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Magnetic properties and crystal structure of novel high anisotropic compounds based on the R–Fe–V system (R≡Y, Nd, Sm, Gd)

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Abstract

We have investigated the crystal structure and magnetic properties of novel ternary compounds of the composition $R_2(Fe_{0.91}V_{0.09})_{17}$ (R≡Y, Nd, Sm, Gd). X-ray diffraction showed that their crystal structure is a superstructure of a new type based on the $CaCu_5$ structure, but with lattice parameters five times larger than those of $CaCu_5$. The Curie temperature and saturation magnetization of the compounds studied fall into the ranges 440–520 K and 15–30 μ_B $(f.u.)^{-1}$ at 4.2 K respectively. The influence of dissolved cobalt, carbon and nitrogen on the magnetic properties of the compounds $R_2(Fe_{0.91}V_{0.09})_{17}$ has been studied.

1. Introduction

During recent years much attention has been paid to the search for new iron–rare earth compounds with non-cubic structures and high values of saturation magnetization, Curie temperature and anisotropic field strength which might serve as starting materials for permanent magnets. Compounds exhibiting such magnetic properties are expected to exist among the series of alloys from the iron-rich region of the R–Fe system (R, rare earth element or yttrium). Compounds with crystal structures which were previously unknown in the binary R–Fe system have been stabilized by alloying with a small quantity of a third element. Examples of such ternaries are the compounds with a tetragonal crystal structure: $R(Fe,M)_{11}$ ($M=Si+C$) and $R(Fe,M)_{12}$ (M≡Ti, V, W, Mo, Cr, Si, Re) as well as the well-known $R_2Fe_{14}M$ (M≡B, C) which now provide a basis for the production of the most powerful permanent magnets.

In the R–Fe–V system we have discovered new compounds corresponding to the composition $R_2(Fe,V)_{17}$ but with a crystal structure different from those of the known R_2Fe_{17} compounds. From X-ray studies of a $Y_2(Fe_{0.91}V_{0.09})_{17}$ single crystal [1] it was found that its structure is a superstructure of a new type based on that of the $CaCu_5$-type phase but with lattice parameters five times larger than those of the latter. The aim of this paper is to report on

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the crystal structure and magnetic properties of a series of novel ternary $R_2(Fe,V)_{17}$ intermetallics and to reveal their potential possibilities as materials for permanent magnets.

2. Experimental procedure

The alloys were prepared by induction or arc melting followed by annealing in a pure helium atmosphere at 1000 °C for 50 h. The crystal structure was investigated in an RKU–114M chamber using chromium and iron radiation or with a DRON-type X-ray diffractometer using Cr $K\alpha$ and Fe $K\alpha$ radiation. The preferred, i.e. easiest, orientation axis for magnetization was found from the intensities of lines on diffractograms of magnetically oriented powders. The magnetic moment M was measured with a vibrating sample magnetometer on powders in fields of up to 7.2 MA m^{-1} in a superconducting magnet or in fields of up to 1.6 MA m^{-1} in an electromagnet. The Curie temperatures T_C were obtained from low field $M(T)$ measurements ($H \approx 16 \times 10^3$ A m^{-1}).

3. Crystal structure

A novel $R_2(Fe_{0.91}V_{0.09})_{17}$ phase (we shall denote it as the Z phase) was identified for R=Y, Nd, Sm and Gd. Such a phase also exists for R=Tb but we have not succeeded in preparing the alloy free of other phases. No traces of the Z phase were found in alloys with other elements R. It is possible that the $Ce_2(Fe_{0.95}V_{0.05})_{17}$ and $Y_2(Fe_{0.91}V_{0.09})_{17}$ alloys [2] have the structure of the Z phase.

As was mentioned above, the $Y_2(Fe_{0.91}V_{0.09})_{17}$ phase has a hexagonal crystal lattice and can be identified as a superstructure based on the $CaCu_5$ structure but with lattice parameters approximately five times larger than those of $CaCu_5$. In compounds where R=Nd, Sm or Gd the situation was found to be more complicated. Figure 1 shows the X-ray diffractogram obtained from $Sm_2(Fe_{0.91}V_{0.09})_{17}$ at 300 K. The location of diffraction peaks for the crystal structure similar to that of $Y_2(Fe_{0.91}V_{0.09})_{17}$ is indicated at the top of the diagram. It may be remembered that the reflections with indices h,k,l divisible by five are the basic ones, *i.e.* they are the same for this superstructure and for the $CaCu_5$ structure; the rest of the reflections belong to the superstructure. There is an additional peak between the (555) and (00.10) lines which was absent for $Y_2(Fe_{0.91}V_{0.09})_{17}$. In addition, the (555) and (00.10) lines have approximately equal intensities and the intensity of the (5.0.10) line is almost twice as large as that of the (10.0.5) line, whereas the (555) and (10.0.5) lines in $Y_2(Fe_{0.91}V_{0.09})_{17}$ are substantially more intense than are (00.10) and (5.0.10) respectively, just as in diffractograms of $SmCo_5$ and Sm_2Fe_{17}.

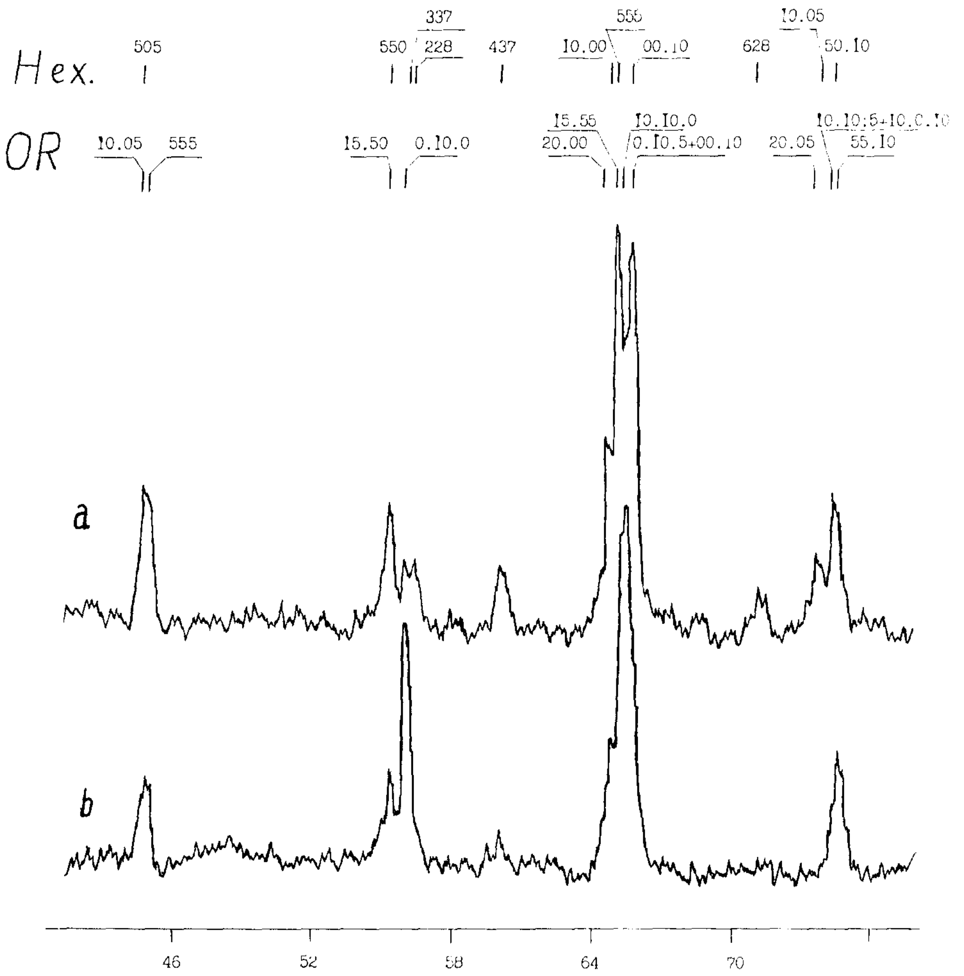

Fig. 1. X-ray diffractograms of $Sm_2(Fe_{0.91}V_{0.09})_{17}$: a, isotropic powder; b, anisotropic powder, aligned in magnetic field. The indices of the lines are shown at the top of the figure for hexagonal (Hex) and orthorhombic (OR) structures.

Such differences can be explained by assuming the presence of a crystal lattice distortion in $Sm_2(Fe_{0.91}V_{0.09})_{17}$ such that one of the three $\{11\bar{2}0\}$ plane systems has a slightly smaller interplanar distance than the other two. In this case the lattice is orthorhombic (OR); all the lines except (00.10) will be split. The locations and indices of split basic lines in orthorhombic notation are shown in Fig. 1. (No locations or indices of superstructure reflections are shown, for the sake of simplicity.) It is clear from the figure why an additional line appeared and the line intensities changed.

It is well-known that a hexagonal lattice may be described in orthorhombic notation. In this case the correlation between the lattice parameters is $a = b \times 3^{1/2}$. We shall introduce the parameter $\delta = b \times 3^{1/2}/a$ which is a measure of the deviation of the $R_2(Fe,V)_{17}$ crystal lattice from the hexagonal. For $Sm_2(Fe,V)_{17}$ $\delta=0.987$; for $Y_2(Fe,V)_{17}$ $\delta=1$ (a hexagonal lattice).

The diffractogram for $Sm_2(Fe,V)_{17}$ powder aligned in a magnetic field normal to the sample surface is shown in Fig. 1(b). It can be seen that the $(0.10.0)_{OR}$ line is sharply intensified; in contrast, the $(15.5.0)_{OR}$ and $(20.0.5)_{OR}$ lines are quite weak in comparison with those for an unaligned sample. Apparently this means that the preferred direction of magnetization for $Sm_2(Fe,V)_{17}$ is parallel to the $[010]_{OR}$ direction.

Quite similar diffraction patterns were obtained for alloys with R = Nd and Gd. The lattice parameters of Z phases containing various elements, R (OR notation) are listed in Table 1. The deviation of δ from unity is greatest for the alloy where R = Nd and is equal to zero for R = Y.

The structure of the Z phase lattice is not exactly of the hexagonal $CaCu_5$ type, but is distorted and may be considered as an orthorhombic lattice. The degree of deviation from a hexagonal structure is quite small and is different for alloys with different elements R. One of the three $\langle 11\bar{2}0\rangle$ axes is shorter than the other two and this also coincides with the direction in which the alloy is most easily magnetized. This fact and also the absence of lattice distortion in the alloy containing the non-magnetic yttrium ion make it possible to suppose that the lattice distortion in alloys with R = Nd, Sm and Gd is due to spontaneous magnetostriction of the R sublattice. To verify this supposition an investigation of the diffraction patterns was carried out on the $Sm_2(Fe_{0.91}V_{0.09})_{17}$ alloy using an X-ray high temperature vacuum chamber at 300–700 K. Up to 530 K no change in the diffraction patterns was observed; above 640 K the diffraction patterns showed evidence of a composition change in the sample layer, probably because of evaporation of samarium. The Curie temperature of the alloy is equal to 490 K; hence the orthorhombic distortion of the lattice is retained above T_C.

The atomic arrangement in the unit cell of the Z phase has not yet been established. The new crystal structure is most probably obtained by replacing one-third of all the R atoms by two iron or vanadium atoms (the so-called dumbbell arrangement) as occurs in the Th_2Ni_{17} and Th_2Zn_{17} structures. However, the manner of the dumbbell arrangement in the unit cell of the Z phase is quite different from that in these other structures. There is probably some alternation of dumbbells and R atoms or iron and vanadium atoms along one of the $\langle 11\bar{2}0\rangle$ directions, and as a result this direction becomes distinct from the others. In this case it is not clear why the crystal lattice of $Y_2(Fe_{0.91}V_{0.09})_{17}$ is hexagonal. The structure of this alloy has been found from electron diffraction patterns [1] to be very dispersed although its diffractogram is typical of single crystals. This may mean that the alloy consists of small domains of an orthorhombic phase with common [001] axes but that their [010] axes are turned to each other by 60°. A small deviation of the crystal lattice from the hexagonal might not be revealed because of the presence of such fine structure. A similar situation occurs in CoPt and FePt alloys [3, 4] where small domains in the total volume of the tetragonal phase are observed with intermediate stages of ordering. In

TABLE 1

Lattice parameters (in orthorhombic notation) and magnetic properties of $R_2(Fe_{0.91}V_{0.09})_{17}$ compounds and their nitrides

R	$R_2(Fe_{0.91}V_{0.09})_{17}$							$R_2(Fe_{0.91}V_{0.09})_{17}N_{2.5}$	
	Lattice parameters				T_c (K)	$M\{\mu_B$ (f.u.)$^{-1}\}$[a]	Preferred direction[b]	T_c (K)	Preferred direction[b]
	a (nm)	b (nm)	c (nm)	$\delta = 3^{1/2}\ b/a$					
Y	4.209	2.430	2.090	1.00	439	25.3	In (001) plane	706	In (001) plane
Nd	4.280	2.431	2.104	0.984	480	30.6	In (001) plane	706	In (001) plane
Sm	4.260	2.427	2.099	0.987	490	24.9	In (001) plane	743	[001] axis
Gd	4.245	2.430	2.086	0.991	524	14.5	In (001) plane	728	In (001) plane

[a] 4.2 K.

[b] 300 K.

this case the main reflections in the X-ray diffractograms show patterns arising from the tetragonal phase with a lesser degree of tetragonality or may even show patterns typical of a distorted cubic phase.

4. Magnetic properties

The intrinsic magnetic properties of $R_2(Fe_{0.91}V_{0.09})_{17}$ have been investigated (Table 1). The compounds are ferromagnetic with Curie temperatures falling within the range 440–520 K. The T_C value of the compound containing a non-magnetic yttrium ion is approximately the same as that of phases with magnetic neodymium, samarium and gadolinium ions. This means that the Fe–Fe exchange interaction makes the main contribution to the T_C values. The contribution from the R–Fe exchange interaction is highest for the compound with R = Gd (the highest T_C value).

The magnetic moments measured on oriented powders in a field of 7.2 MA m^{-1} at 4.2 K varied from 14.5 (R = Gd) to 30.6 μ_B $(f.u.)^{-1}$ (R = Nd). This means that the magnetic moments of the R and iron sublattices are parallel or antiparallel for light or heavy rare earths respectively. Taking into account that the R and vanadium components in $Y_2(Fe_{0.91}V_{0.09})_{17}$ are non-magnetic one can estimate the average magnetic moment per iron atom as $\bar{\mu}_{Fe} = 1.63$ μ_B from the saturation moment of the compound.

In the alloys where R = Y the three $\langle 11\bar{2}0 \rangle$ axes in the basal plane of the hexagonal lattice are the directions in which the alloys are most easily magnetized; hence the iron sublattice in these compounds has a preferred-plane anisotropy. As was mentioned above, the preferred directions in the alloys with R = Nd, Sm and Gd also lie in the (001) plane but among three $\langle 11\bar{2}0 \rangle$ axes only one is the preferred axis. Because single crystals were not available we could not estimate the value of the magnetic anisotropy energy in the (001) plane. However, taking into account that the orthorhombic distortion δ is close to unity and the Z phase is a superstructure based on the hexagonal $CaCu_5$ structure one can expect the value of the anisotropy energy in the (001) plane for the Z phase to be substantially smaller than in any plane containing the *c* axis. We have derived some support for this idea from an analysis of magnetization curves from measurements on $Sm_2(Fe_{0.91}V_{0.09})_{17}$ powders along and perpendicular to the preferred direction: the magnetic anisotropic behaviour in this case is more characteristic of preferred plane than of a preferred axis. Therefore none of the $R_2(Fe_{0.91}V_{0.09})_{17}$ compounds with R = Nd, Sm or Gd or with R = Y can be considered as promising permanent magnet materials.

5. Alloying of the Z phase with cobalt, carbon and nitrogen

It is known that the type and value of magnetocrystalline anisotropy in R–3d compounds may be changed under the influence of some alloying elements. Recently it has been reported [5, 6] that for Sm_2Fe_{17} which shows preferred plane anisotropy at room temperature, an appreciable enhancement of the uniaxial samarium sublattice anisotropy was observed as a result of the influence of carbon or nitrogen dissolved in the crystal lattice. This resulted in a change in orientation of the direction of greatest ease of magnetization, to the c axis in this compound. However, substitution of cobalt for iron in Sm_2Fe_{17} decreases the 3d sublattice plane anisotropy and as a consequence a change in orientation of the preferred direction also takes place here [7].

We have studied the influence of these alloying elements on the crystal structure and magnetocrystalline anisotropy of Z phases. The $Sm_2(Fe_{0.91-x}Co_xV_{0.09})_{17}$ alloys up to $x=0.2$ are entirely composed of the Z phase. The substitution of cobalt for iron causes almost no change in the lattice parameters and no change in the preferred direction of magnetization is observed. When $x \geqslant 0.3$ the phase with the Th_2Zn_{17} structure appears instead of the Z phase. The Curie temperature rises when x increases and reaches 673 K when $x=0.2$. The specific magnetization measured in a field of 1.6 MA m^{-1} along the preferred direction also increases (Fig. 2).

When alloyed with carbon according to the formula $Y_2(Fe_{0.91}V_{0.09})_{17}C_x$ the Z phase was the only one up to $x=1.0$; at $x=1.4$ the samples also contained a phase with the Th_2Zn_{17} structure. The lattice parameter a and the unit cell volume increased slightly under the influence of dissolved carbon (by about 0.5% and 1% respectively). At $x=1.0$ the T_C value had increased by 30°; the magnetic moment also rose slightly ($M_{4.2K}=26.5$ μ_B $(f.u.)^{-1}$). In $Sm_2(Fe_{0.91}V_{0.09})_{17}C_x$ samples where $x=0.5$ there are considerable amounts of the phase with the Th_2Zn_{17} structure and also a solid solution based on α-Fe together with the Z phase. The lattice parameters of the Z phase in this alloy are a little larger than when $x=0$; this means that a small amount of carbon is dissolved in this alloy (apparently, essentially less than in the

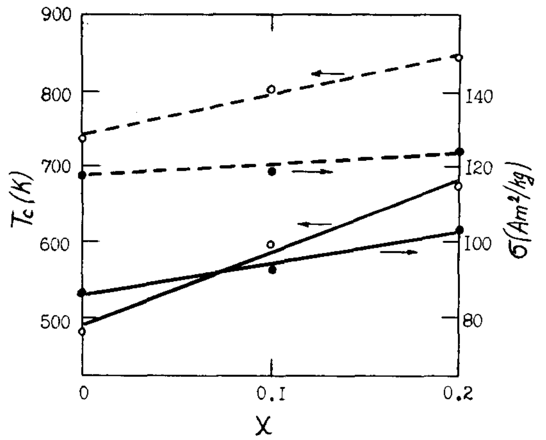

Fig. 2. Curie point and specific magnetization at 300 K *vs.* composition x for $Sm_2(Fe_{0.91-x}Co_xV_{0.09})_{17}$ compounds (full lines) and their nitrides (broken lines).

Z phase with R = Y). When $x = 0.75$ the Z phase disappears entirely and the samples consist of the Th_2Zn_{17} phase alone. No change in the preferred magnetization direction was observed as an effect of carbonization.

Nitrogenation of Z phases was achieved by annealing powders with a particle size d of less than 50 μm in an atmosphere of nitrogen at $p = 1.25$ bar. After the $Sm_2(Fe_{0.91-x}Co_xV_{0.09})_{17}$ powders ($x \leqslant 0.2$) had been annealed at 350–650 °C the type of crystal structure was still the same. The change in the lattice parameters a, $b \times 3^{1/2}/a$, $c \times 3^{1/2}/a$ and the unit cell volume after nitrogenation for 1 h at different temperatures is shown in Fig. 3. It can be seen that there was no noticeable change in these values at 350–450 °C. The lattice parameters increased appreciably at 550–650 °C and as a result the unit cell volume rose by 6%. Figure 4 shows the variation of the lattice parameters after nitrogenation at 650 °C *vs.* the time of annealing. It can be seen that saturation was almost reached in 15 min. After the powders had been annealed a certain amount of solid solution based on α-Fe + Co was observed. Apparently, this is a consequence of the evaporation and oxidation of samarium. The quantity of this phase increased with rising temperature and increasing duration of annealing.

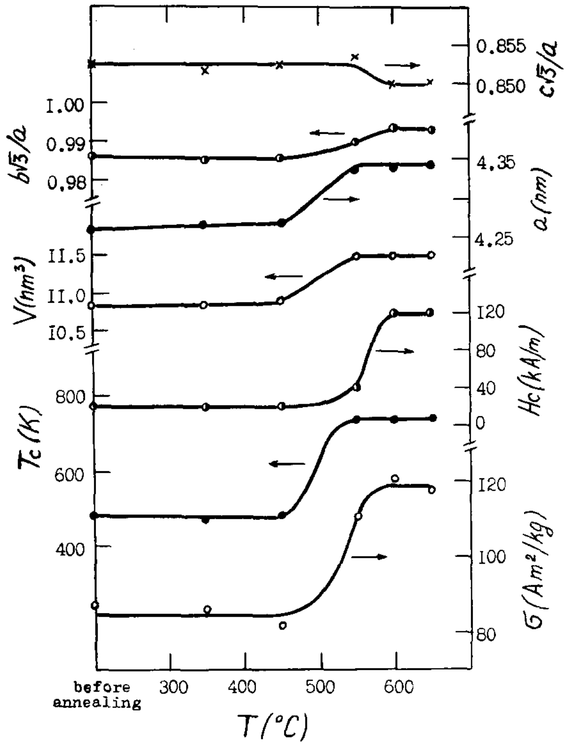

Fig. 3. Lattice parameters, unit cell volume, Curie point, specific magnetization and coercive force at 300 K *vs.* temperature of annealing for 1 h in nitrogen atmosphere.

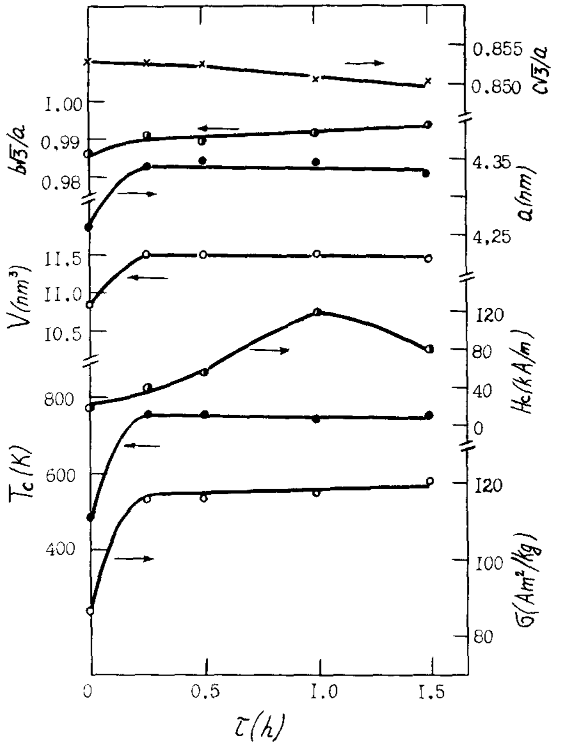

Fig. 4. Lattice parameters, unit cell volume, Curie point, specific magnetization and coercive force at 300 K of $Sm_2(Fe_{0.91-x}Co_xV_{0.09})_{17}$ compounds *vs.* time of annealing at 650 °C in nitrogen atmosphere.

Controlled annealing of the alloys for 1–3.5 h at 650 °C in a vacuum or a helium atmosphere did not lead to any change in the lattice parameters. This confirms the assumption that parameter growth is connected with nitrogenation of the Z phase. The nitrogen atoms, apparently, occupy the interstitial sites. The nitrogen content in the alloys was estimated by means of gravimetric measurements. It was found to be equal approximately to 2.5 atoms per formula unit. The most effective temperature for nitrogenation was deduced, which is typically 550–650 °C.

When studying the nitrogenation process we paid particular attention to one interesting peculiarity: the unit cell volume reached its final value in 15 min at 650 °C or in 1 h at 550 °C, but in spite of this the parameter ratios $b\times 3^{1/2}/a$ and $c\times 3^{1/2}/a$ only had intermediate values. This may mean that there is an order in the location of the nitrogen atoms and the ordering process is more durable than the nitrogen absorption.

Nitrogenation of the alloys at 750 °C did not lead to the appearance of $Sm_2(Fe_{0.91-x}Co_xV_{0.09})_{17}N_{2.5}$; samarium nitride and a solid solution based on α-Fe + Co were observed.

The X-ray diffraction patterns revealed that nitrogenation of the alloys had resulted in a change in the direction most easily magnetized in the

$Sm_2(Fe_{0.91-x}Co_xV_{0.09})_{17}$ phase: at 300 K the preferred axis was parallel to [001].

Figure 3 shows the variation of the Curie temperature, specific magnetization σ and coercive force H_c at 300 K *vs.* annealing temperature in a nitrogen atmosphere. After annealing at 550–650 °C the powders absorbed nitrogen and a noticeable increase in T_C and σ was observed. The first parameter T_C increased by 250° and the second by 35%. The changes in T_C and σ vs. annealing time at 650 °C (Fig. 4) are the same as those of the lattice parameters. The coercive force also increased (to 120 kA m^{-1}) but it reached its maximum value not immediately after the change in direction most easily magnetized, but later when, perhaps, the nitrogen atoms were becoming ordered in the alloy. The highest value of T_C (840 K) was reached after nitrogenation for 1 h at 650 °C in alloys containing cobalt (Fig. 2).

As was mentioned above the direction most easily magnetized in $Sm_2(Fe_{0.91}V_{0.09})_{17}N_{2.5}$ is parallel to the [001] axis. To estimate the field anisotropy H_a the field dependence of the magnetization was measured on oriented powders of the alloy (Fig. 5). The sharp increase in σ in fields up to 0.4 MA m^{-1} is connected, apparently, with the ease of the magnetization process in a solid solution based on α-Fe. The field anisotropy of the Z phase is obtained as a field strength, where linear extrapolations of curves representing the directions easiest and most difficult to magnetize intersect each other. It was found that $H_a = 19$ MA m^{-1} at 4.2 K and $H_a = 13.5$ MA

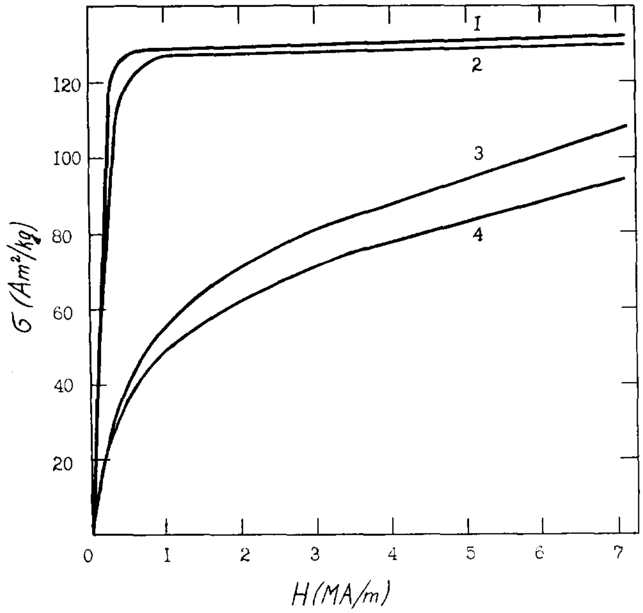

Fig. 5. Magnetization curves for textured powder of $Sm_2(Fe_{0.91}V_{0.09})_{17}N_{2.5}$ alloy measured in magnetic field parallel (1 and 2) or perpendicular (3 and 4) to the preferred direction: 1 and 4, $T = 4.2$ K; 2 and 3, $T = 260$ K.

m^{-1} at 260 K. One can expect that $Sm_2(Fe_{0.91}V_{0.09})_{17}N_{2.5}$ also has a fairly high uniaxial anisotropy energy at room temperature.

Nitrogenation of the Z phase containing other elements R at 550–650 °C also resulted in an increase in the unit cell volume which was approximately the same as in the case where R = Sm. The Curie temperatures also rose but there was no change in the direction most easily magnetized (Table 1).

The interatomic distances increased under the influence of the dissolved nitrogen. The increase in T_C for $Y_2(Fe_{0.91}V_{0.09})_{17}N_{2.5}$ was the same as for the Z phase with magnetic rare earth ions. Therefore we can suppose that the sharp increase in the Curie temperatures after nitrogenation of all the compounds investigated is connected with an increase in the exchange Fe–Fe interactions owing to the increase in the Fe–Fe distances. The increase in magnetization σ at 300 K is connected mostly with the increase in T_C because the magnetic moment scarcely changes throughout the interval 4.2–300 K (Fig. 5, curves 1 and 2).

Thus $Sm_2(Fe_{0.91}V_{0.09})_{17}N_{2.5}$ is a magneto–uniaxial compound with sufficiently high values of the Curie temperature, the magnetic moment and the field anisotropy. It can be considered as a starting material for permanent magnets with a maximum energy product $(BH)_m$ of up to 260 kJ m^{-3}. However, powders of these alloys have a rather low coercive force. It should also be noted that the magnetization of the compounds studied is less than that of Sm_2Fe_{17}, $Sm_2Fe_{17}C_x$ and $Sm_2Fe_{17}N_x$ owing to the presence of non-magnetic vanadium.

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