unsubstituted or partially substituted by another element and when the magnetic material of said general formula is derived from an intermetallic compound of tetragonal crystal structure Fe is partially substituted by any element of group IIIA or IVA of the periodic table or a transition metal from another group with the further proviso that in the case of materials derived from said rhombohedral or hexagonal crystal structures the element X' is not boron when the component Z is antimony or bismuth.

It is to be understood that herein the term rare earth element includes the elements yttrium and thorium, and that the groups IIIA, IIIB, IVA, IVB and V of the periodic table are those defined by the CAS version of that table. By hexagonal, rhombohedral and tetragonal crystal structure is meant intermetallic compounds having a crystal structure analogous to Th_2Ni_{17} , Th_2Zn_{17} and $ThMn_{12}$ respectively.

In the case where the material is derived from an intermetallic compound of hexagonal or rhombohedral

crystal structure the element R may be samarium alone or a combination of samarium with one or more other rare earth elements selected from lanthanum, cerium, neodymium, praseodymium, erbium, thulium, yttrium, and mischmetal. R may also be yttrium, cerium, neodymium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, or a mixture of two or more thereof. In the case where the material is derived from an intermetallic compound of tetragonal crystal structure, R may be any rare earth element but preferred elements for R are cerium, praseodymium, neodymium, terbium, dysprosium, holmium or a mixture of two or more thereof. Particularly preferred are neodymium or praseodymium alone or in combination with other elements.

In the case of the hexagonal or rhombohedral materials as aforementioned the iron may be substituted by up to 50%, most preferably up to 33% with another element or elements. The element is preferably a magnetic transition metal, most preferably cobalt.

In the case of the tetragonal materials as aforementioned the iron is substituted with any element of group IIIA or IVA of the periodic table or with a transition metal not already included in those groups. Preferred substituents are silicon or aluminium or any of the transition metals titanium, vanadium, molybdenum or chromium.

Where an element X' is included in the materials it is preferably carbon, boron, silicon or zirconium and the value of "a" may be as low as 0.1 with a maximum of 3. Preferably the value of a+b is ≤ 3 .

The component Z may be nitrogen, phosphorus, arsenic, antimony or bismuth or mixtures thereof and of these the particularly preferred element is nitrogen. For example, three materials in accordance with this aspect of the invention which demonstrate the requisite improved magnetic properties are $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$, $\text{Sm}_2\text{Fe}_{17}\text{C}_{1.1}\text{N}_{1.1}$ and $\text{NdFe}_{11}\text{TiN}_{0.8}$.

The magnetic materials of the invention display considerably improved magnetic properties over materials hitherto known. Firstly they have Curie temperatures in excess of 400°C. Secondly, they have improved easy uniaxial anisotropy as demonstrated by X-ray diffraction patterns of the material after a magnetic field has been applied. Thirdly, the magnetic moment is increased and finally the magnetic moment is subject to little variation with time or temperature around ambient temperature. These increased intrinsic magnetic properties are all very favourable for permanent magnet applications.

In accordance with a second aspect of the invention there is provided a process for modifying the magnetic properties of an intermetallic compound comprising at least one or more rare earth elements and the element iron in which the iron is optionally substituted with another element which process comprises heating said intermetallic compound with a gas containing at least one group VA element Z in the substantial absence of oxygen to incorporate the said at least one element Z interstitially into the crystal lattice of the intermetallic compound by a gas-solid reaction. Where the intermetallic compound is of tetragonal crystal structure the iron may be substituted by an element of group IIIA or group IVA of the periodic table or by a transition metal not already included in those groups.

The sample material is preferably placed in a sealed container from which the oxygen can be pumped and the reactive gas added and heated from the outside. Its temperature is raised to a maximum not exceeding about 600°C. Optionally the intermetallic starting material is ground from, for example, an ingot to a particle size of from 0.5 to 50 microns diameter before heating in a suitable gas. The preferred range is 0.5 to 20 microns. Specific additives such as niobium or vanadium may be added to reduce or eliminate free iron present in the ingot facilitating the development of coercivity in the resulting modified metallic material. Alternatively, the starting material may be prepared into thin flakes or ribbons by melt spinning or into powder by mechanical alloying or spray casting. The heating may proceed for a period not exceeding 8 hours, but the exact time will depend upon the gas and the solid geometry of the starting material. The precise heating time for any starting material is therefore readily calculable.

Suitable gases to be used in the process include those which produce radicals containing single atoms of a group VA element on contact with hot surfaces such as metal or quartz or by exposure to high frequency radiation, for example gaseous hydrides of the group VA elements.

The preferred magnetic materials of the invention, in which the group VA component Z interstitially inserted into the crystal lattice is nitrogen, may be made from the appropriate intermetallic starting material using gaseous nitrogen, ammonia or hydrazine. When an intermetallic compound of the formula R_2Fe_{17} , or RFe_{11}Ti for example, is heated with nitrogen and the gas pressure monitored, a decrease in pressure occurs which begins at about 350°C and continues until the temperature reaches 650°C. The initial decrease in pressure is attributed to the reaction of nitrogen with the exemplified intermetallic compound and its incorporation into the R_2Fe_{17} or $\text{R}(\text{FeTi})_{12}$ crystal lattice. That a new compound incorporating R, Fe and N has been formed is borne out by the fact that after the heating process the sample has increased weight and there is an increase in the crystal lattice parameters i.e. unit cell volume, as shown by X-ray diffraction.

The process of producing the new preferred materials may also be carried out using ammonia instead of nitrogen. In this case there is a rise in pressure starting at approximately 350°C. The rise in pressure is explained

by the fact that at 350°C the ammonia decomposes to nitrogen and hydrogen. The nitrogen is taken up by the intermetallic sample as evidenced by a weight gain and increased crystal lattice parameters. It appears that once the temperature exceeds about 650°C the newly formed material decomposes to alpha-Fe and nitrides of the rare earth element or elements.

In accordance with a third aspect of the invention the new magnetic material produced as described herein is used for fabricating permanent magnets.

A preferred process by which this may be achieved comprises milling the magnetic material with a metal such as aluminium, copper or zinc or a solder or an organic powder or resin, magnetically aligning the material by applying a magnetic field and then heating to a temperature not sufficient to decompose the material. Preferably the magnetic material is milled with zinc. This process of forming a magnet serves to increase the coercivity essential for forming magnets.

The following figures and tables give data relating to the magnetic properties of certain preferred intermetallic compounds of the invention and by way of example demonstrate the improvement in magnetic properties over known magnetic materials.

Table 1

The data in this table demonstrate the effect of incorporating nitrogen interstitially into the crystal lattice of compounds of the formula R_2Fe_{17} with respect to crystal lattice parameters, Curie temperature (T_c) and spontaneous magnetization per unit mass (6_s). These nitrogen-containing compounds were prepared by the process of heating in nitrogen gas in accordance with the invention.

The lattice parameters are determined by X-ray diffraction. R is represented by 12 different rare earth elements.

The spontaneous magnetization per unit mass (6_s) is converted to spontaneous magnetization per unit volume (M_s) by multiplying the value 6_s by the density of the magnetic material.

Compound	Structure type	a (nm)	c (nm)	T _c (°C)	6 _s (JT ⁻¹ Kg ⁻¹)
Ce ₂ Fe ₁₇	Th ₂ Zn ₁₇	0.847	1.232	-32	0
Ce ₂ Fe ₁₇ N _{2.8}	"	0.873	1.265	440	160
Pr ₂ Fe ₁₇	"	0.857	1.242	17	82
Pr ₂ Fe ₁₇ N _{2.5}	"	0.877	1.264	455	167
Nd ₂ Fe ₁₇	"	0.856	1.244	57	77
Nd ₂ Fe ₁₇ N _{2.3}	"	0.876	1.263	459	178
Sm ₂ Fe ₁₇	"	0.854	1.243	116	100
Sm ₂ Fe ₁₇ N _{2.3}	"	0.873	1.264	476	159*
Gd ₂ Fe ₁₇	"	0.851	1.243	204	46
Gd ₂ Fe ₁₇ N _{2.4}	"	0.869	1.266	485	115
Tb ₂ Fe ₁₇	"	0.845	1.241	131	51
Tb ₂ Fe ₁₇ N _{2.3}	"	0.866	1.266	460	96
Dy ₂ Fe ₁₇	Th ₂ Ni ₁₇	0.845	0.830	94	50
Dy ₂ Fe ₁₇ N _{2.8}	"	0.864	0.845	452	115
Ho ₂ Fe ₁₇	"	0.844	0.828	54	49
Ho ₂ Fe ₁₇ N _{3.0}	"	0.862	0.845	436	115
Er ₂ Fe ₁₇	"	0.842	0.827	23	32
Er ₂ Fe ₁₇ N _{2.7}	"	0.861	0.846	424	134
Tm ₂ Fe ₁₇	"	0.840	0.828	-13	0
Tm ₂ Fe ₁₇ N _{2.7}	"	0.858	0.847	417	137
Lu ₂ Fe ₁₇	"	0.839	0.826	-18	0
Lu ₂ Fe ₁₇ N _{2.7}	"	0.857	0.848	405	147
Y ₂ Fe ₁₇	"	0.848	0.826	52	92
Y ₂ Fe ₁₇ N _{2.6}	"	0.865	0.844	421	164

*Extrapolated value

The data presented in Table 1 demonstrate that the interstitial nitride phase R₂Fe₁₇Nb, where b is about 2.6, exists across the entire rare-earth series from Ce to Lu. The unit cell volume of the crystal lattice increases by 5 to 9% on forming the nitride and the Curie temperature T_c and spontaneous magnetization 6_s are greatly increased. Data further indicate that substitutions exist between nitrides of different rare earths so that properties such as magnetization or anisotropy field may be optimised for particular applications having regard to the cost of the particular rare earth component.

Table 2

The data in the table demonstrate the effect on crystal lattice parameters, Curie temperature (T_c) and the spontaneous magnetic moment per unit volume (M_s) of incorporating nitrogen into the crystal lattice of compounds of the formula: Y₂Fe₁₇C_{1.0} and Sm₂Fe₁₇C_{1.1}. Again the novel compounds were prepared by heating in

a nitrogen-containing gas in accordance with the invention.

5	Compound	Structure type	a (nm)	c (nm)	T _c (°C)	$\mu_0 M_S^*$ (T)
	Y ₂ Fe ₁₇ C _{1.0}	Th ₂ Ni ₁₇	0.855	0.833	239	1.25
	Y ₂ Fe ₁₇ C _{1.0} N _{1.4}	"	0.867	0.851	428	1.46
10	Sm ₂ Fe ₁₇ C _{1.1} **	Th ₂ Zn ₁₇	0.858	1.244	207	1.11
	Sm ₂ Fe ₁₇ C _{1.1} N _{1.1}	"	0.873	1.270	471	1.53

15 * at 18°C

** values are sensitive to conditions of heat treatment after melting the alloys.

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The data again demonstrate the improvement in magnetic properties, T_c, magnetization and unit cell volume, by interstitial incorporation of nitrogen into the crystal lattice of compounds of the general formula R_xFe_yX'_z.

25 Table 3

The data presented in this table demonstrate the improved easy uniaxial anisotropy with, as an example, compounds where R is samarium. The value for easy uniaxial anisotropy represented by the anisotropy field B_a, in Tesla was obtained by aligning the rhombohedral c-axis in the direction of an applied magnetic field. From magnetization curves on oriented powders with the field applied parallel and perpendicular to the alignment direction the values for B_a shown in this table were obtained.

Compound	B _a (T)
Sm ₂ Fe ₁₇	< 1.0
Sm ₂ Fe ₁₇ N _{2.3}	>12.0
35 Sm ₂ Fe ₁₇ C _{1.1}	4.0
Sm ₂ Fe ₁₇ C _{1.1} N _{1.0}	>8.0

Table 4

40 The data in this table presented give deduced values for iron-iron and iron-rare earth exchange interactions based on the variation in Curie temperature for the different heavy rare earths.

Compound	$n_{R-Fe} (\mu_0)$	$n_{Fe-Fe} (\mu_0)$
45 R ₂ Fe ₁₇	225	181
R ₂ Fe ₁₇ N _y	208	515

50 It is deduced that the iron-iron interactions are enhanced by a factor of 2.5 in the new nitride compounds while iron-rare earth interactions are only slightly decreased.

Table 5

55 The data presented in the table demonstrate the effect of incorporating nitrogen interstitially into the crystal lattice of compounds of the formula RFe₁₁Ti with respect to crystal lattice parameters, (a and c), Curie temperature (T_c), average hyperfine field B_{hf}, in Tesla, and anisotropy. The starting materials were prepared by heating in a nitrogen-containing gas in accordance with the process of the invention. The particular process

conditions in each case are given in the table.

5	Compound	a(nm)	c(nm)	T _c (°C)	B _{hf} (T)	anisotropy	processing
	Nd(Fe ₁₁ Ti)	0.856	0.478	270	21.5	c-axis	
10	Nd(Fe ₁₁ Ti)N _{0.7}	0.879	0.487	475	28.0	c-axis	40' at 450°C in N ₂
	Sm(Fe ₁₁ Ti)	0.855	0.479	311	25.5	c-axis	
	Sm(Fe ₁₁ Ti)N _{0.8}	0.864	0.484	496	29.1	c-plane	30' at 480°C in N ₂
15	Sm(Fe ₁₁ Ti)N _{0.9}	0.865	0.486	490			heat to 550°C @ 10°/min in NH ₃
	Dy(Fe ₁₁ Ti)	0.850	0.478	257	24.4	c-axis	
20	Dy(Fe ₁₁ Ti)N _{0.6}	0.867	0.480	473	28.2	c-axis	60' at 450°C in N ₂
	Tb(Fe ₁₁ Ti)	0.852	0.479	281	24.2	c-axis	
25	Tb(Fe ₁₁ Ti)N _{0.5}	0.864	0.482	477	28.5	c-axis	40' at 450°C in N ₂
	Y(Fe ₁₁ Ti)	0.851	0.479	251	23.5	c-axis	
30	Y(Fe ₁₁ Ti)N _{0.8}	0.862	0.481	460	28.8	c-axis	60' at 480°C in N ₂

The interstitial incorporation of an element of group VA of the periodic table, for which the example is nitrogen, into selected intermetallic compounds of the formula R₂Fe₁₇ or R₂Fe₁₇X_a or R(FeM)₁₂ or R₂(FeM)₁₇ where M is a substituent element as hereinbefore defined and the improved magnetic properties achieved thereby is further demonstrated by data presented in the figures in which:-

Figure 1 is a thermopiezic curve for absorption of nitrogen gas by Y₂Fe₁₇ showing the drop in pressure of gas in the chamber as nitrogen is taken up by the sample. The pressure values on cooling demonstrate that the nitrogen remains absorbed by the Y₂Fe₁₇ sample;

Figure 2 shows the isothermal reaction of nitrogen with Y₂Fe₁₇ powder, having an average grain size of approximately 2 microns diameter at 400°C, 450°C and 500°C, the value y being the number of moles of nitrogen atoms incorporated into a mole of the sample. The data indicate that the optimum temperature range for the operations of the process of the invention is between about 450°C and 600°C;

Figure 3 is a thermopiezic curve for absorption of ammonia gas by Y₂Fe₁₇ at an atmosphere of approximately 1 bar. The curves of heating demonstrate an increase in pressure due to uptake of nitrogen from the ammonia. There is an increase in weight after heating the sample to 550°C which is attributed to nitrogen absorption.

Figure 4 shows ⁵⁷Fe Mössbauer spectra at room temperature of Y₂Fe₁₇ before (a) and after (b) heating to 500°C in 1 bar ammonia. The changes in Curie temperature and magnetic moment are reflected in the ⁵⁷Fe Mossbauer spectra in which the average hyperfine field at 20°C, <B_{hf}> increases from 10 Tesla for Y₂Fe₁₇ to 30 Tesla for Y₂Fe₁₇N_{2.6};

Figure 5 shows the X-ray diffraction patterns of Y₂Fe₁₇ powder heated in a thermopiezic analyser in nitrogen at 10°C/minute up to the temperatures of 500°C, 550°C, 600°C, 700°C and 850°C. Powders of the formula R₂Fe₁₇ where R is another rare earth element behave similarly.

The figure shows the appearance of a phase with expanded lattice parameters which co-exists with the unexpanded phase after treatment up to 550°C. The Y₂Fe₁₇N_{2.6} phase forms clearly at 600°C and on heating up to 700°C or above the alloy decomposes to YN and αFe;

Figure 6 shows X-ray diffraction patterns of Y₂Fe₁₇ powder after heating in nitrogen gas isothermally at

500°C for two hours. The extended heat treatment produces the $\text{Y}_2\text{Fe}_{17}\text{N}_{2.6}$ compound at a lower temperature than shown in the previous figure but further heat treatment to 850°C results in decomposition to YN and αFe .

Figure 7 is a thermopiezic curve for $\text{Y}_2\text{Fe}_{17}\text{C}_{1.0}$ heated from room temperature in an atmosphere of approximately 1 bar ammonia. Again an increase in pressure at about 370°C is observed;

5 Figure 8 shows the dependence of the Curie temperature (a) $T_c(^{\circ}\text{C})$ and the unit cell volume of the lattice (b) $V(\text{\AA}^3)$ on the maximum heating temperature T_m for $\text{Y}_2\text{Fe}_{17}\text{C}$. For the sample treated at 450°C and 500°C there co-exist two R_2Fe_{17} -type phases one with the larger unit cell volume and higher Curie temperature and the other with the smaller unit cell volume and lower Curie temperature. The more the crystal lattice is expanded the higher the Curie temperature. There is also a substantial increase in spontaneous magnetic moment ($\mu_0 M_s$) to 1.46 Tesla (see Table 2);

10 Figure 9 shows Mossbauer spectra at room temperature of $\text{Y}_2\text{Fe}_{17}\text{C}_{1.0}$ before (a) and after (b) heating in 1 bar ammonia at 550°C. The average hyperfine field at 18°C $\langle B_{\text{hf}} \rangle$ increases from 25.3 Tesla to 30.8 Tesla after the ammonia treatment;

15 Figure 10 is a thermopiezic curve for $\text{Sm}_2\text{Fe}_{17}\text{C}_{1.1}$ heated from room temperature in an atmosphere of approximately 1 bar ammonia. Again an increase in pressure is shown at about 350°C. Analysis of the sample after heating to 600°C reveals that the material retains the rhombohedral ($\text{Th}_2\text{Zn}_{17}$ -type) structure with increased lattice parameters. From the increase in mass the nitrogen content is estimated to be 1.1 nitrogen atoms per $\text{Sm}_2\text{Fe}_{17}\text{C}_{1.1}$ formula unit;

20 Figure 11 is an X-ray diffraction pattern of $\text{Sm}_2\text{Fe}_{17}\text{C}_{1.1}\text{N}_{1.1}$ powder before (a) and after (b) orientation in an applied field of 1.2 Tesla for one hour. The figure demonstrates the strong uniaxial anisotropy possessed in particular where R is samarium;

25 Figure 12 shows magnetization curves at 18°C of oriented samples of $\text{Sm}_2\text{Fe}_{17}\text{C}_{1.1}$ before (a) and after (b) treatment in 1 bar ammonia up to 600°C. Curves are shown for the field applied parallel ($\parallel$) and perpendicular ($\perp$) to the axis of orientation. From these magnetization curves the values for $\mu_0 M_s$ shown in Table 2 and B_a shown in Table 3 are obtained;

Figure 13 shows the X-ray diffraction patterns of a) $\text{Sm}_2\text{Fe}_{17}$ powder with an average particle size of $1\mu\text{m}$ and b) the same powder heated at 500°C in nitrogen gas for two hours to form $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.4}$;

30 Figures 14a and b show the radial distribution functions deduced from extended X-ray absorption fine structure data on the same samples as Figure 13. The peak appearing at 2.5 Å shows the presence of approximately three nitrogen atoms at a distance 2.5 Å from a samarium atom in the nitride;

Figures 15a and b show the crystal structure of the rhombohedral and hexagonal 2:17 structure, indicating the sites occupied by nitrogen; Figure 15a is the rhombohedral crystal structure and Figure 15b is the hexagonal crystal structure. Large circles represent rare earths, small shaded circles represent iron and small black circles represent nitrogen sites 9e or 6h.

35 Figure 16 is a histogram of the particle size distribution of a typical $\text{Sm}_2\text{Fe}_{17}$ powder used for nitrogen absorption;

Figure 17 shows the variation of the diffusion coefficient for nitrogen in the $\text{Sm}_2\text{Fe}_{17}$ powder as a function of inverse temperature.

40 Figure 18 shows magnetization curves at 18°C for an oriented sample of $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ after treatment with ammonia. Again curves are shown for the field applied parallel ($\parallel$) and perpendicular ($\perp$) to the axis of orientation. From these the values of the anisotropy field B_a are obtained as shown in Table 3. The value of B_a for $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ is given as >12.0 Tesla but in fact the curves shown in the figure indicate it may be as high as 20 Tesla;

45 Figure 19(a) is a thermopiezic curve for a powder made from a cast ingot of $\text{Sm}_2\text{Fe}_{17}$ heated in nitrogen. Figure 19(b) is a thermopiezic curve for a powder made from an ingot and annealed for 100 hours at 950°C and heated in nitrogen. The differences in the two sets of curves clearly demonstrate that the treatment temperature required to form the $\text{R}_2\text{Fe}_{17}\text{N}_b$ phase varies depending on the metallurgical composition of the ingot used to make the powder;

50 Figure 20 shows X-ray diffraction patterns of the compounds $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.3}$, $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ and $\text{Er}_2\text{Fe}_{17}\text{N}_{2.7}$ after an applied field of 1.2 Tesla. In the case of $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ the c-axis is aligned parallel to the applied field indicating strong uniaxial anisotropy. However in the case where R is Nd or Er there is a tendency for the c-axis to be aligned perpendicular to the direction of the applied magnetic field;

Figure 21 shows the crystal structure of the tetragonal 1:12 compound showing sites occupied by nitrogen. The coding of the circles is as described for Figures 15a and 15b;

55 Figure 22 shows a thermopiezic trace for absorption of nitrogen gas by $\text{Sm}(\text{Fe}_{11}\text{Ti})$. The material was heated at a rate of 10°C/minute at approximately 1 bar nitrogen. The figure demonstrates that the optimum temperature range for operation of the process is similar to that of the R_2Fe_{17} compounds;

Figure 23 shows room temperature ^{57}Fe Mössbauer spectra of $\text{Sm}(\text{Fe}_{11}\text{Ti})$ before (a) and after (b) heating in

a nitrogen containing gas in accordance with the invention. The average hyperfine field increases from 25.5 Tesla in (a) to 29.1 Tesla in (b), reflecting the changes in Curie temperature and iron magnetic moment.

Figure 24 shows X-ray diffraction patterns of powders of $\text{Sm}(\text{Fe}_{11}\text{Ti})$ (a) and $\text{Sm}(\text{Fe}_{11}\text{Ti})\text{N}_{0.8}$ (b) oriented in a magnetic field of 1.2 Tesla. The strong uniaxial anisotropy of $\text{Sm}(\text{Fe}_{11}\text{Ti})$ is transformed to easy-plane anisotropy in the interstitial nitride $\text{SmFe}_{11}\text{TiN}_{0.8}$ demonstrating a change in sign of the second-order crystal field coefficient A_{20} from negative to positive. Hence the strong uniaxial anisotropy observed for interstitially-modified 1:12 structure compounds of rare-earths with a negative Stevens coefficient $\alpha_J(\text{Nd}, \text{Er}, \text{Tm})$, neodymium in particular;

Figure 25 is an illustration of interstitial nitrogen atoms around the rare earth in the rhombohedral or hexagonal 2.17 structure (a) and in the tetragonal 1.12 structure (b). The electric field gradient experienced by the rare-earth, quantified in the parameter A_{20} , is mainly produced by surrounding interstitial atoms in the materials of the invention. It is negative for the configuration of the 2.17 compounds and positive for configuration of the 1.12 compounds;

Figure 26 illustrates some of the effects of cobalt substitution for iron in materials of the invention having the rhombohedral or hexagonal crystal structure.

Figure 26(a) indicates the nitrogen content achieved by treating finely-ground powders of the $\text{R}_2(\text{Fe}_{17-c}\text{Co}_c)\text{N}_b$ type formula where c is the number of cobalt atoms in nitrogen gas at temperatures ranging from 400-600°C.

Figure 26(b) illustrates a broad maximum in magnetization with a transition metal substitute where R is Y and $c=0.2$.

Figure 26(c) shows that the transition metal substituents make a positive contribution to the anisotropy when c is >0.1 ;

Figure 27 is an illustration of the development of hysteresis in a powder of $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ comprising first and second quadrant demagnetizing curves of samples aligned and magnetized in a pulsed field of 8 Tesla.

The data represented are as follows:-

- a) Powder of $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ dispersed in epoxy resin
- b) Powder of $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ milled with Zn powder (25 wt %)
- c) Powder of $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ milled with Zn powder (15 wt %) and heat treated at 400°C for two hours.

Figure 27 indicates the magnetic properties of permanent magnets produced from the magnetic materials of the invention and methods by which the coercivity and hysteresis may be developed. For example in 21(c) the material is milled with 15 wt % Zn and heated to 400°C to produce a magnet having a coercivity of 0.5 Tesla and a maximum energy product of 86KJm^{-3} .

The data shown in Figure 27 establishes conclusively that $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ and the related compounds of the invention can be effectively processed to make magnets.

Further, thin films of materials of the invention may be exploited for magnetic or magneto-optic recording.

Claims

1. A magnetic material of the general formula:



which is derived from an intermetallic compound of rhombohedral, hexagonal or tetragonal crystal structure wherein R is one or more rare earth elements, X' is an element of groups IIIA, IIIB, IVA or IVB of the periodic table, Z is one or more elements of group VA of the periodic table, x is a value from 0.5 to 2, y is a value from 9 to 19, a is a value from 0 to 3, b is a value from 0.3 to 3 and wherein when the magnetic material of said general formula is derived from an intermetallic compound of rhombohedral or hexagonal crystal structure Fe is unsubstituted or partially substituted by another element and when the magnetic material of said general formula is derived from an intermetallic compound of tetragonal crystal structure Fe is partially substituted by any element of group IIIA or IVA of the periodic table or a transition metal from another group with the further proviso that in the case of materials derived from said rhombohedral or hexagonal crystal structures the element X' is not boron when the component Z is antimony or bismuth.

2. A magnetic material as claimed in claim 1 wherein when the material of said general formula is derived from an intermetallic compound of tetragonal crystal structure $a=0$.

3. A magnetic material as claimed in claim 1 or 2 wherein R is samarium or neodymium.

4. A magnetic material as claimed in claim 1 or claim 3 wherein when the material of said general formula is

derived from an intermetallic compound of hexagonal or rhombohedral crystal structure R is samarium.

- 5 5. A magnetic material as claimed in claim 1 wherein when the material of said general formula is derived from an intermetallic compound of hexagonal or rhombohedral crystal structure R is samarium in combination with one or more rare earth elements selected from yttrium, lanthanum, cerium, neodymium, erbium, thulium and mischmetal.
- 10 6. A magnetic material as claimed in claim 1 wherein when the material of said general formula is derived from an intermetallic compound of hexagonal or rhombohedral crystal structure R is yttrium, lanthanum, cerium, praseodymium, neodymium, gadolinium, terbium, dysprosium, erbium, thulium, ytterbium or lutetium or a mixture of two or more thereof.
- 15 7. A magnetic material as claimed in any of claims 1,2 or 3 wherein when the material is derived from an intermetallic compound of tetragonal crystal structure R is yttrium, thorium, cerium, praseodymium, neodymium, terbium, dysprosium or holmium or a mixture of two or more thereof.
- 20 8. A magnetic material as claimed in any preceding claim wherein the element Fe is up to 33% substituted with a transition metal.
- 25 9. A magnetic material as claimed in claim 8 wherein when the material of said general formula is derived from an intermetallic compound of hexagonal or rhombohedral crystal structure the transition metal is cobalt.
- 30 10. A magnetic material as claimed in any one of claims 1,2,3 or 7 wherein when the material of said general formula is derived from an intermetallic compound of tetragonal crystal structure the element Fe is partially substituted by titanium, vanadium, molybdenum or chromium.
- 35 11. A magnetic material as claimed in any one of claims 1,2,3 or 7 wherein the material of said general formula is derived from an intermetallic compound of tetragonal crystal structure the iron is partially substituted by aluminium or silicon.
- 40 12. A magnetic material as claimed in any of claims 1,3,4,5 or 6 wherein when the material is derived from an intermetallic compound of rhombohedral or hexagonal crystal structure X' is carbon, boron, silicon or zirconium and a is a value from 0.1 to 3.
- 45 13. A magnetic material as claimed in claim 12 wherein $a+b \leq 3$.
- 50 14. A magnetic material as claimed in any preceding claim wherein Z is nitrogen.
- 55 15. A magnetic material as claimed in any one of claims 1 to 13 wherein component Z is a combination of nitrogen with one or more other group VA elements.
16. A magnetic material as claimed in any one of claims 1 to 13 wherein component Z is one or more of P, As, Sb and Bi.
17. A magnetic material as claimed in claim 14 which has the formula $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ or $\text{Sm}_2\text{Fe}_{17}\text{C}_{1.1}\text{N}_{1.1}$ or $\text{NdFe}_{11}\text{TiN}_{0.8}$.
18. A process for modifying the magnetic properties of an intermetallic compound comprising at least one or more rare earth elements and the element iron in which the iron is optionally substituted with another element which process comprises heating said intermetallic compound with a gas containing at least one group VA element Z in the substantial absence of oxygen to incorporate the said at least one element Z interstitially into the crystal lattice of the intermetallic compound by a gas-solid reaction.
19. A process as claimed in claim 18 wherein when the intermetallic compound is of tetragonal crystal structure the iron is substituted by any element of group IIIA or group IVA of the periodic table or by a transition metal from another group.

20. A process as claimed in claim 18 or claim 19 wherein the gas is one which produces radicals containing single atoms of the group VA element Z on contact with hot surfaces such as metal or quartz or by exposure to high frequency radiation.
- 5 21. A process as claimed in claim 20 wherein the gas is a gaseous hydride of the group VA element Z.
22. A process as claimed in any one of claims 18 to 21 which produces a magnetic material as defined in any one of claims 1 to 17.
- 10 23. A process as claimed in claim 20 wherein the group VA element Z is nitrogen and the gas is nitrogen, ammonia or hydrazine.
24. A process as claimed in any one of claims 18 to 23 wherein said intermetallic compound is heated to a temperature not exceeding 650°C.
- 15 25. A process as claimed in any one of claims 18 to 24 wherein said intermetallic compound is ground to a particle size of 1 to 50 microns diameter.
26. A process as claimed in claim 25 wherein the said ground compound is heated for up to 8 hours.
- 20 27. Use of the magnetic material as claimed in any one of claims 1 to 17 for fabricating a permanent magnet.
28. The use as claimed in claim 27, wherein a magnet is formed by a process comprising the steps of:-
 a) milling said magnetic material with a metal such as aluminium, copper or zinc or an organic powder or resin
 25 b) generating magnetic alignment in the said material by applying a magnetic field and
 c) heating the milled product to a temperature sufficiently low to prevent decomposition of the magnetic material.
- 30 29. The use as claimed in claim 28 wherein in the magnet fabricating process the magnetic material is milled with from 5 to 20 wt % zinc.
30. A permanent magnet comprising a magnetic material as claimed in any one or claims 1 to 17.
- 35 31. A permanent magnet comprising a magnetic material which is produced by the process of any one of claims 18 to 26.

Claims for the following Contracting State: ES

- 40 1. A process for modifying the magnetic properties of an intermetallic compound comprising at least one or more rare earth elements and the element iron in which the iron is optionally substituted with another element which process comprises heating said intermetallic compound with a gas containing at least one group VA element Z in the substantial absence of oxygen to incorporate the said at least one element Z interstitially into the crystal lattice of the intermetallic compound by a gas-solid reaction.
- 45 2. A process as claimed in claim 1 wherein when the intermetallic compound is of tetragonal crystal structure the iron is substituted by any element of group IIIA or group IVA of the periodic table or by a transition metal from another group.
- 50 3. A process as claimed in claim 1 or claim 2 wherein the gas is one which produces radicals containing single atoms of the group VA element Z on contact with hot surfaces such as metal or quartz or by exposure to high frequency radiation.
4. A process as claimed in claim 3 wherein the gas is a gaseous hydride of the group VA element Z.
- 55 5. A process as claimed in claim 3 wherein the group VA element Z is nitrogen and the gas is nitrogen, ammonia or hydrazine.

6. A process as claimed in any one of claims 1 to 5 wherein said intermetallic compound is heated to a temperature not exceeding 650°C.
7. A process as claimed in any one of claims 1 to 6 wherein said intermetallic compound is ground to a particle size of 1 to 50 microns diameter.
8. A process as claimed in claim 7 wherein the said ground compound is heated for up to 8 hours.
9. A process as claimed in claim 1 in which the intermetallic compound has a rhombohedral, hexagonal or tetragonal crystal structure and has the general formula:

$$R_xFe_yX'_a$$
 wherein R is one or more rare earth elements, X' is an element of groups IIIA, IIIB, IVA or IVB of the periodic table, x is a value from 0.5 to 2, y is a value from 9 to 19 and a is a value from 0 to 3 and wherein when the intermetallic compound is of rhombohedral or hexagonal crystal structure, Fe is unsubstituted or partially substituted by another element and when the intermetallic compound is of tetragonal crystal structure Fe is partially substituted by any element of group IIIA or IVA of the periodic table or a transition metal from another group.
10. A process as claimed in claim 9 wherein the product is a magnetic material of the general formula:-

$$R_xFe_yX'_aZ_b$$
 wherein R, X' x, y and a are as defined in claim 9, Z is one or more elements of group VA of the periodic table and b is a value from 0.3 to 3.
11. A process as claimed in claim 9 or 10 wherein when the intermetallic compound is of tetragonal crystal structure a=0.
12. A process as claimed in any one of claims 9 to 11 wherein R is samarium or neodymium.
13. A process as claimed in any one of claims 9,10 or 12 wherein when the intermetallic compound is of hexagonal or rhombohedral crystal structure R is samarium.
14. A process as claimed in claim 9 or claim 10 wherein when the intermetallic compound is of hexagonal or rhombohedral crystal structure R is samarium in combination with one or more rare earth elements selected from yttrium, lanthanum, cerium, neodymium, erbium, thulium and mischmetal.
15. A process as claimed in claim 9 or claim 10 wherein when the intermetallic compound is of hexagonal or rhombohedral crystal structure R is yttrium, lanthanum, cerium, praseodymium, neodymium, gadolinium, terbium, dysprosium, erbium, thulium, ytterbium or lutetium or a mixture of two or more thereof.
16. A process as claimed in any one of claims 9,10 or 11 wherein when the intermetallic compound is of tetragonal crystal structure R is yttrium, thorium, cerium, praseodymium, neodymium, terbium, dysprosium or holmium or a mixture of two or more thereof.
17. A process as claimed in any of claims 9 to 16 wherein the element Fe is up to 33% substituted with a transition metal.
18. A process as claimed in claim 17 wherein when the intermetallic compound is of hexagonal or rhombohedral crystal structure the transition metal is cobalt.
19. A process as claimed in any one of claims 9,10 or 11 wherein when the intermetallic compound is of tetragonal crystal structure the element Fe is partially substituted by titanium, vanadium, molybdenum or chromium.
20. A process as claimed in any one of claims 9,10 or 11 wherein when the intermetallic compound is of tetragonal crystal structure the element Fe is partially substituted by aluminium or silicon.
21. A process as claimed in any of claims 9,10,12,13,14 or 15 wherein when the intermetallic compound is of rhombohedral or hexagonal crystal structure X' is carbon, boron, silicon or zirconium and a is a value from

0.1 to 3.

22. A process as claimed in claim 21 wherein $a+b \leq 3$.

5 **23.** A process as claimed in any one of claims 9 to 22 wherein Z is nitrogen.

24. A process as claimed in any one of claims 9 to 22 wherein Z is a combination of nitrogen with one or more other group VA elements.

10 **25.** A process as claimed in any one of claims 9 to 22 wherein Z is one or more of P, As, Sb and Bi.

26. Use of the modified intermetallic compound as made by the process as claimed in any preceding claim for fabricating a permanent magnet.

15 **27.** The use as claimed in claim 26, wherein a magnet is formed by a process comprising the steps of:-
a) milling said modified intermetallic compound with a metal such as aluminium, copper or zinc or an organic powder or resin
b) generating magnetic alignment in the said modified compound by applying a magnetic field and
c) heating the milled product to a temperature sufficiently low to prevent decomposition of the modified
20 compound.

28. The use as claimed in claim 27 wherein in the magnet fabricating process the modified intermetallic compound is milled with from 5 to 20 wt % zinc.

25 **29.** A permanent magnet comprising a modified intermetallic compound which is produced by the process as claimed in any one of claims 1 to 25.

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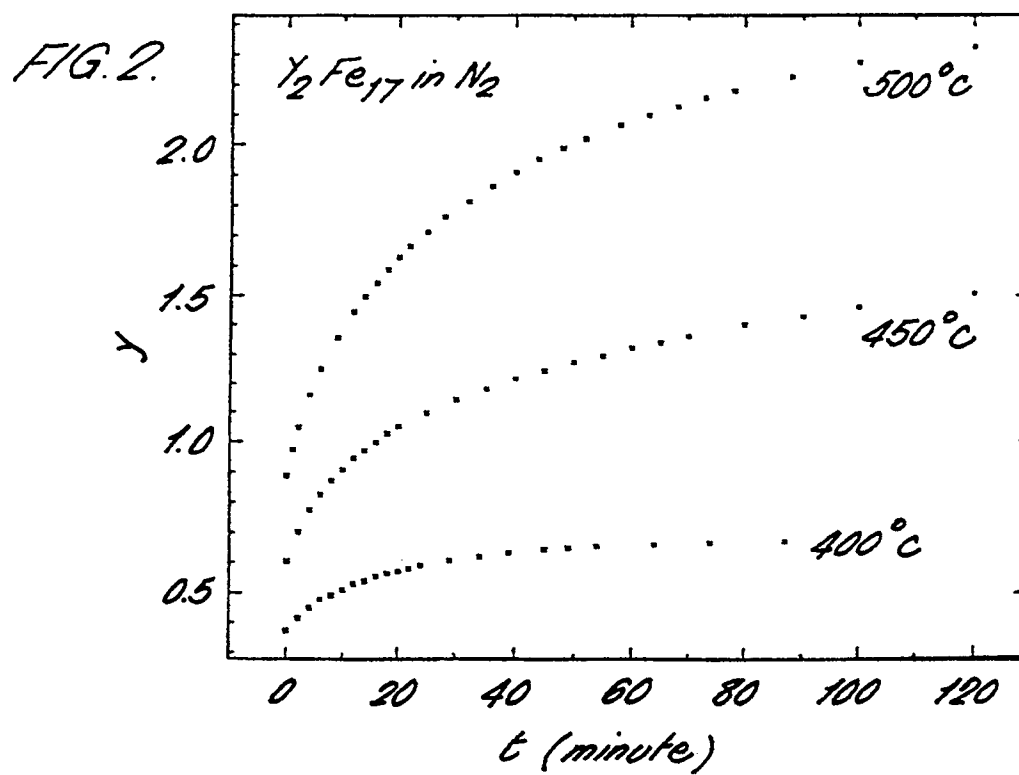
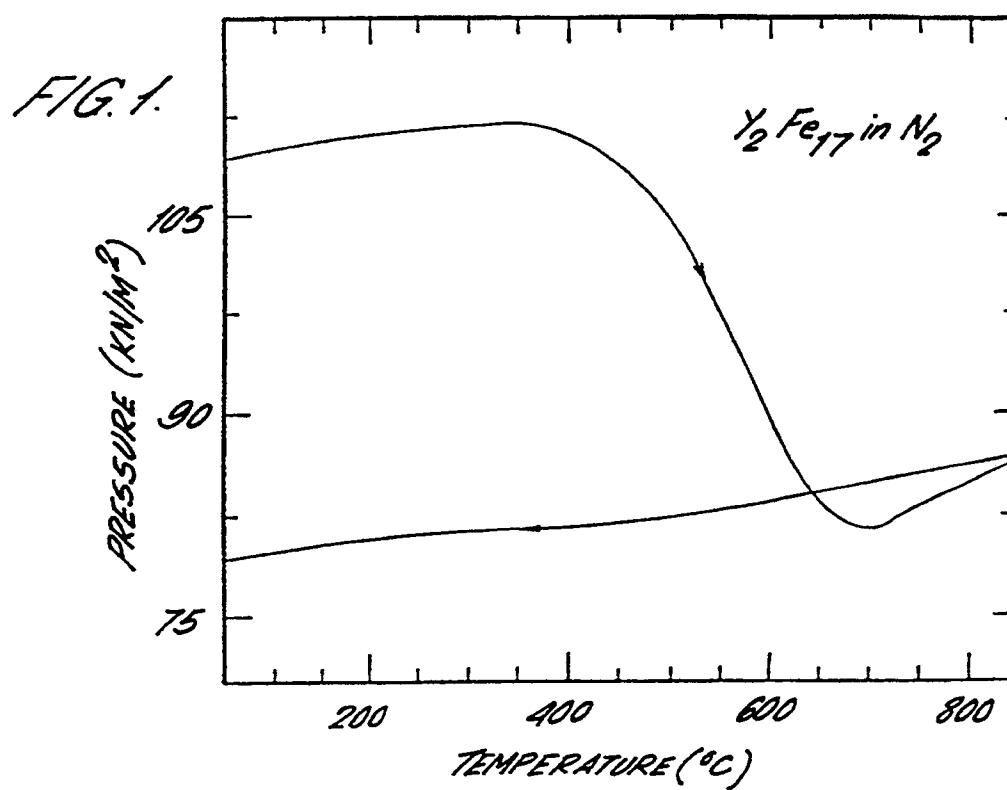


FIG. 3.

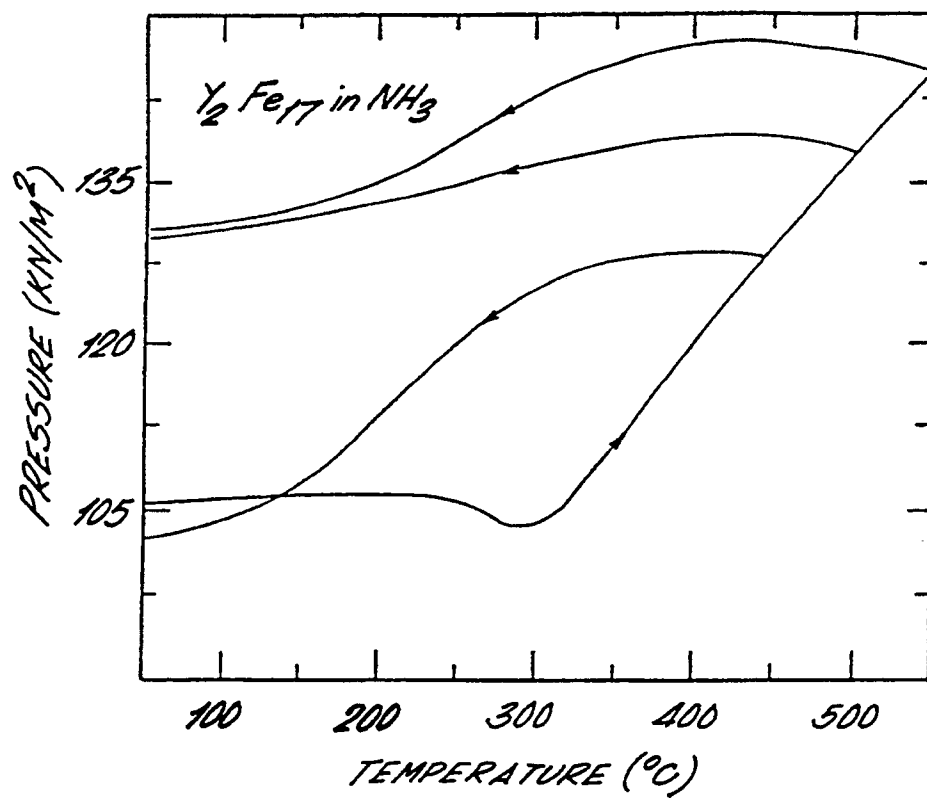


FIG. 4.

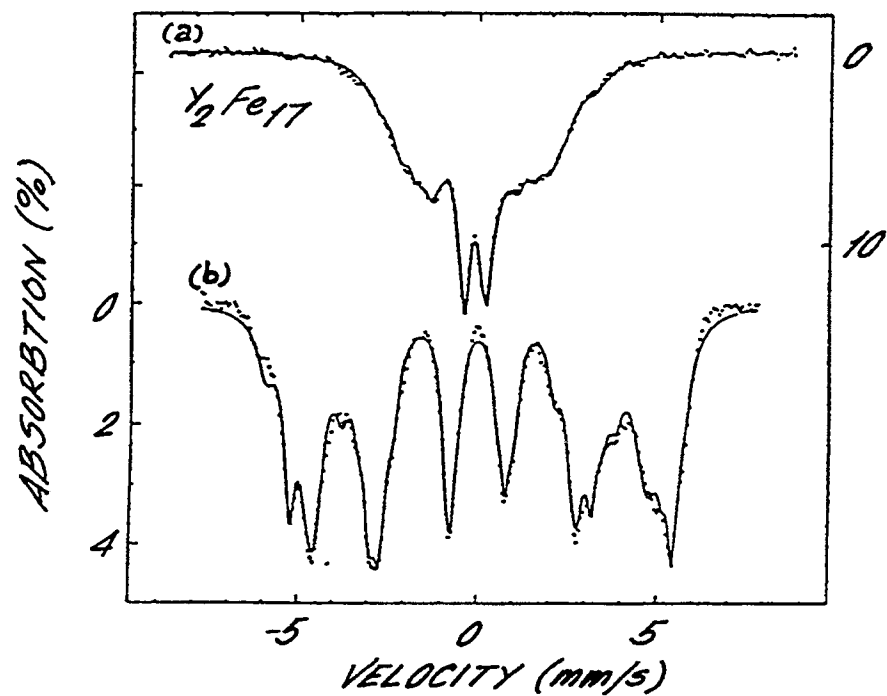


FIG. 7.

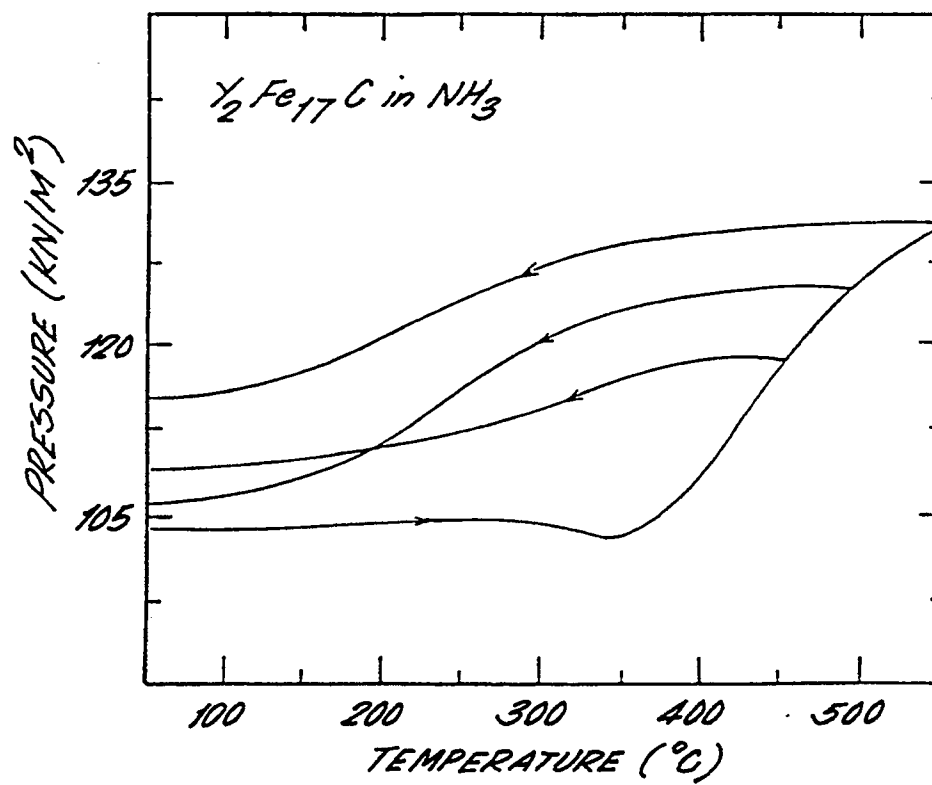


FIG. 5.

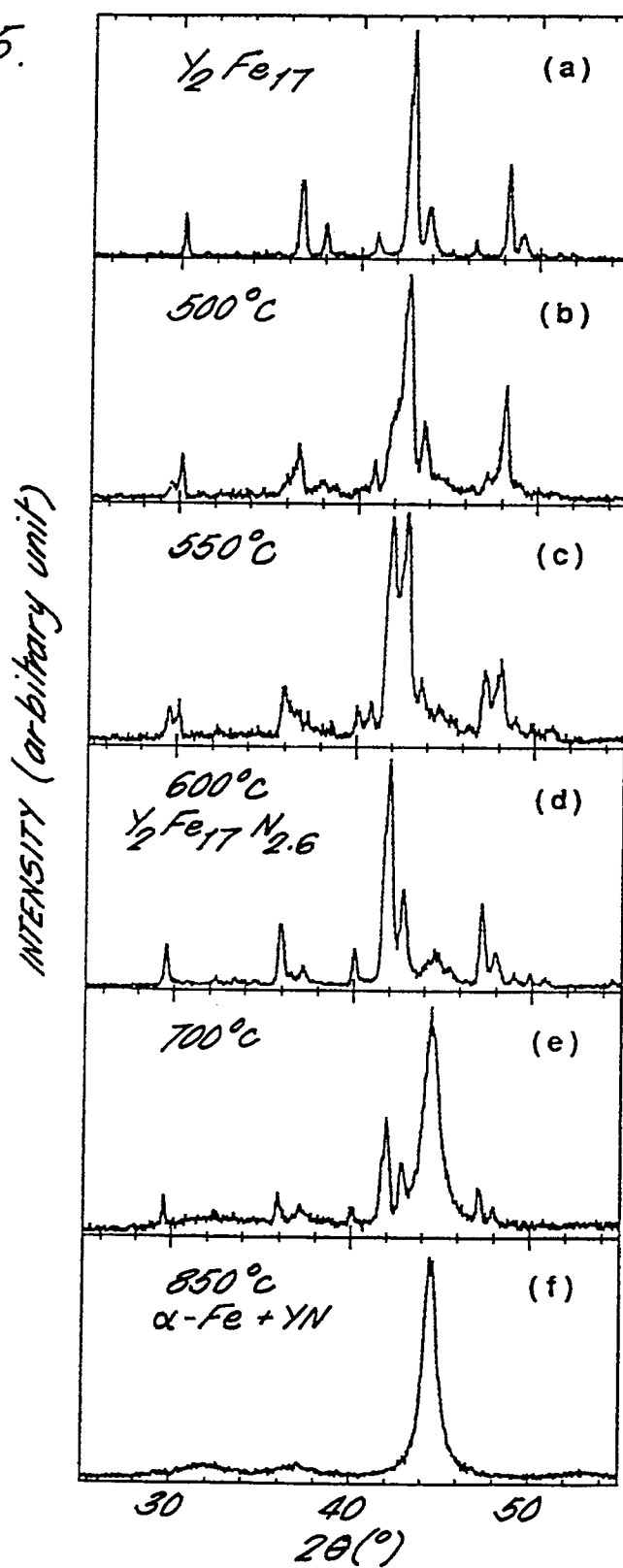


FIG. 6.

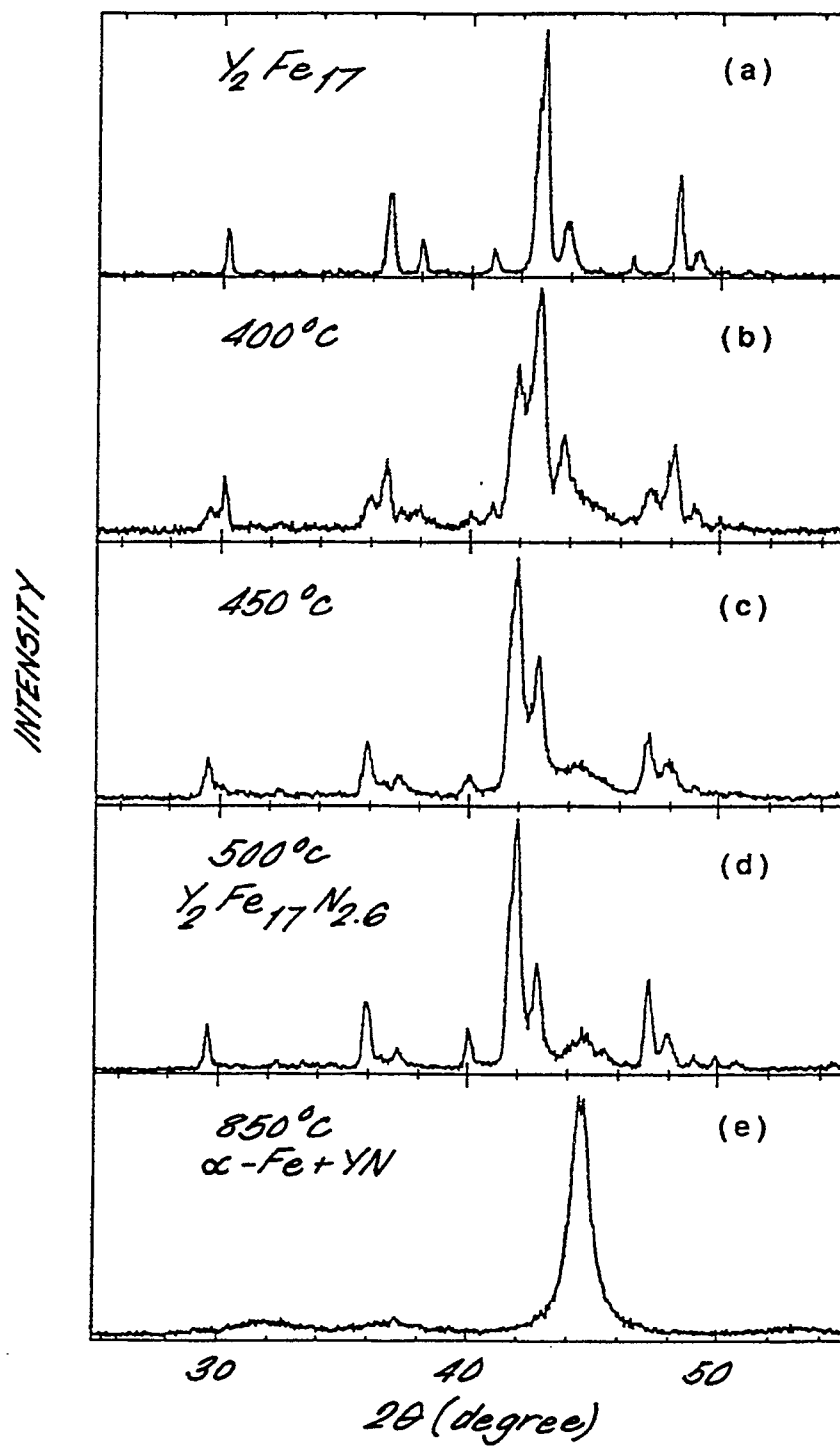


FIG. 8.

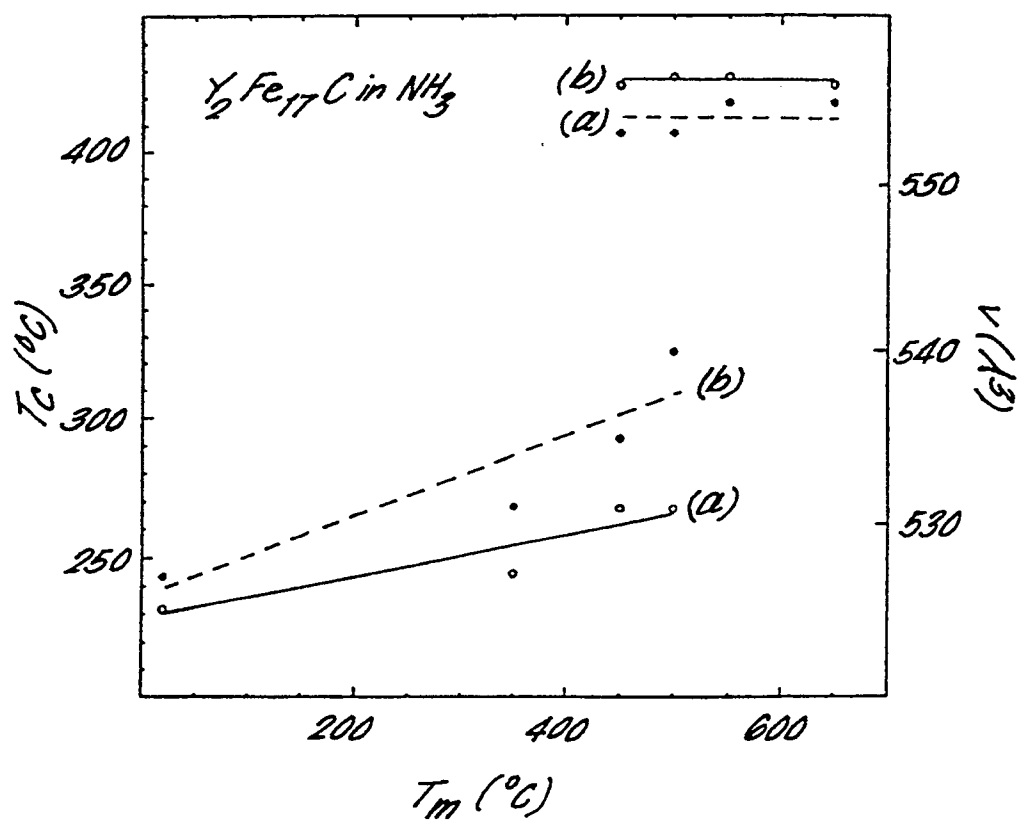


FIG. 9.

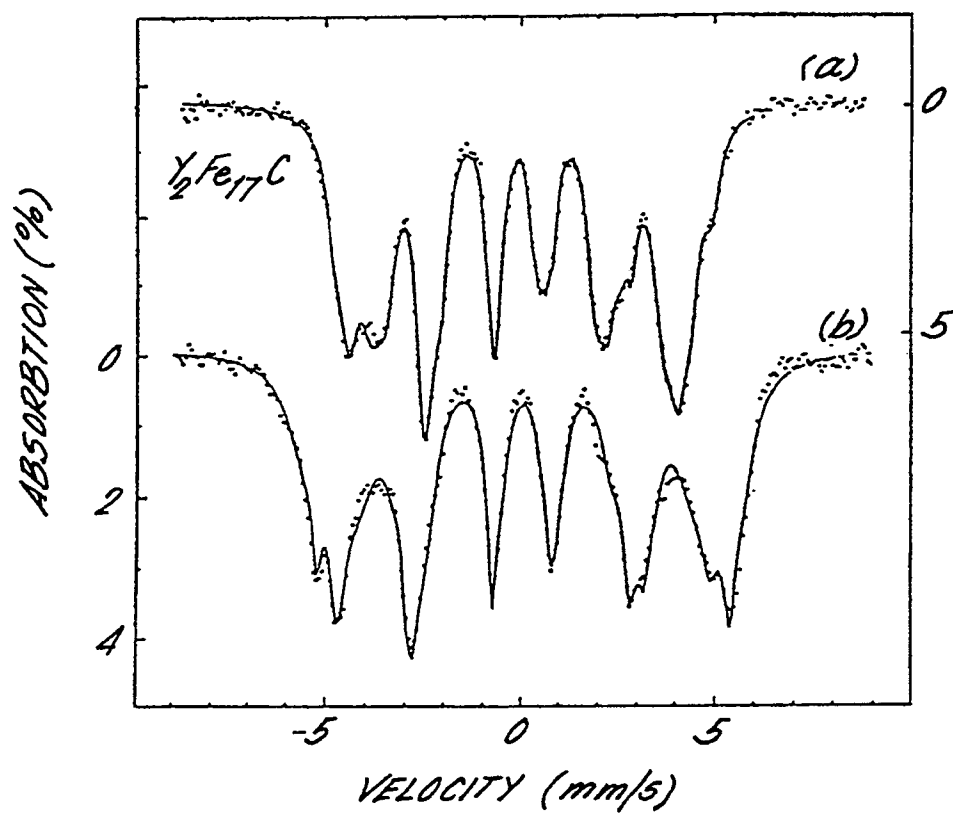


FIG. 10.

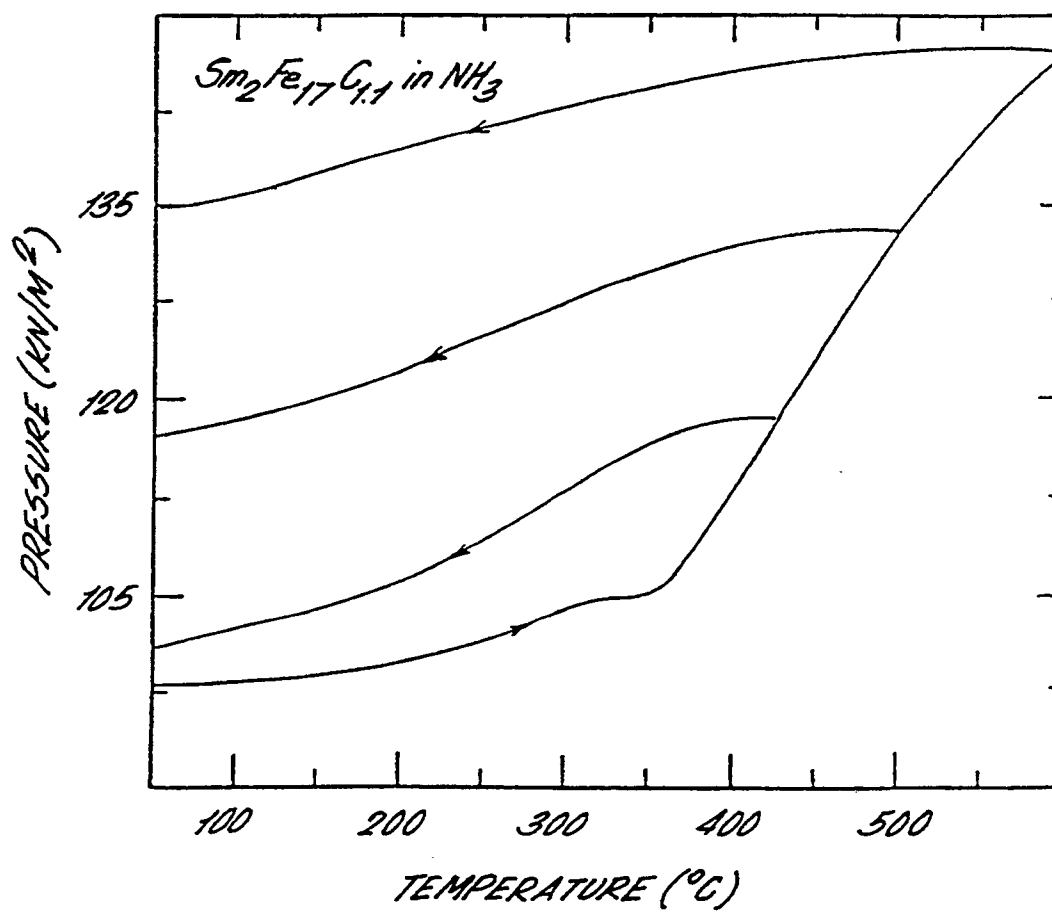


FIG. 11.

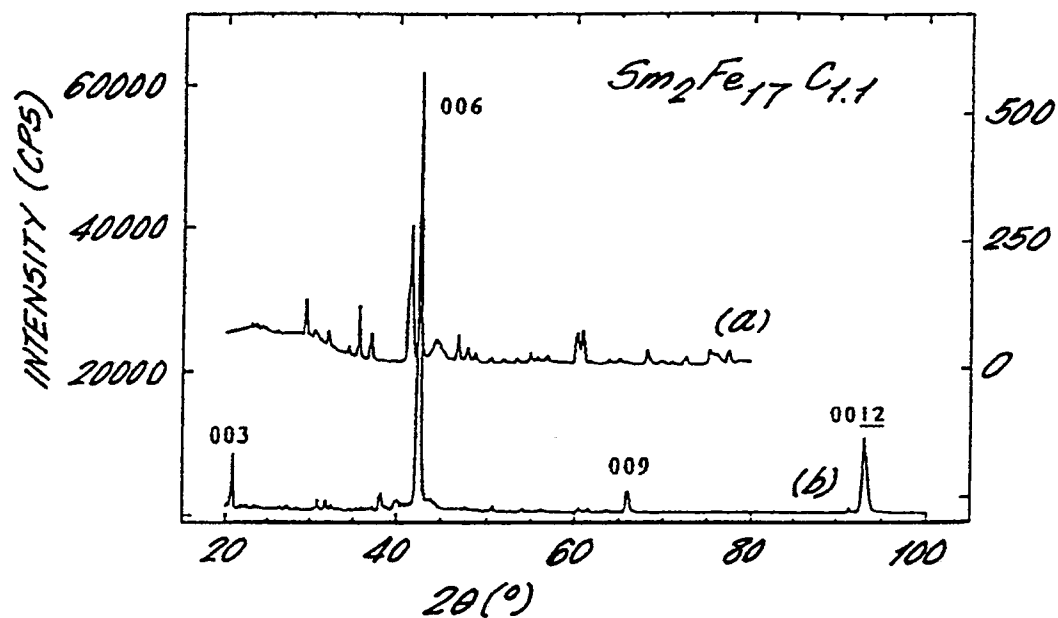


FIG. 12.

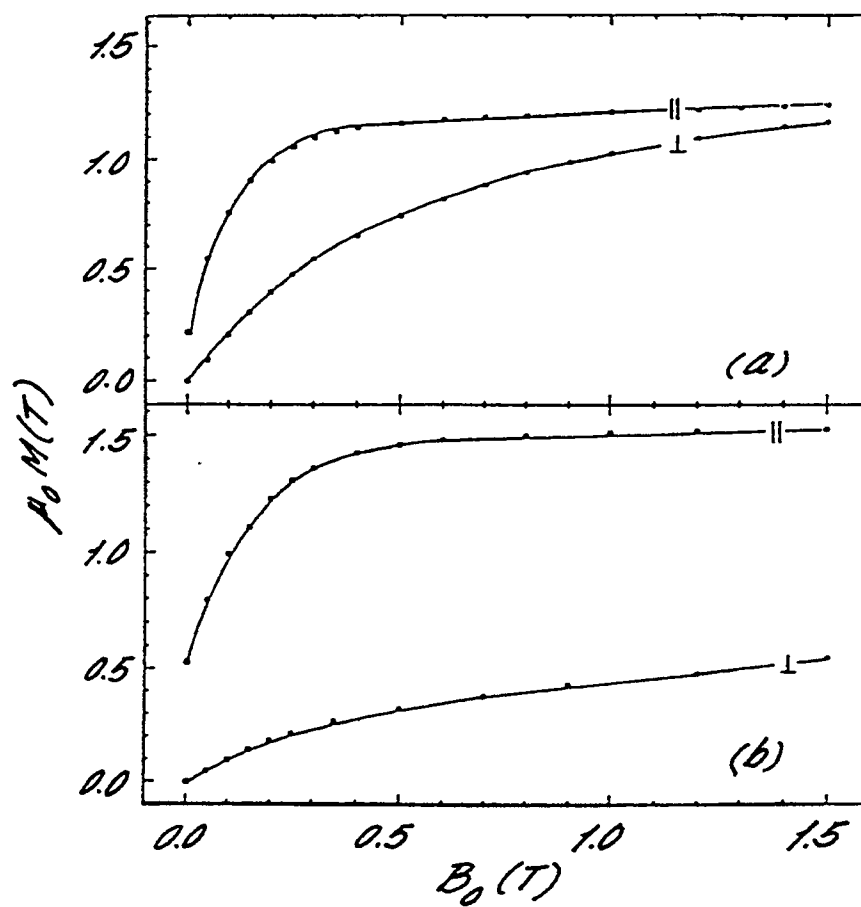


FIG. 13.

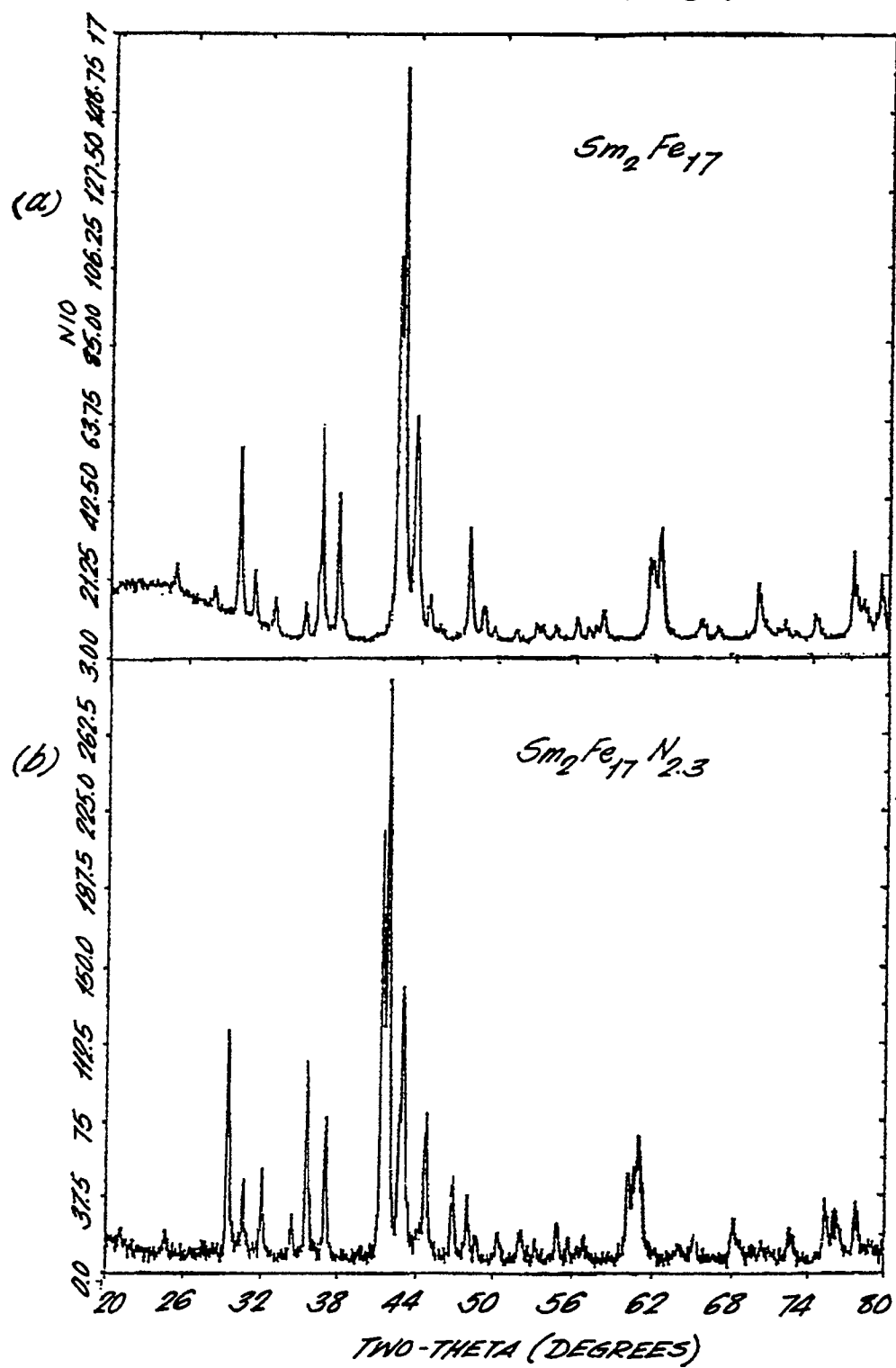


FIG. 14.

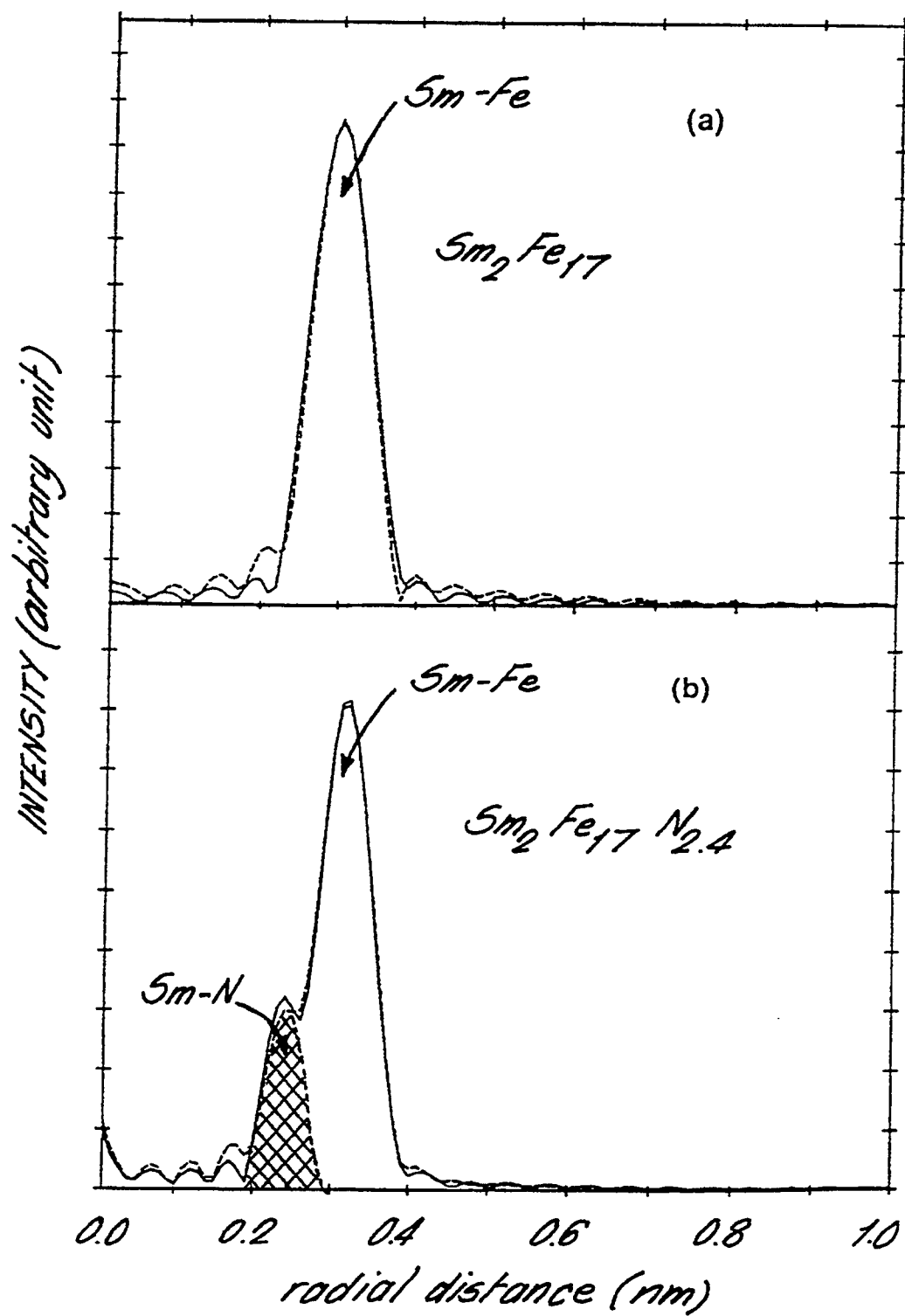


FIG. 15a.

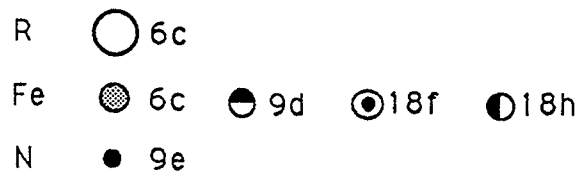
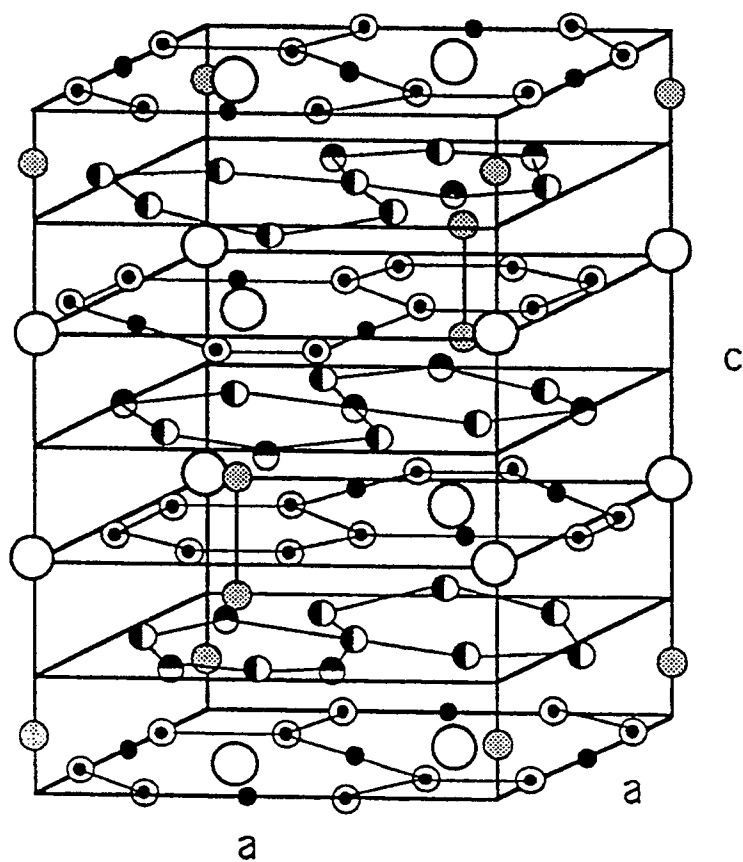


FIG. 15b.

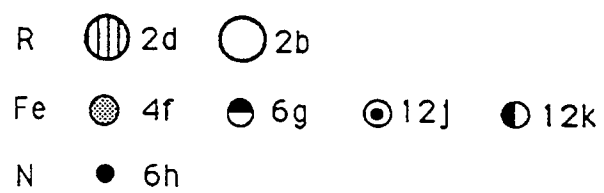
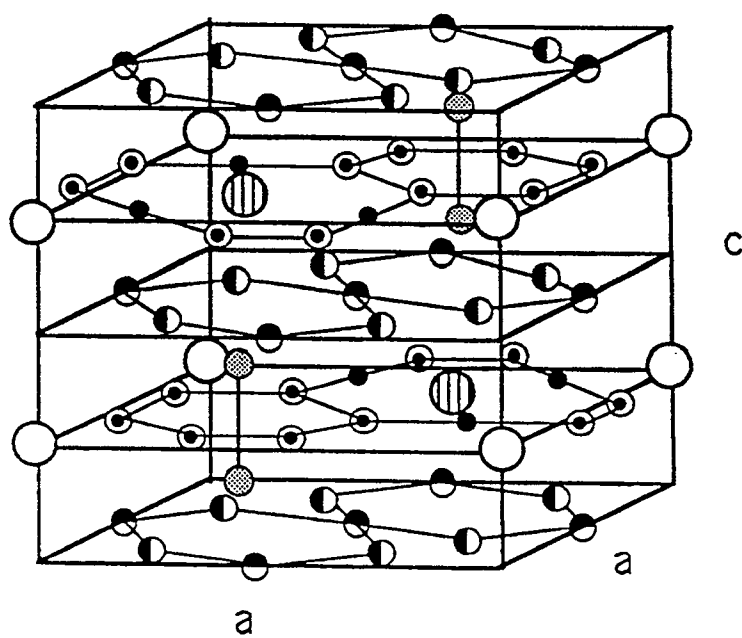


FIG. 16.

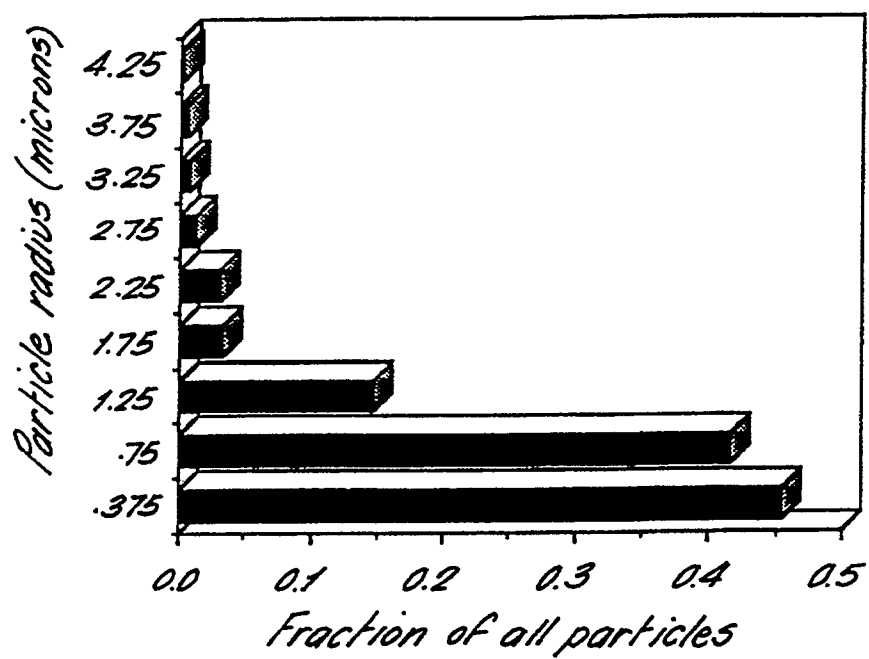
Particle size distribution.

FIG. 17.

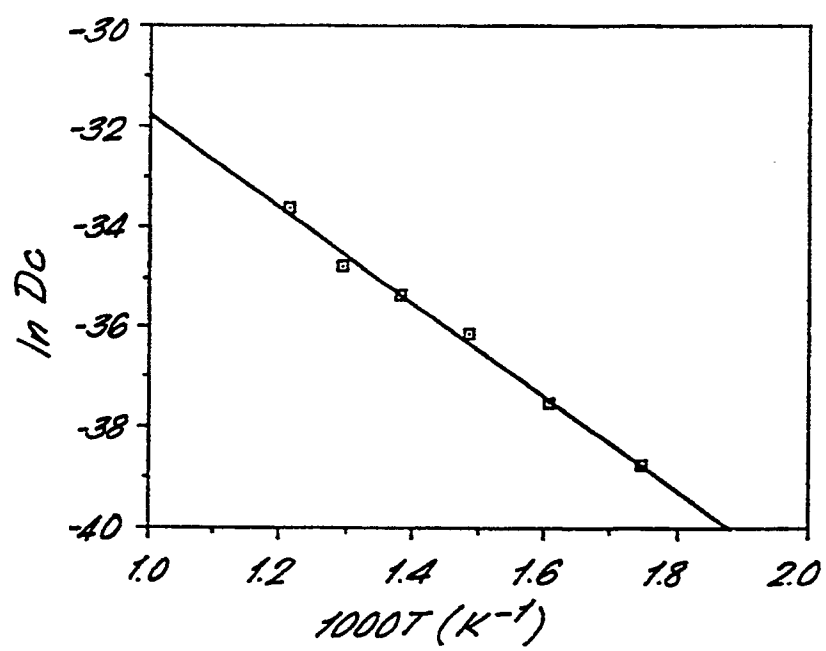


FIG. 18.

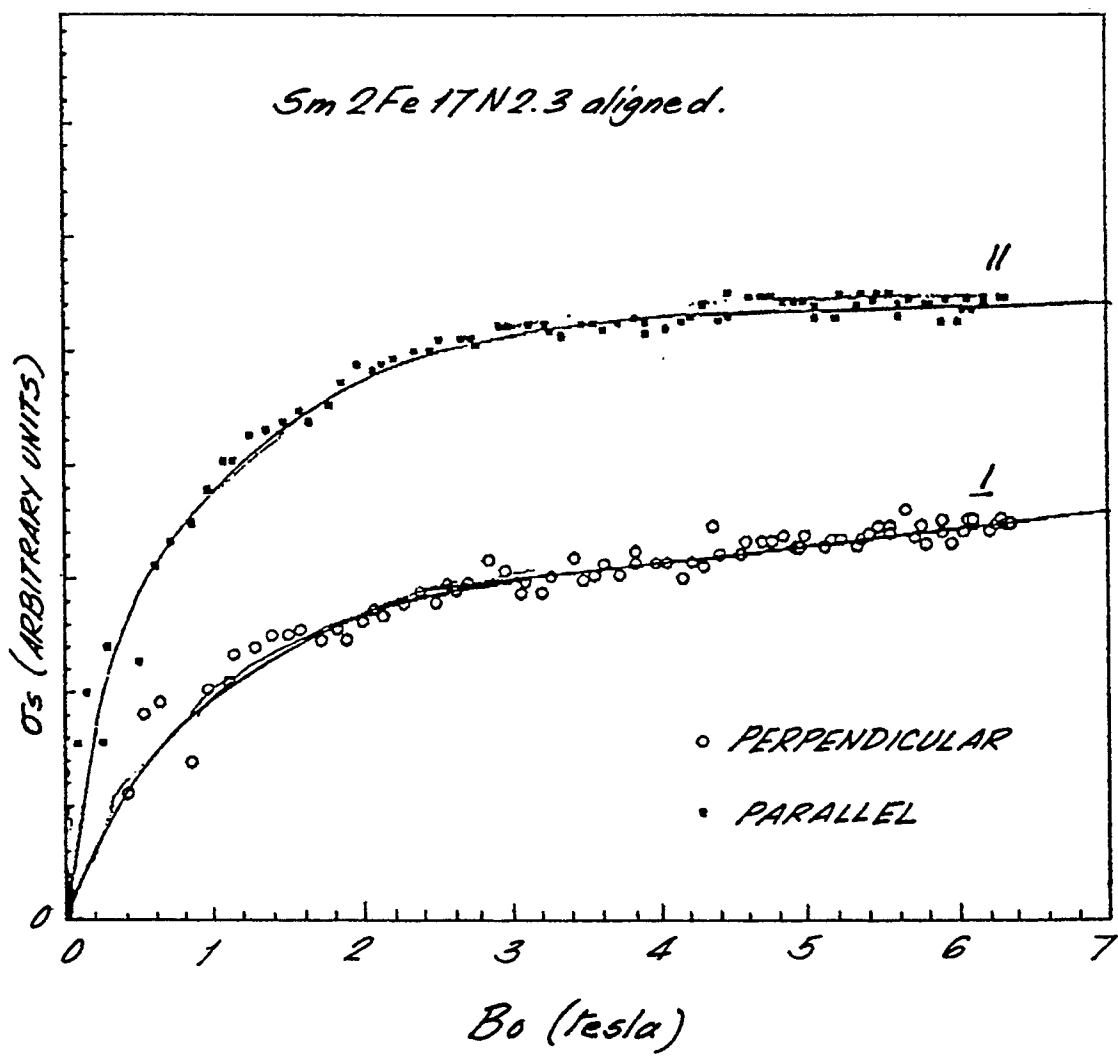


FIG. 19.

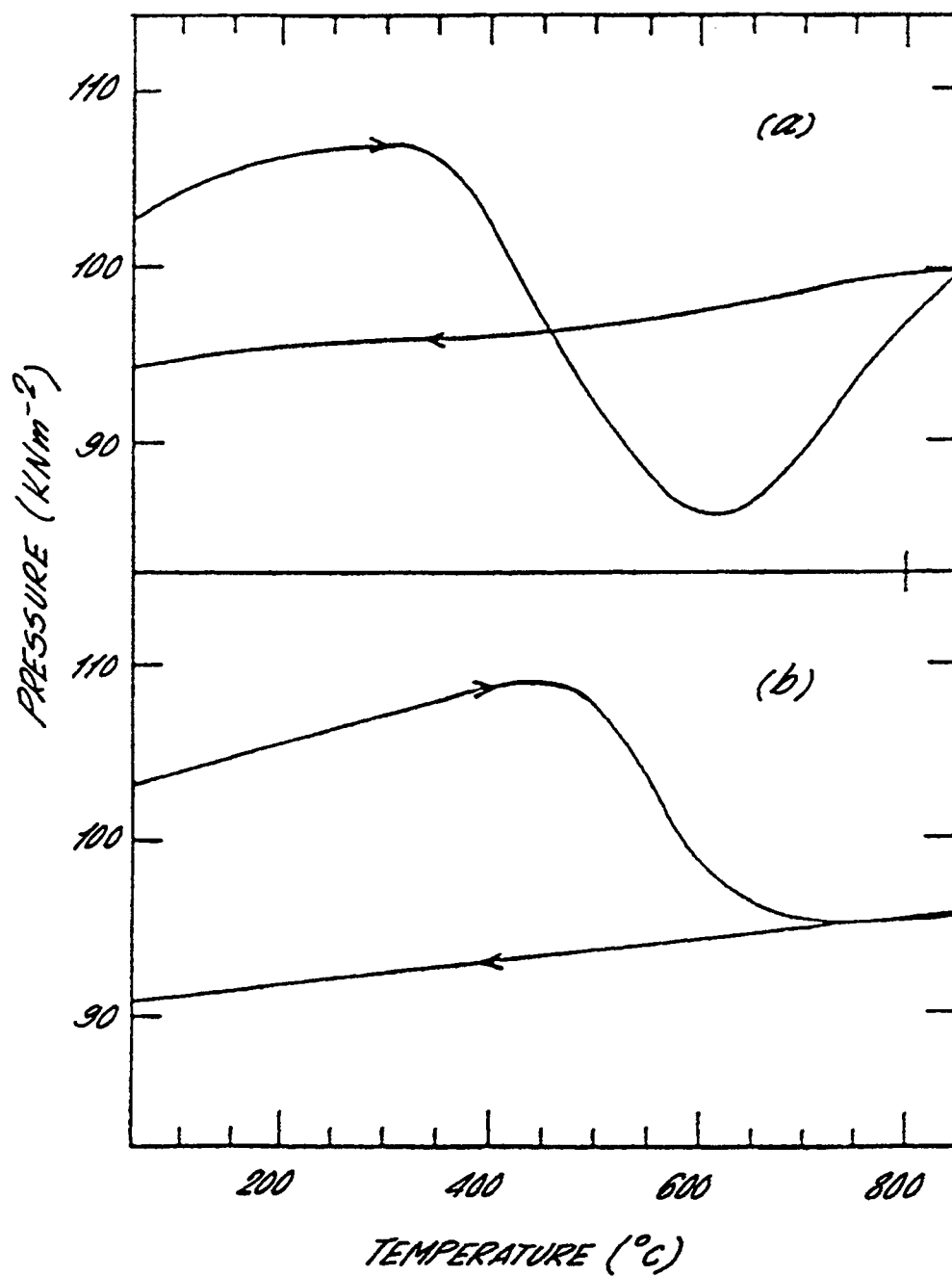


FIG. 20.

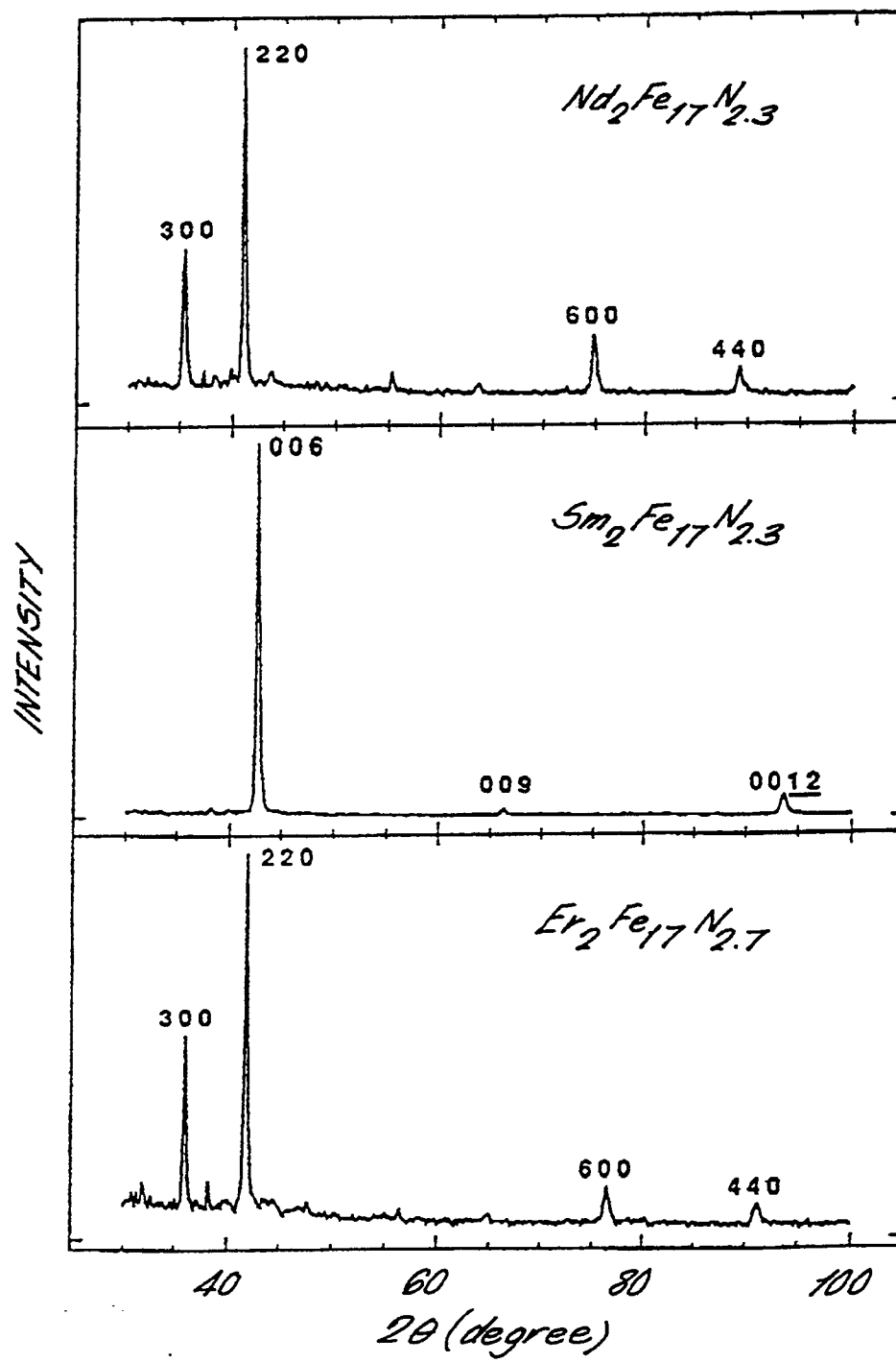


FIG. 21.

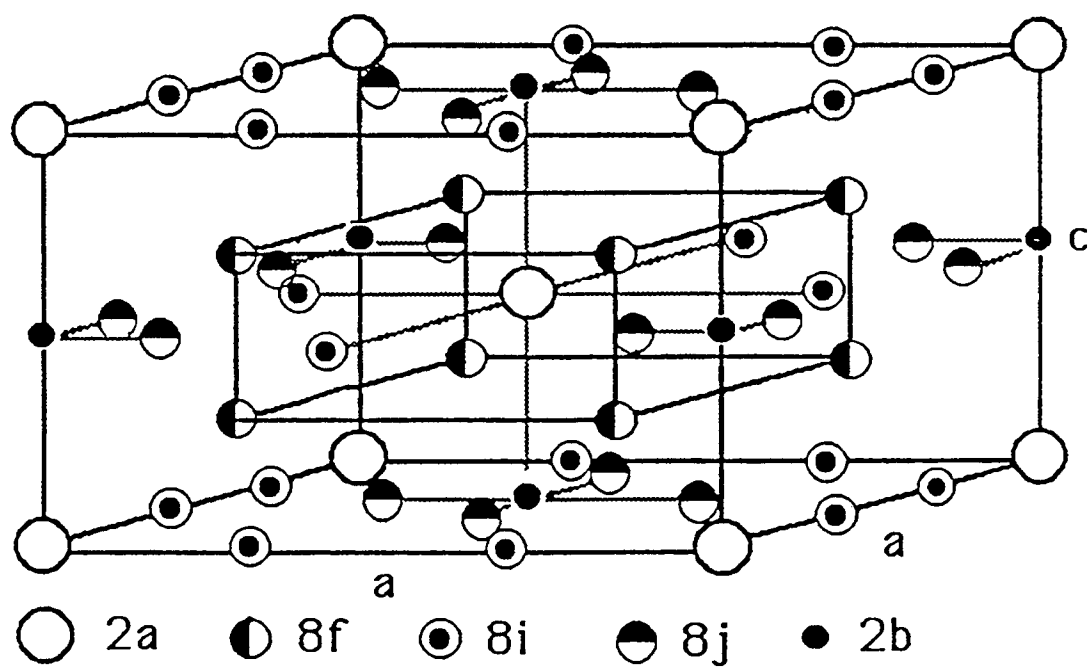


FIG. 22.

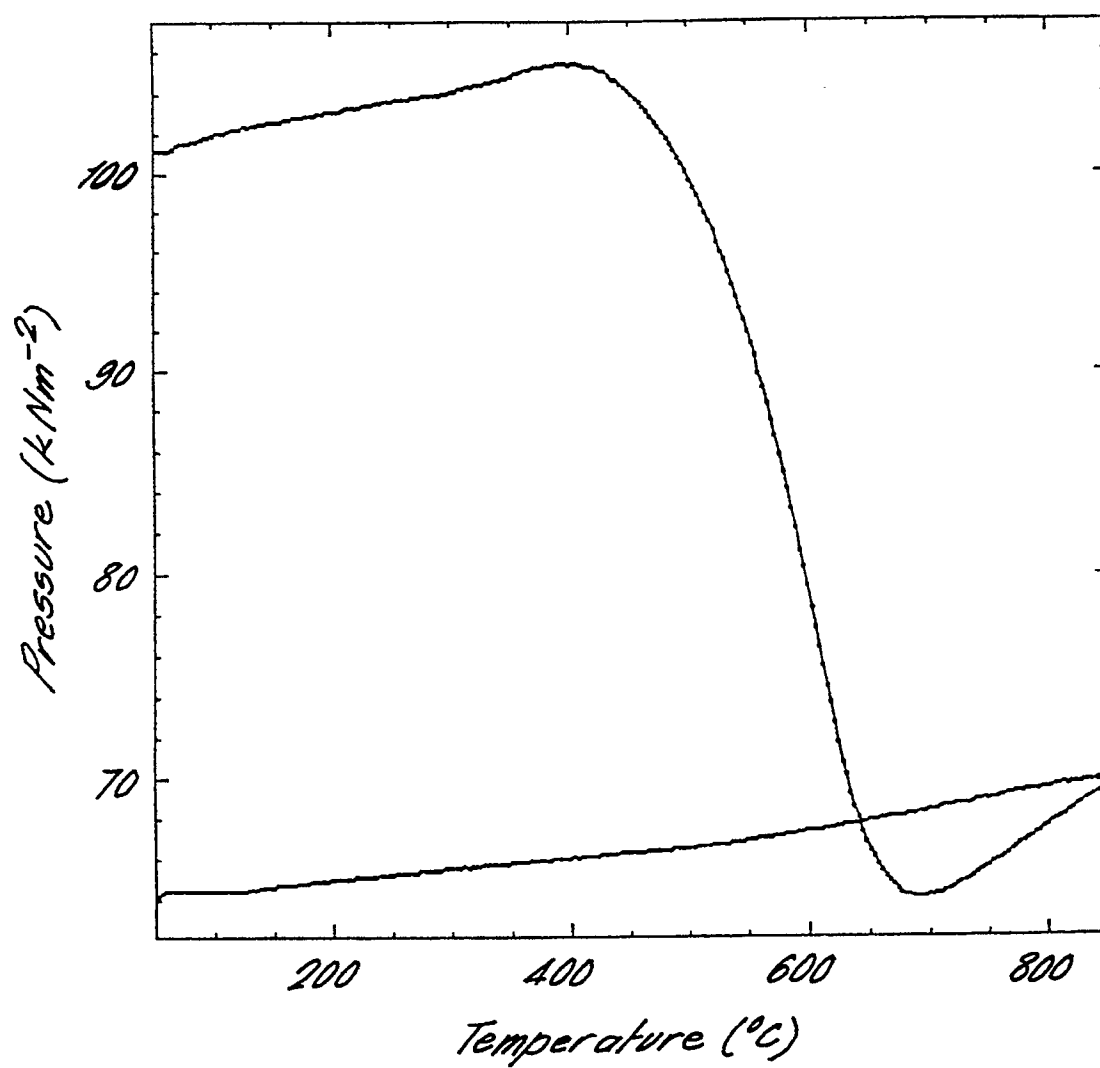
 $\text{SmFe}_{11}\text{Ti}$ in N_2 

FIG. 23.

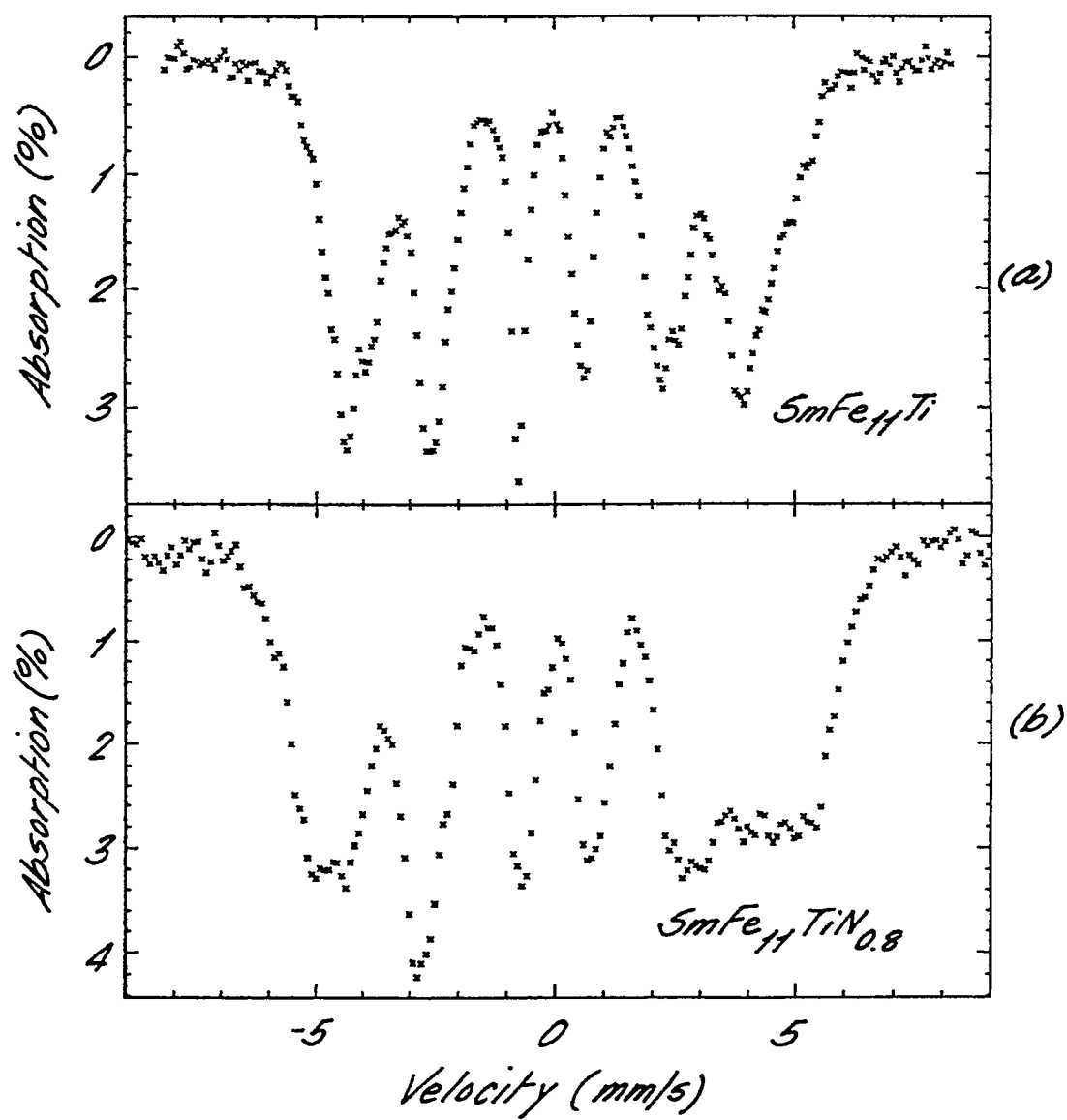


FIG. 24.

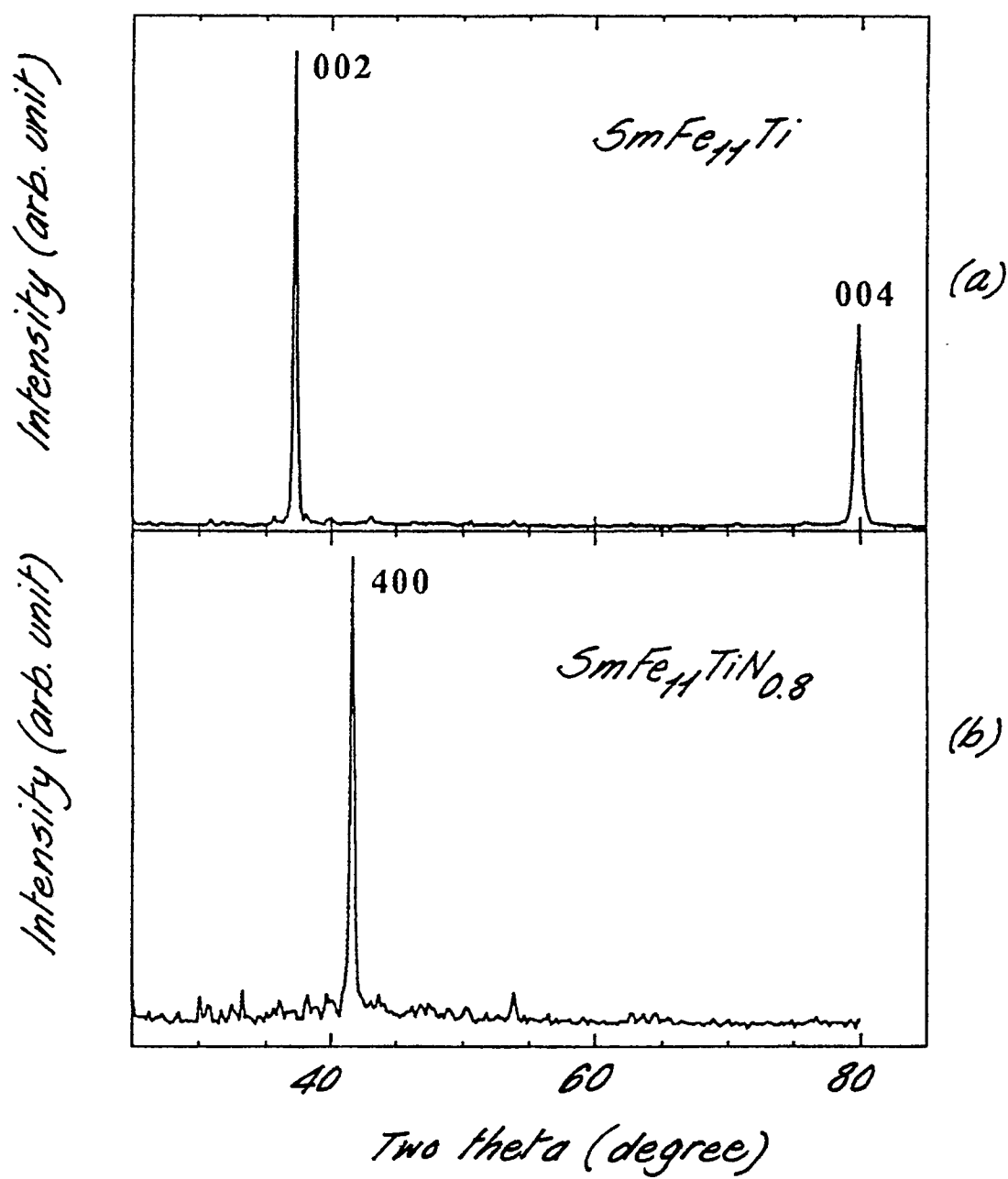


FIG. 25.

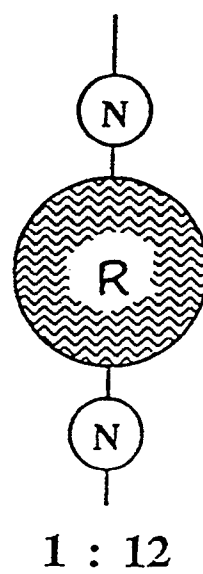
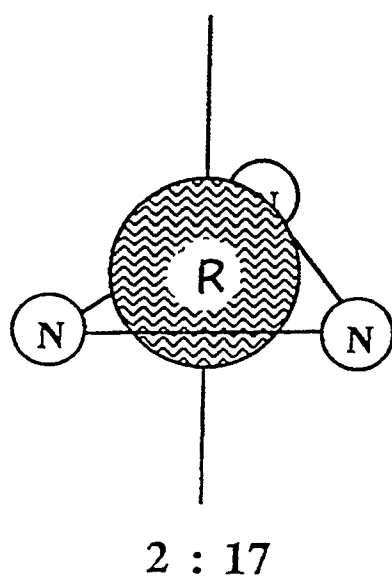


FIG. 26a.

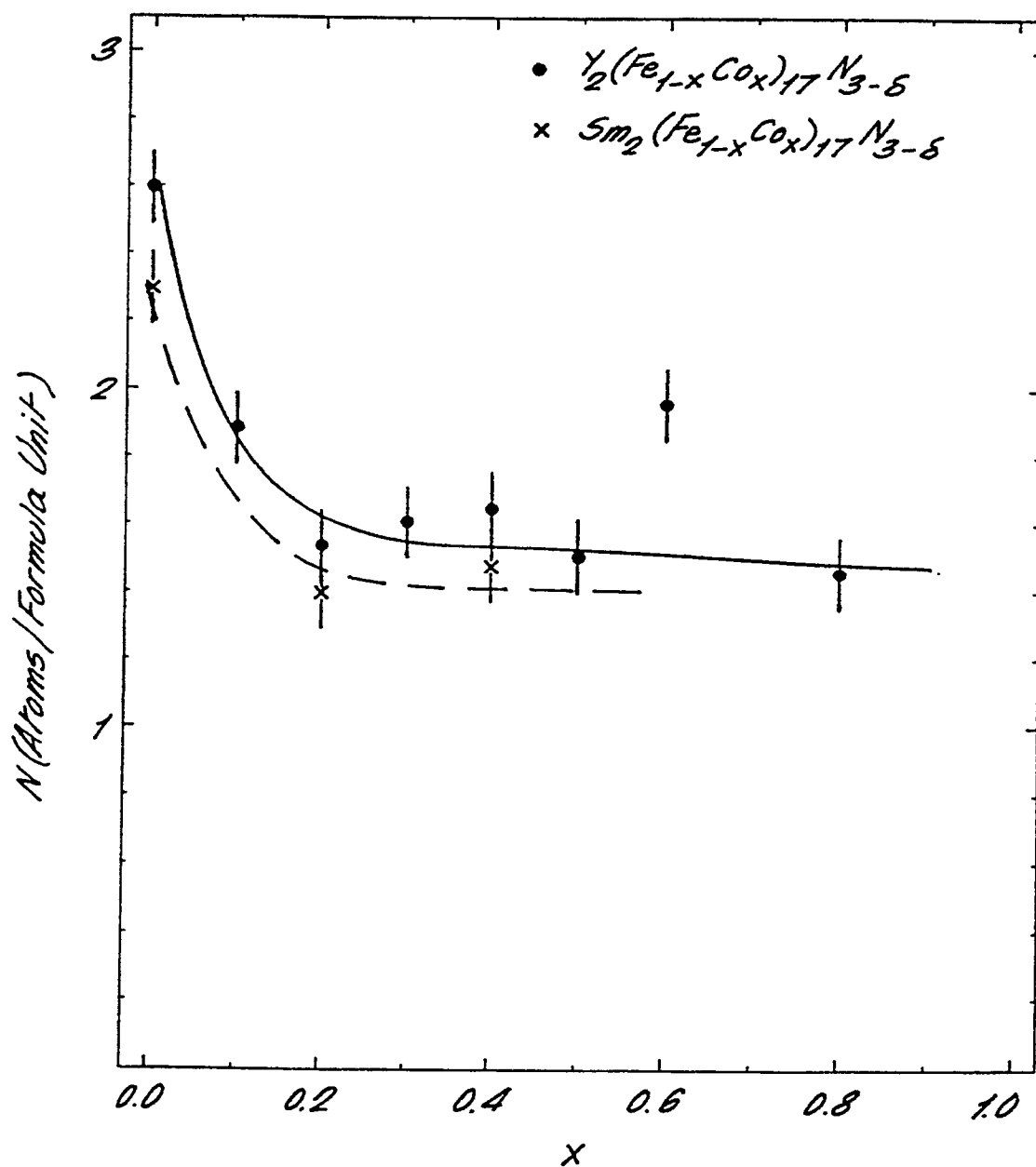


FIG. 26b.

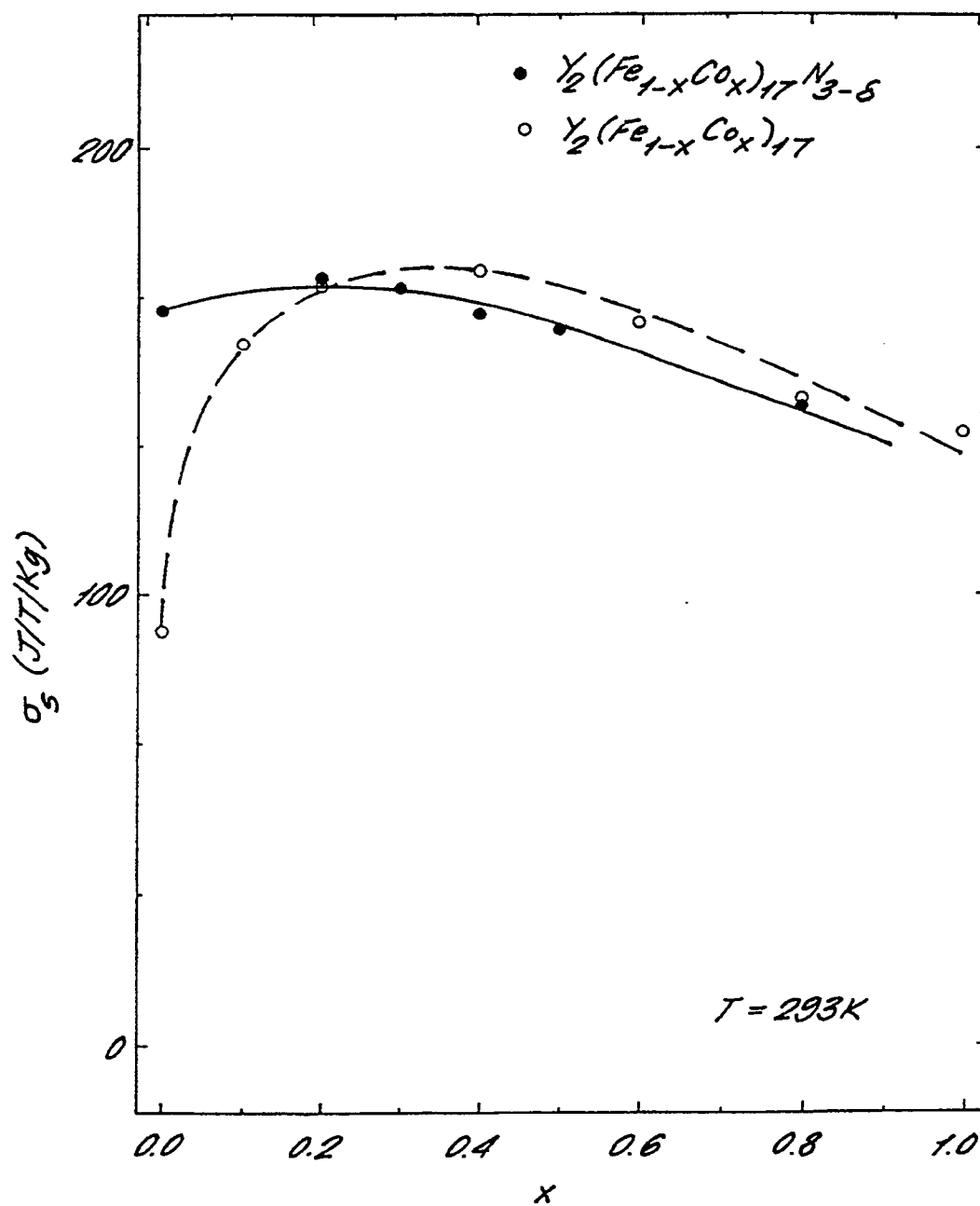


FIG. 26c.

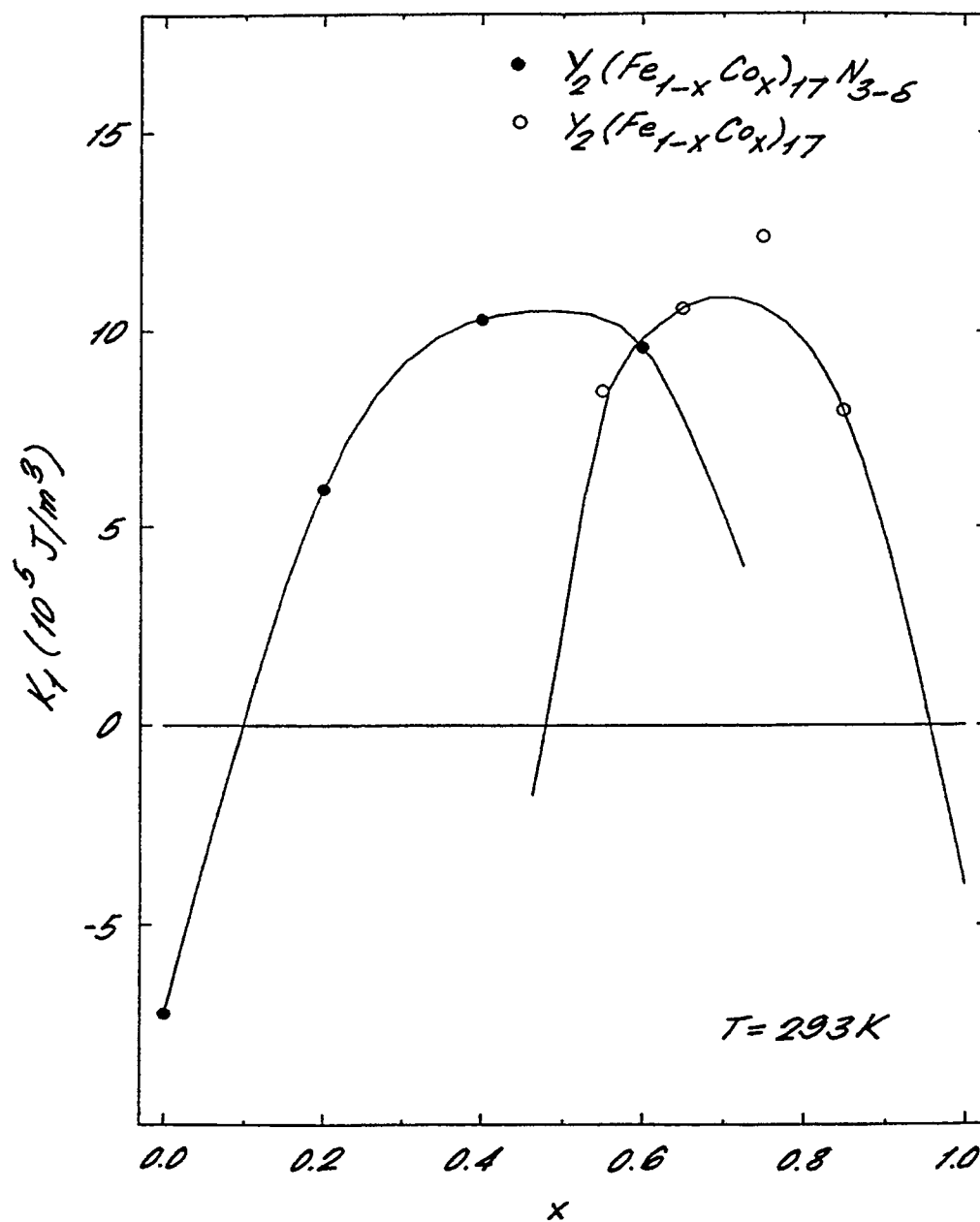


FIG. 27.

